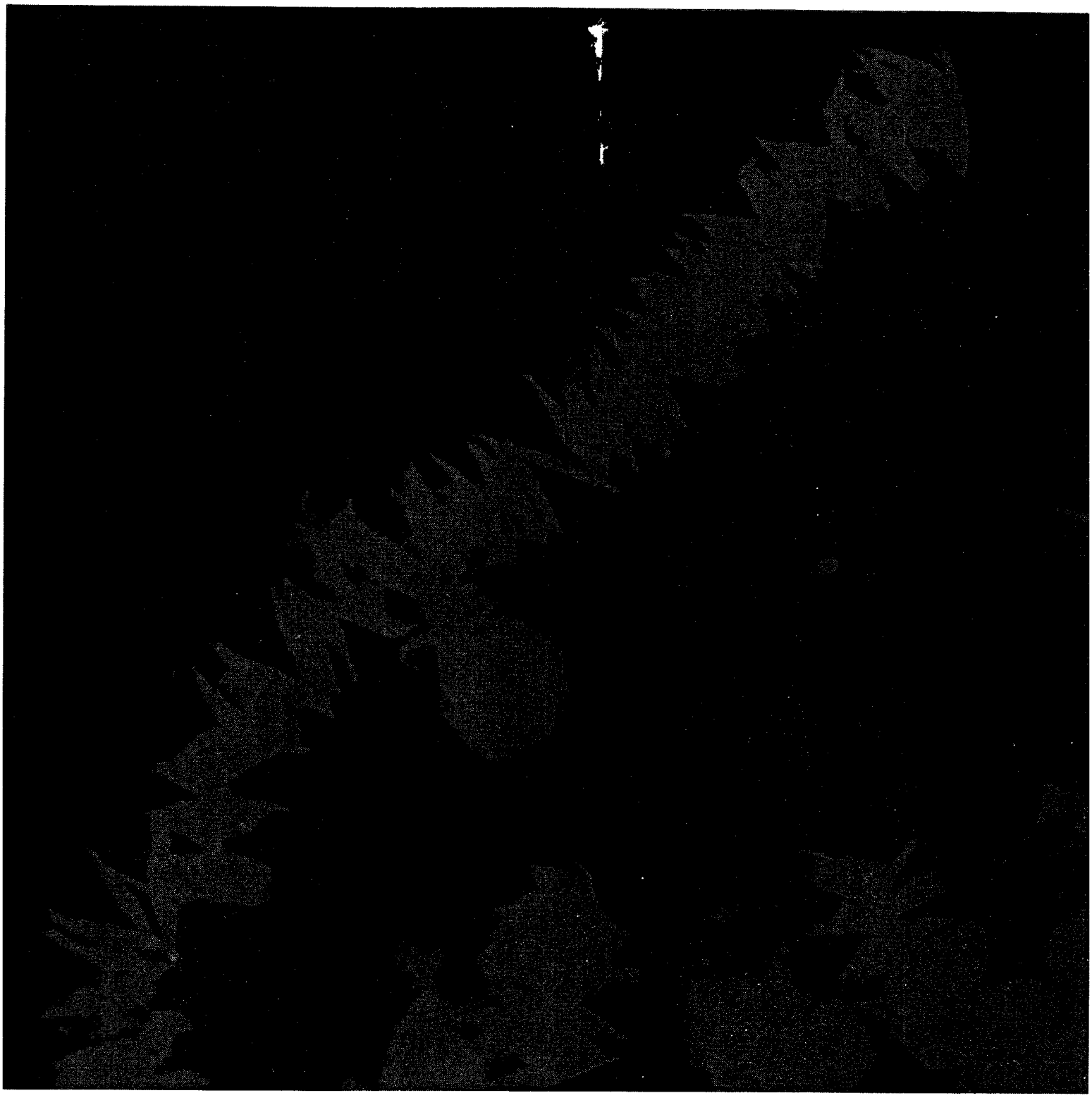
Stereoregular Polymers and Stereospecific Polymerizations

The Contributions of Giulio Natta and his school to Polymer Chemistry

Volume 1

Edited by G. Natta and F. Danusso

Istituto di Chimica Industriale del Politecnico, Milan



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PREFACE

STEREOREGULAR polymers and stereospecific polymerizations have now been known for some years. These discoveries aroused great interest not only in the field of macromolecular chemistry, but also in those of industrial chemistry and of chemistry in general. This interest has increased steadily, and development on this subject continues and is fully open to progress in the future.

It may thus be of some significance to collect in a single work the papers of those researchers in whose laboratories took place the discovery of synthetic polymers and of the first stereospecific polymerization processes. This significance, apart from a historical aspect, consists mainly in the usefulness this collection may have for a scientist working in the same or in related fields. This is especially true considering that a number of the original papers were published in Italian or in languages other than English, and therefore could not be directly read by all interested scientists who are more usually familiar with the English language. Hence the proposal of Pergamon Press Ltd. to collect in one or more volumes all the papers published by my Institute on the subject.

The first volume comprises all the papers, in chronological order, submitted for publication from the discovery of the stereoregular polymers (March 1954) to 1959 inclusive. The papers numbering 170, it was not considered convenient to re-publish all of them integrally. Therefore some papers have been reported as abstracts. The unabridged form has been adopted for some of the most important papers and for the lectures delivered at Conferences and on different occasions. The latter, in fact, being reviews on the results obtained at different times, summarize the successive stages of research. This aspect of the lectures has been held advantageous, although this has involved some repetition of information and concepts.

Among the papers from 1954 and 1959 can be found the first announcement of the discovery of stereoregular polymers and the description of the first syntheses and industrial production of stereoregular polymers of aliphatic and vinylaromatic α-olefins and of diolefins. In addition to the subsequent developments of these initial findings, the first syntheses of olefin copolymers are described and all the papers on the kinetics and the reaction mechanisms are included.

The study of the structure of crystallizable polymers and of the conformational properties of stereoregular macromolecules advanced together with the chemical research and with the studies on the physical, mechanical and thermodynamic properties of the new polymers in the solid state or in bulk, and in solution.

Finally some papers concern the commercial production of the first plastics and rubbers obtained from synthetic stereoregular polymers and the application of isotactic polypropylene in the production of textile fibres and films.

The new polymers described in the period covered by this first volume were predominantly hydrocarbons. Corresponding polymers of non-hydrocarbon monomers and polytactic polymers were described soon after and will be presented in subsequent volumes.

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Chimica e Industria **42,** 125 (1960) [18 Dec. 1959] 869

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1

CRYSTALLINE HIGH POLYMERS OF α-OLEFINS

by G. NATTA, P. PINO, P. CORRADINI,* F. DANUSSO,+ E. MANTICA,#
G. MAZZANTI,§ and G. MORAGLIO+

(10 Dec. 1954)
[*J. Amer. Chem. Soc.* **77,** 1708 (1955)]

No crystalline polymers of olefinic hydrocarbons containing asymmetric carbon atoms in the principal chain of the macromolecules have been reported. Such a lack of crystallinity has been explained[1] by considering such polymers as copolymers of two types of random distributed monomeric units, differing only in the configuration of their dissymmetric group.

Using various heterogeneous solid catalysts which will be described elsewhere,[2] we have synthesized linear crystalline polymers of α-olefins and we are now reporting some properties of crystalline polypropylene, poly-α-butylene, and polystyrene. Depending on the structure of the catalyst, different amounts (ranging from 0 to 100 per cent) of the polymerization products are crystallizable and can be separated easily from the much more soluble non-crystalline polymers by solvent extraction. In the case of polypropylene and polystyrene the X-ray diagrams of drawn fibres show reflections from about fifty different planes. Both equatorial and higher order X-ray reflections of polystyrene may be indexed on the basis of a hexagonal cell with $a = 21{\cdot}9$ Å, and $c = 6{\cdot}65$ Å (space-group $R3c$ or $R\bar{3}c$) One of the two different crystal forms we observed for the poly-α-butylene seems to have a similar cell with $a = 17{\cdot}3$ Å and $c = 6{\cdot}7$ Å. We have not yet collected sufficient data to establish the correct unit cell of polypropylene : the identity period along the fibre axis c is, in this case, $6{\cdot}50$ Å ; the equatorial X-ray reflections may be indexed on the basis of an oblique cell with $a = 6{\cdot}56$ Å, $b = 5{\cdot}46$ Å, and $\gamma = 106°\ 30'$.

TABLE 1. PHYSICAL PROPERTIES OF "CRYSTALLINE" AND "AMORPHOUS" (NON CRYSTALLIZABLE) POLYPROPYLENE, POLY-α-BUTYLENE AND POLYSTYRENE

	Intrinsic viscosity[a] ($cm^3/g \times 10)^2$	*Identity period along the chain* (Å)	*X-ray density* (g/cm^3)	*Density* (D_{25}^{25})	*X-ray*[d] *or dilatometric*[e] *transition point* (°C)	*Melting point* (°C)	*Solubility*[f]		
							Ether	*n-Heptane*	*Toulene*
Polypropylene									
(a) h. m. w. "crystalline"	2·40[b]	6·50±0·05	0·94	0·92	158–160[d]	..	i.	i.	s.
(b) l. m. w. "crystalline"	0·17[b]	(6·50±0·05)	0·94	0·91	148–150[d]	..	i.	sl.s.	s.
(c) "amorphous"	0·55[b]	...	...	0·85	...	75	s.	s.	v.s.
Poly-α-butylene									
(a) "crystalline"	1·02[b]	6·7 ±0·1	0·96	0·91	126–128[d]	..	i.	s.	v.s.
(b) "amorphous"	0·35[b]	...	...	0·87	...	65	s.	v.s.	v.s.
Polystyrene									
(a) "crystalline"	3·8[c]	6·65±0·05	1·12	1·08	230[d,e]	..	i.	i.	v.s.

[a] Concentrations at 25°. [b] Tetralin as solvent at 135°. [c] Benzene as solvent at 25°. [d] Temperature at which all the X-ray reflections of crystals disappear. As will be demonstrated in subsequent papers, the melting temperatures of sterically purer fractions were much higher. [e] First order transition point from dilatometric data. [f] i., insoluble; sl.s., slightly soluble; s., soluble; v.s., very soluble.

In Table 1 the physical properties of the crystalline polypropylene and poly-α-butylene have been compared with those of the corresponding solid non-crystallizable substantially linear polymers obtained as by-products by the same polymerization processes.

The new crystalline polyhydrocarbons show higher melting point, higher density and lower solubility in organic solvents than the corresponding "amorphous" polyhydrocarbons having intrinsic viscosity of the same order of magnitude.

The infrared spectra* of crystalline polypropylene, of melted samples of the same polymer and of the "amorphous" polypropylene, show between 2 and 7·5 μ the high adsorption regions characteristic of hydrocarbons. The wavelengths of the absorption bands between 7·5 and 15 μ in normal and polarized light are presented in Table 2. Most of the differences between the infrared spectrum of the

* A Beckmann IR 2, a Perkin-Elmer model 112, and a Perkin-Elmer model 21 spectrometer with NaCl prisms have been used.

TABLE 2. INFRARED SPECTRUM OF DIFFERENT TYPES OF POLYPROPYLENE BETWEEN 7·5 AND 15 μ

Crystallizable polypropylene				
Crystalline product	*Crystalline cold drawn product* ↕ *E-vector*		*Melted product*	*Amorphous non-crystallized polypropylene*
	↕	↔		
7·53 w	...	7·53 w	...	...
7·67 m	7·67 m	...	...	7·67 w
7·71 sh	...	7·72 w	...	...
7·97 m	7·96 m	...	7·97 w	7·97 m
...	...	...	..	8·13 m
8·20	...	8·20 w	...	..
8·57 s	8·56 s	sh	...	...
8·66 sh	sh	8·67 m	8·70 s,b	8·66 s
9·06 w	9·06 w	9·06 w	9·06 w	9·06 sh
9·57 w	9·57 w	...	...	...
9·65 sh	...	...	...	...
10·02 s	10·02 s	10·02 w	10·02 w-m	10·02 w-m
10·28 s	10·28 s	10·28 m	10·28 s	10·28 s
10·64 w	...	10·63 w	...	...
11·12 m	11·12 vw	11·12 m	Wide absorption region	Wide absorption region
11·89 s	11·89 s	11·89 w	between 11 μ and	between 11 μ and
12·36 m	12·36 vw	12·36 m	12·7 μ with absorption	12·7 μ with absorption
			maxima at 12·38 μ and	maxima at 12·3 μ and
			11·2 μ	11·90 μ and shoulder
				at 11·21 μ

vw, very weak; w, weak; m, medium; s, strong; sh, shoulder; b, broad.

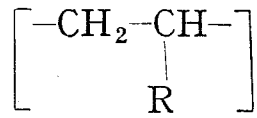
crystalline and of the non-crystalline polypropylene* disappear on melting the crystalline product and reappear after cooling the melted sample.

The large number and the clearness of the X-ray reflections obtained from drawn fibres of the new polyhydrocarbons demonstrate the unusual regularity of their chain structure. By comparing X-ray and density data it is seen that each portion of the principal chain, included in the elementary cell, corresponds to three monomeric units (—CH_2—CHR—) and therefore contains an odd number of asymmetric carbon atoms.

For these reasons we have excluded the presence of sequences of asymmetric carbon atoms having alternatively *d* and *l* configuration in the principal chain of the polymer, as was proposed for the crystalline polyalkylvinyl ethers.[3]

* The infrared spectra of the crystalline and of the linear not crystallizable polypropylene are very different from infrared spectra of branched polypropylene produced using $AlBr_3$ as catalyst.

Since regular sequences of the type *d-l-l* or *l-d-d* do not seem probable, we attribute to the new crystalline polymers a structure in which at least for long portions of the principal chain, all the asymmetric carbon atoms have the same configuration.* In this case, if the principal chain of a crystalline polymer of an α-olefin



is represented arbitrarily as a planar fully extended chain, all the R groups must be placed on the same side of the plane of the principal chain. Such planar structure is impossible because of the steric hindrances among the R groups and, in order to reach the crystalline state, a spiralization of the principal chains must take place.

This hypothesis agrees with the value found for the identity period (6·5—6·7 Å) of all these polymers, which is shorter than the length of a planar and fully extended paraffinic chain corresponding to three monomeric units (7·62 Å).

We suppose that a similar structure may be attributed to the crystalline polyalkylvinyl ethers having identity periods along the principal chain[4] roughly as long as those observed in the crystalline polyhydrocarbons we have prepared, and different properties from ordinary soft polymers.[5]

* We propose to designate as "isotactical chains", from the Greek words *ἴσος* = equal, and *τάττω* = to set up, the polymer chains having such exceptionally regular structures, containing series of asymmetric carbon atoms with the same steric configuration ("isotactical" asymmetric carbon atoms).

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* X-ray structure determinations.
\+ Physical determinations.
\# Infrared spectra determinations.
§ Polymerization of α-olefins.

2

A NEW CLASS OF POLYMERS OF α-OLEFINS WITH AN EXCEPTIONAL REGULARITY OF STRUCTURE*

by G. NATTA

(11 Dec. 1954)
[*Atti Accad. Naz. Lincei, Memorie* (8) **4**, 61 (1955)]
[*J. Polymer Sci.* **16**, 143 (1955)]

SUMMARY

The exceptional properties of a new class of macromolecular hydrocarbons having a linear structure, obtained by polymerization of α-olefins, are described in this paper.

The high melting temperature, the high crystallinity, the slight solubility, and the peculiar mechanical properties of these polymers are attributed to a particular regularity of structure due to the existence, in each macromolecule, of long and ordered sequences of asymmetric carbon atoms having the same steric configuration.

A suggestion is made to call "isotactic" this particular type of arrangement of the asymmetric carbon atoms of the linear macromolecules.

Vinyl polymers, obtained by head-to-tail polymerization of monomers of the $CH_2 = CHR$ type, possess main chains in which asymmetric carbon atoms are alternated with methylenic groups.

The inability of polymers containing successions of —CH_2—CHR— groups to crystallize whenever the R group is larger than the hydrogen atom bound to the tertiary carbon atom, was attributed to the diffe-

* This paper is of preliminary character on the identification and on some general properties of a new and very interesting class of poly-α-olefins, prepared by us, having a remarkable regularity of structure, high crystallinity, exceptional physical and mechanical properties, and is only a part of a whole series of works developed in 1954 with the co-operation of Montecatini Co. and of several research chemists at the Institute of Industrial Chemistry of the Polytechnic School of Milan. More precisely, with the co-operation of Piero Pino, for the organization of research of organic chemistry and discussion of the results; Giorgio Mazzanti, Ettore Giachetti and, at first, Paolo Chini for the preparation and purification of the new polymers; Paolo Corradini for X-ray research; Ferdinando Danusso and Giovanni Moraglio for physical determinations; Enrico Mantica, Mario Peraldo and Luisa Bicelli for I.R. spectrography; and Giuseppe Lutzu for mechanical tests.

rent configuration of the asymmetric carbon atoms. This seems to be the reason why in the chain of these polymers, no regular repetition of constitutive elements identical as far as the space is concerned can exist ; whereas, there is a succession, normally statistically disordered, of two different structural units, which differ from one another only in their steric configurations of the relating asymmetric carbon atoms.

All the polymers derived from the olefins of the aforesaid type, in which R is an alkyl group, are liquid or amorphous solids.

The presence of methyl side groups (with an actual van der Waals' radius of about 2 Å) or of other groups of even larger size was moreover considered, in this type of polymers, as a certain hindrance to the formation of fully planar zigzag chains of paraffins stretched on a plane.

According to Flory,[1] a better condition to obtain a chain with a regular planar structure would entitle the alternate succession, along the chain, of asymmetric carbon atoms with opposite steric configurations. A similar structure had been proposed for crystalline polyvinylisobutyl ethers, prepared by C. E. Schildknecht, S. T. Gross, H. R. Davidson, I. M. Lambert, A. O. Zoss[2] operating at very low temperatures with an extremely slow polymerization rate.

Steric hindrances decrease only if the R groups possess (as F, OH) a radius smaller than 1·4 Å, that is, if their size is not considerably larger than that of the hydrogen atom bound to the carbon atom ; in that case, the formation of the rigid zigzag planar chain, which is typical of the rhombic structure of paraffins, is still possible.

Therefore, we were extremely surprised, toward the beginning of March 1954, when we discovered that the fractionation of solid high-molecular-weight polymers of propylene, which we prepared by adopting procedures and conditions suitable for obtaining polymers with essentially linear chains (that is without branchings longer than those in the R group), gave a considerable portion of crystalline polymers, as revealed by X-ray examination.

Later on, we prepared crystalline polymers of other aliphatic α-olefins and of styrene, and we probed into their structures, in order to understand the essence of these new products.

In another communication we will report the general methods that allowed us to obtain remarkable amounts of these crystalline polymers, or to produce at will amorphous non-crystallizable polymers. This topic is still under investigation.

We only refer here to the methods used by us for separating crystalline polymers, to their peculiar properties and the relationship between such properties and the structure of the chains.

SEPARATION OF THE CRYSTALLINE POLYMERS FROM THE AMORPHOUS ONES AND THEIR PROPERTIES

Fractionation of some crude polymers of propylene, carried out by extraction with solvents, done in March 1954, yielded a series of fractions whose properties did not appear to have a regular function with respect to the molecular weight. For instance, ether-soluble fractions of molecular weight higher than 40,000 were highly crystalline up to at least 130°C, whereas acetone-insoluble fractions but ether-soluble, of molecular weight lower than 35,000 were completely amorphous even at low temperature. Intermediate fractions did not appear to have a polymeric composition with intermediate properties, but rather to exist as a heterogeneous mixture of two parts : one crystalline and one amorphous.

Having observed this phenomenon, we studied how these anomalies had occurred, and why they did not occur when the polymers obtained were fractionated by adopting the polymerization conditions normally used.

Therefore, we performed subsequent extraction runs of the crude polymers with a series of solvents with a solvent power, at their boiling temperature, in the increasing order : acetone, ethyl acetate, ether, n-heptane, benzene, toluene.

With regard to polypropylene, the ether extract is completely amorphous, while the n-heptane insoluble product is completely crystalline. With regard to poly-α-butylene, a separation of the two types of products may be performed with boiling ether. Crystalline polystyrene may be easily separated from the amorphous one due to its insolubility in boiling n-heptane.

Some characteristic properties common to polypropylene, polybutenes, polystyrenes, concerned with both types of polymers separated by us in the way described above, are compared in Table 1.

TABLE 1

Polymers	*Amorphous non-crystallizable*	*Crystalline*
Appearance	Elastic at a temperature above that of the 2nd order transition, vitreous at a lower temperature	Can be pressed at temperatures near to the temperature of the 1st order transition to tough and flexible lamina
X-ray examination	Typical bands of the prevailingly amorphous linear polymers	Crystallinity up to 120 °C at least
Polarized-light I.R. spectra	Absence of dichroism	Strong dichroism
Thermal analysis	Melting or softening at temperatures below 110°C	Temperature of the 1st order transition > 120°C
Density	Low	High
Behaviour with regard to the mechanical deformations	Viscoelastic at temperatures higher than the temperature of the 2nd order transition	Orientation of the crystals and corresponding anisotropies
Tensile strength	Low	Very high in the oriented polymers

Even if the measurements of the intrinsic viscosity (performed on about one hundred samples) had generally given higher values for the crystalline polymers than for the amorphous ones (which had been separated from the same crude product), this, notwithstanding the difference of properties of the two types of products, would not have been attributed to the difference of molecular weights.

In fact, we could separate fractions, some crystalline, others amorphous, that in solution have the same intrinsic viscosity, and very likely similar molecular weights. As we shall see later these are polymers that in both cases are essentially linear.

Furthermore, crystalline products have been obtained by thermal depolymerization of highly crystalline polypropylenes, having an average molecular weight of about 100,000; and this also occurred when the molecular weight decreased to values (3000–5000) much lower than those of a great number of completely amorphous polypropylenes, which have molecular weights higher than 20,000.

The properties of some fractions of the two types of polypropylenes and of polybutenes are compared in Table 2. Intrinsic viscosities

TABLE 2

Polymer	*Intrinsic viscosity* (10^2 *cm³/g*)	*Experimental density*	*Temp. of the ist order transition*	*Temp. of incipient melting*	*Solubility in*		
					Ether	*n-heptane*	*Toluene*
Crystalline high-molecular-weight polypropylene	2·40	0·92	158–160	—	i.	i.	s.
Crystalline low-molecular-weight polypropylene	0·17	0·91	149	—	i.	s.	s.
Amorphous polypropylene	0·55	0·85	—	75	s.	s.	v.s.
Crystalline poly-α-butene	1·02	0·91	126–128	—	i.	s.	v.s.
Amorphous poly-α-butene	0·35	0·87	—	65	s.	v.s.	v.s.

were determined in tetralin, at 135°C. The indicated transition temperature represents the temperature at which the X-ray diffraction bands, typical of the crystalline phase, disappear completely. Solubilities in various solvents are indicated at their boiling temperature (i., insoluble, s., soluble, v.s., very soluble).

Even more marked differences have been observed when comparing crystalline and amorphous polystyrenes. A comparison is made herein between commercial amorphous polystyrenes and a polystyrene having the following properties: it is insoluble in acetone, ether, n-heptane, but soluble in toluene; it has an intrinsic viscosity at 25°C: $[\eta] = 3 \cdot 8 \times 10^2$ cm³/g (determined in benzene solutions); it remains crystalline up to above 200°C, and has a temperature of the first order transition of 213°C, as determined by dilatometric means:

	Density	*Transition temperature*	
Crystalline polystyrene	1·08	213°C	(1st order)
Amorphous polystyrene	1·04–1·065	70–100°C	(2nd order)

The remarkable differences existing between the physical properties of the two types of polymers must be attributed to a common reason, which must be looked for in the structures of the main chains of the macromolecules.

LINEARITY OF THE MAIN CHAIN

From the literature on macromolecular chemistry, it can be seen that remarkable differences in physical properties may be derived from the presence or from the absence of frequent branchings of the high polymer main chains. For instance, unbranched polymethylene, as obtained by decomposition of diazomethane with BF_3, is highly crystalline, whereas polyethylene, obtained by initiation of free radicals

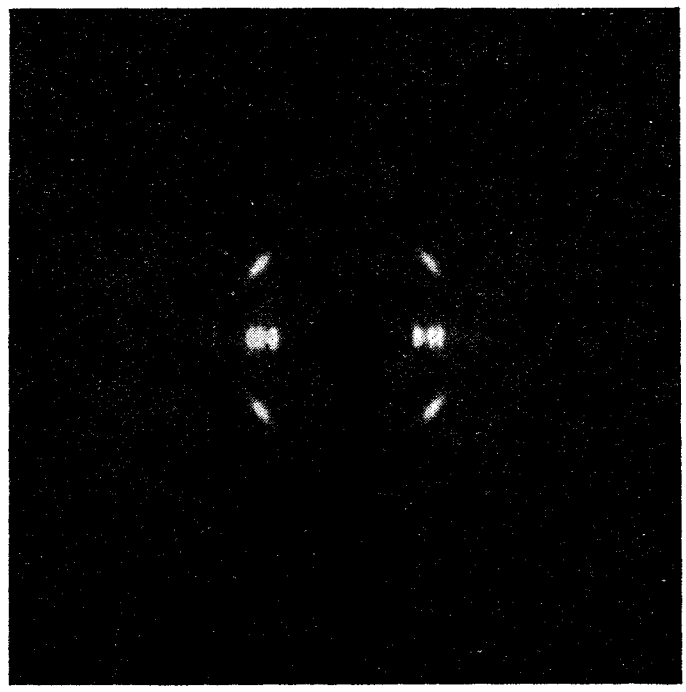


FIG. 1. Fibre spectrum of a crystalline polypropylene.

at high temperature, is considerably branched and normally it contains about 50 per cent of the amorphous fraction ; polyethylene of the preceding type, to which we had grafted a great number of ethyl branchings, was completely amorphous.

The high crystallinity observed in some polypropylenes and polystyrenes prepared by us (see Figs. 1 and 2) is not consistent with the presence of frequent branchings in the main chain of the polymer.

Also the ether-soluble amorphous polypropylene (a by-product of the preparation of crystalline polypropylene) should not be considerably branched, because when molecular weights are higher than 5000, it should have the consistency of a solid, whereas from the literature it may be seen that branched polypropylenes, obtained with $AlBr_3$,[5] are viscous liquids even when molecular weights have values of many tens of thousands.

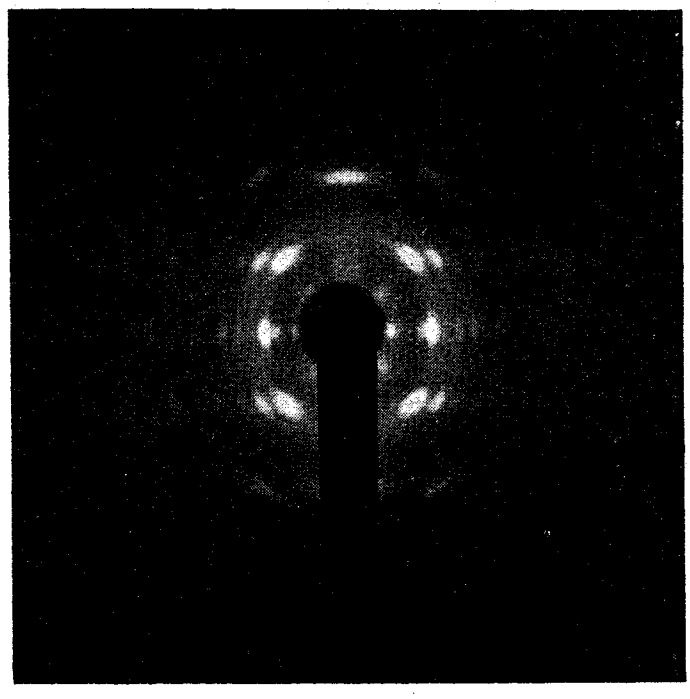


Fig. 2. Fibre spectrum of a crystalline polystyrene.

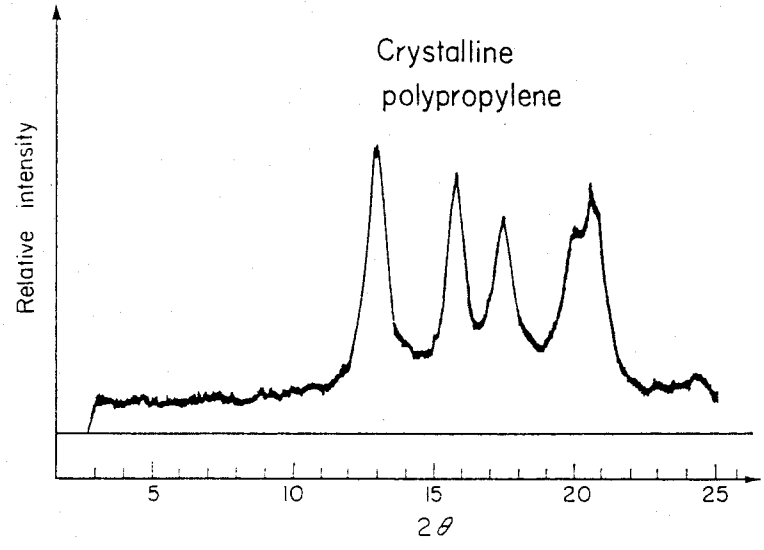


Fig. 3. X-ray spectrum of a crystalline polypropylene registered with a Geiger counter (Cu$K\alpha$).

The X-ray spectrum of an amorphous polypropylene, cured after sulphochlorination with the introduction of about 1 per cent of sulphur, and maintained under stress, shows the main band characteristic of the amorphous polymer, corresponding to 5·3 Å, on the equator of the spectrum; this suggests the parallel orientation of the linear chain segments, normally distanced by groups of size not larger than that of the methyl group.

The great similarity existing between the I.R. spectra of the ether-soluble and ether-insoluble polypropylenes, when examined in the molten state, demonstrates that in both cases the degree of branching cannot be very different. One must, therefore, conclude that even the ether-soluble solid polymer cannot be much branched. Its I.R. spectra are quite different from the spectra obtained by examining branched polypropylenes obtained with $AlBr_3$.

On the contrary, one observes great differences in the I.R. spectra of the crystalline product, which in the oriented state shows high dichroism (Table 3).

TABLE 3. I.R. SPECTRUM OF POLYPROPYLENE BETWEEN 7·5 AND 15 μ

Crystalline polypropylene				
Crystalline product stretched. Direction of streching ↔				
Crystalline product	*Electric vector* ↔	*Electric vector* ↕	*Molten product*	*Amorphous non-crystallizable polypropylene*
7·53 w	—	7·53 w		
7·67 m	7·67 m	—	—	7·67 w
7·71 sh	—	7·72 w	—	—
7·97 m	7·96 m	—	7·97 w	7·97 m
				8·13 m
8·20 w	—	8·20 w	—	—
8·57 s	8·56 s	sh		
8·66 sh	sh	8·67 m	8·70 s,b	8·66 s
9·06 w	9·06 w	9·06 w	9·06 w	9·06 sh
9·57 w	9·57 w	—	—	—
9·65 sh	—	—	—	—
10·02 s	10·02 s	10·02 w	10·02 w-m	10·02 w-m
10·28 s	10·28 s	10·28 s	10·28 s	10·28 s
10·64	—	10·63 w	—	—
11·12 m	11·12vw	11·12 m	Broad absorption region between 11 and 12·7 μ with minimum bands at 12·3 and 11·2 μ	Broad absorption region between 11 and 12·7 μ with minimum bands at 11·12 and 12·33 and shoulder at 11·90 μ
11·89 s	11·89 s	11·89 w		
12·36 m	12·36 vw	12·36 m		

vw, very weak; w, weak; m, medium; s, strong; sh, shoulder; b, broad.

It is known that the I.R. spectra of optically active compounds possessing asymmetric carbon atoms differ from the I.R. spectra of racemic compounds, only when examined in the solid state; they do

not differ in the dissolved or molten states. By examining the I.R. spectra, one may obviously conclude that the structures of the two types of products are different because the distribution of the asymmetric carbon atoms (of different configuration) along the chain is also different. This distribution should be statistical in the amorphous polymers and ordered in the crystalline ones.

X-RAY EVIDENCE OF THE EXCEPTIONAL STRUCTURAL REGULARITY OF CRYSTALLINE POLYMERS (FIGS. 3, 4,5)

Here we report only a few X-ray data, which helped us to solve the problem concerned with the structure of our prepared polymers.

Fibre spectra have been obtained on products drawn at temperatures slightly higher than the temperature of the first order transition, and subsequently stretched at lower temperatures (Table 1).

We report some results obtained by examining such photograms : that is the identity period along the fibre axis c, and the a' and b' projections on a plane perpendicular to the c axis of the a and b constants of the elementary unit cell, these last being chosen as the lowest, interpreting the observed $hk0$ reflections.

Polypropylene

$c = 6{\cdot}50 \pm 0{\cdot}05$
$a' = 6{\cdot}56 \pm 0{\cdot}05$
$b' = 5{\cdot}46 \pm 0{\cdot}05$
$\gamma' = 106°30'$
$d_{001} = 6{\cdot}34$ Å

Volume of the elementary unit cell = 222·4 Å^3.
Density of a unit cell containing 3 monomeric units = 0·936.
Experimental density = 0·922.

Polystyrene and Poly-α-butene

	Polystyrene	*Poly-α-butene*
$a' = b'$	12·64±0·05 Å	10·0±0·1 Å
c	6·65±0·05 Å	6·7±0·1 Å
γ'	120°	120°
Volume of the elementary unit cell	921·5 Å^3	580·2 Å^3
Density calculated for a unit cell containing 6 monomeric units	1·124	0·96
Experimental density	1·085	0·915

In another communication we will refer to the dimorphism of polybutene (see Fig. 5), which, upon its recrystallization from solutions, can yield crystals having a different structure.

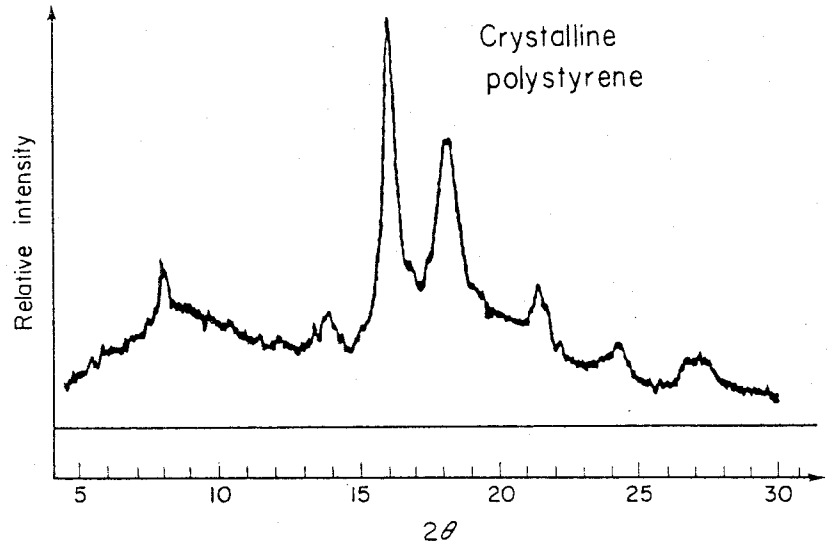


FIG. 4. X-ray spectrum of a crystalline polystyrene registered with a Geiger counter (Cu$K\alpha$).

The great clearness and the high number of reflections (belonging to different layers) that appear in our X-ray photograms of the oriented fibres are only consistent with a great regularity of structure; therefore, they must be attributed to a sequence of perfectly identical structural units along the fibre axis coinciding with the chain axis.

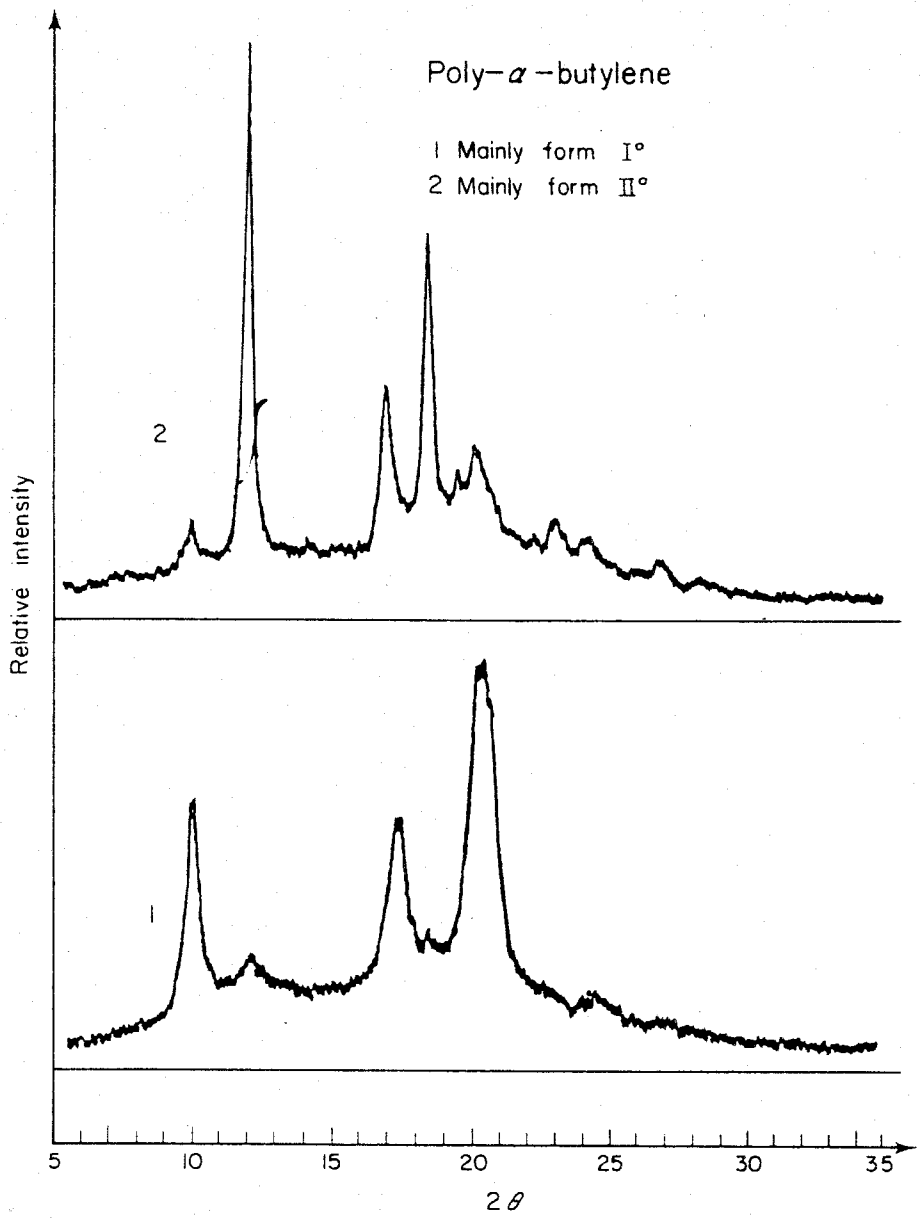


FIG. 5. X-ray spectrum registered with a Geiger counter ($Cu\overline{K}\alpha$) of a crystalline polybutene in the two observed structural modifications.

STRUCTURES OF THE CHAINS OF "ISOTACTIC" CRYSTALLINE POLYMERS

The exceptional regularity of structure of the crystalline polymers examined here, could be attributed to one of the following structural hypotheses :

(1) All the neighbouring asymmetric carbon atoms have the same steric configuration, at least for long segments of the chain.

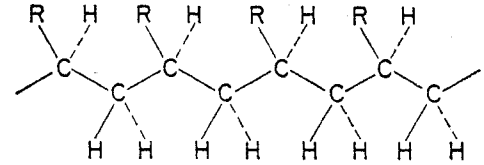
(2) Each chain possesses several asymmetric carbon atoms of different configurations, but the succession of asymmetric atoms of both configurations occurs with a determined regularity.

We think it is possible to exclude the latter hypothesis, because the dentity period found along the chain axis (of about 6·5 Å) corresponds, iat least in the most studied case of polypropylene, to three —CH_2— —CHR— monomeric units, which are probably placed as a helix along the crystal axis. A regular succession of the same number of asymmetric carbon atoms of different steric configurations would require an even number of such units in the identity period. The case of a regular succession of 2 units of one type and of a unit of the other type has not been taken into account, it being extremely improbable.

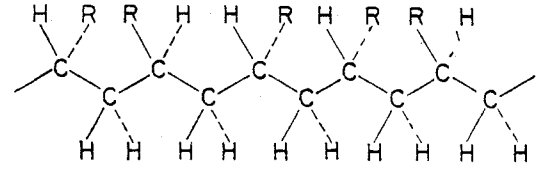
Since we give a great importance to this phenomenon, for the knowledge of a vast class of synthetic macromolecules, whose production has already been started and will be largely developed in the future, we have called, for the sake of simplicity, the asymmetric carbon atoms of equal configuration and belonging to one chain : "isotactic", an adjective from the Greek, meaning : placed in the same order (*ἴσος* = equal, and *τάττω* = to place in order). Thus, we will call "isotactic" those chains and molecules containing isotactic carbon atoms, and also those polymers containing isotactic molecules ; "isotacticity" will be the name of this phenomenon.

In order to clarify the structures of the "isotactic" chains, we should imagine the main zigzag paraffinic chain of the polymer to stretch arbitrarily on a plane. In this case the R groups may be (I) all above or all below the plane of the chain (which in the following scheme corresponds to the plane of the sheet), or else may be statistically distributed (II) :

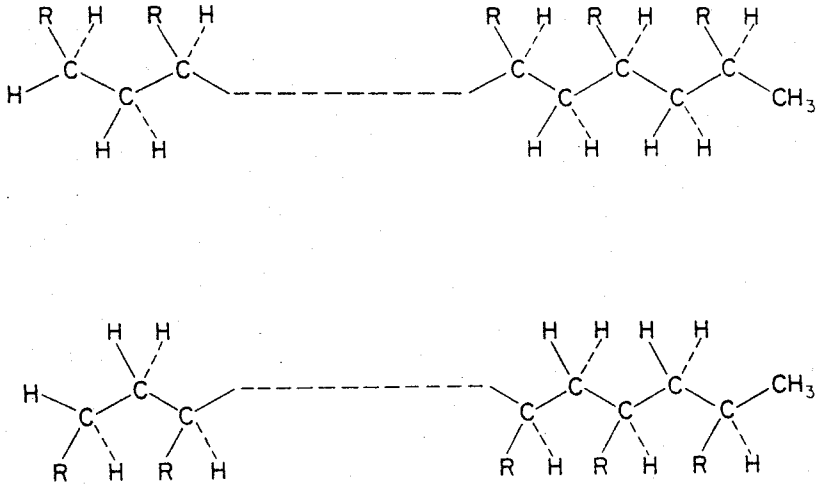
(I) isotactic structure



(II) non-isotactic structure



Obviously an isotactic molecule may have two different configurations, as results from Fig. 2, where for example, we have indicated two types of non-superimposable saturated isotactic (enantiomorphous) molecules, where one is the mirror image of the other :



If one reverses one of the two macromolecules (that is : if one places the head of the macromolecule where its tail was, and rotates it by 180° around its axis), the two macromolecules would be superimposable for almost all their length, with the exception of the end groups.

With regard to the optical activity of each dissolved macromolecule, it can be seen that marked phenomena of internal compensation occur within the asymmetric carbon atoms, which are equidistant from the centre of each isotactic chain, whereas a statistical compensation occurs in each non-isotactic chain. Furthermore, the presence of statistical mixtures of two classes of enantiomorphous molecules is a further reason for the disappearance of every optical activity in these dissolved synthetic polymers.

The isotactic polymers, as we have observed, differ remarkably from the non-isotactic ones in the solid state, not only in their behaviour with regard to polarized light, but also in their nonvectorial properties, melting temperature, solubility and density, etc. The differences of properties observed by us are much greater than the differences generally observed among the low-molecular-weight compounds containing asymmetric carbon atoms with different configurations.

In the case of our macromolecular compounds, this is due to the existence of a great number, often thousands, of asymmetric atoms in each molecule, and to their co-operation in emphasizing an effect that should be negligible if limited to a very small number of sterically differentiated atoms.

The poly-α-olefins, described by us in this communication, represent the first examples of polyhydrocarbons, where the presence of isotactic structural orders has been demonstrated.

We think, however, that the presence of isotactic chains, probably of the same type, causes the crystallinity that was surprisingly observed in some synthetic polymers, whose structures were normally non-isotactic, such as polyvinylbutene, which shows an identity period along the chain axis of 6·2 Å.

Isotacticity occurs automatically when macromolecules are prepared by the condensation of asymmetric molecules of the same configuration containing two different reactive groups bound to the asymmetric carbon atoms; e.g. in the condensation of *l*-α-amino acids. The chains of a great number of fibrous, crystallizable proteins must be considered as isotactic.

We believe that this phenomenon may occur in other synthetic polymers, and presents a possibility of producing new types of macromolecules, of particular properties, very different from those of the corresponding non-isotactic linear polymers.

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3. These procedures are being patented.
4. G. NATTA and P. CORRADINI, *La Ricerca Sci.* Suppl , 695 (1955) (presented at the Macromolecular Chemistry Conference — Milan, Turin, Sept.–Oct. 1954).
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3

THE CRYSTALLINE STRUCTURE OF A NEW TYPE OF POLYPROPYLENE

by G. NATTA and P. CORRADINI

(11 Dec. 1954)
[*Atti Accad. Naz. Lincei, Memorie* (8) **4**, 73 (1955)]

ABSTRACT

The X-ray spectra of a new, high crystalline type of polypropylene are described here and qualitatively interpreted. It is observed that the presence of crystallinity is not dependent on molecular weight.

The fractionation of polymers with different solvents yields products having more or less regularity of structure, hence, a more or less high degree of crystallinity.

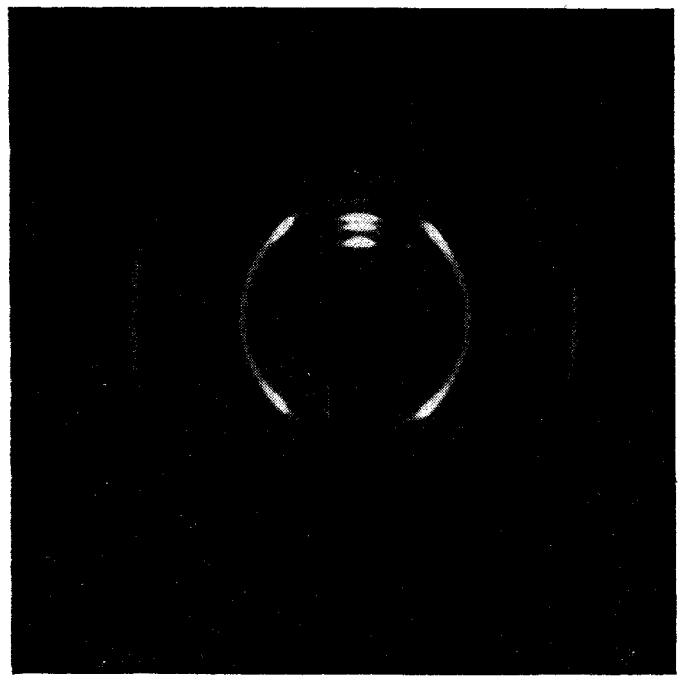


FIG. 1. Fibre spectrum of the polypropylene indicated in Fig. 1 of paper 2 with fibre axis perpendicular to the Weissenberg camera axis.

The presence of tertiary carbon atoms along the chain gives rise to many isomeric possibilities. Only an *isotactic* structure is in accordance with the fibre identity period (6·5 Å). In fact, three monomeric units repeat within the identity period. Figure 1 of paper 2 and Figure 1 of this paper show the fibre spectra of typical sample.

A qualitative correlation of intensities permits one to establish the conformation of the chain (a threefold helix), as can be seen from Fig. 2, subsequently confirmed in other papers.

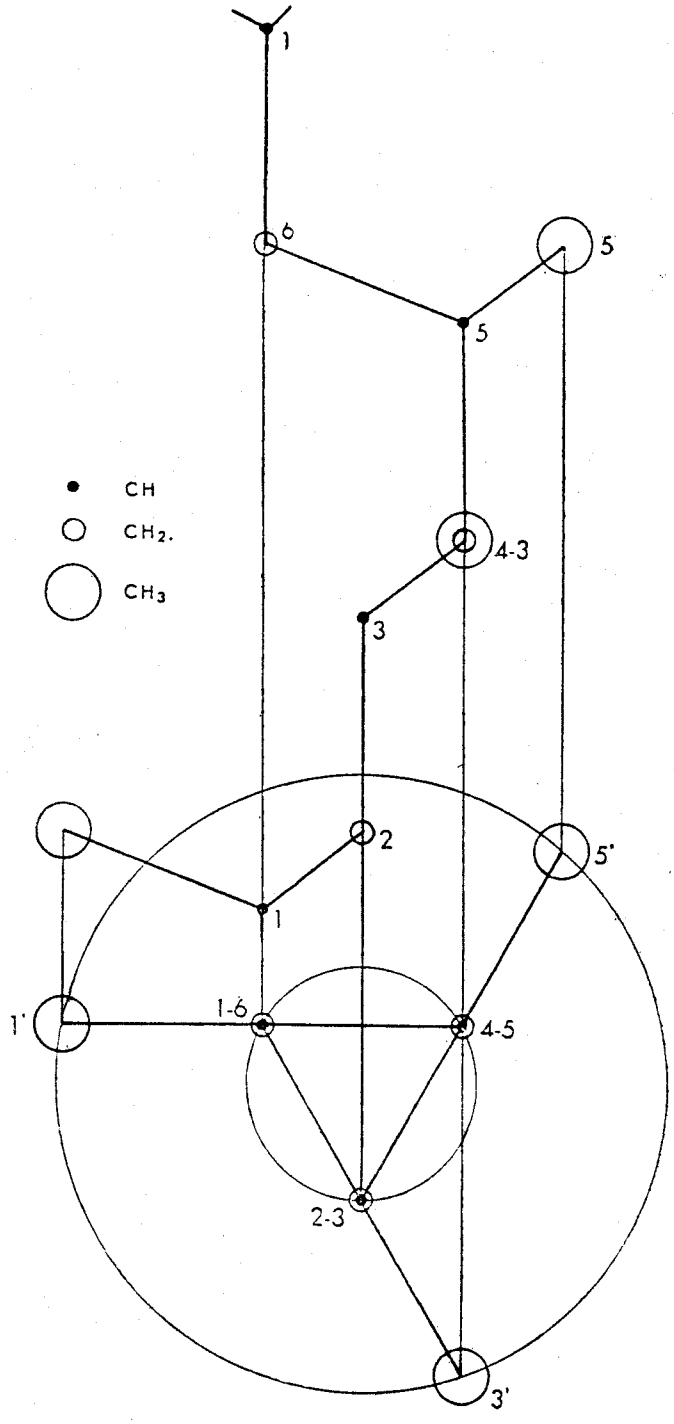


FIG. 2. Side and end views of a chain portion corresponding to the identity period of crystalline polypropylene.

4

THE CRYSTALLINE STRUCTURE OF ISOTACTIC POLYSTYRENE

by G. NATTA and P. CORRADINI

(15 Jan. 1955)
[*Rend. Accad. Naz. Lincei* (8) **18**, 19 (1955)]

ABSTRACT

The Geiger spectra of crystalline isotactic polystyrene are discussed.

It is observed that samples quenched from the melt are amorphous and become highly crystalline if maintained for some time at a temperature slightly lower than their melting temperature.

From the fibre spectra the identity period along the fibre axis is $6 \cdot 65 \pm 0 \cdot 05$ Å.

The $hk0$ intensities are qualitatively interpreted with the aid of structure factor graphs. A threefold helix structure of the chain is postulated thus establishing the isotacticity of the polymer.

5

THE CRYSTALLINE STRUCTURE OF ISOTACTIC POLYSTYRENE

by G. NATTA and P. CORRADINI

(25 May 1955)
[*Makromol. Chemie* **16**, 77 (1955)]

ABSTRACT

The X-ray fibre spectra of isotactic polystyrene are fully interpreted in this paper.

Polystyrene crystallizes in the space-group $R3c$ ($R\bar{3}c$) with unit cell constants $a = 21{\cdot}9$, $c = 6{\cdot}65$ Å.

From space-group considerations it follows that the only conformation of the chain is that of a threefold helix. A first approximation model of chain packing obtained from the study of $hk0$ reflections is proposed (Fig. 1). This approximation will be confirmed and refined in subsequent papers.

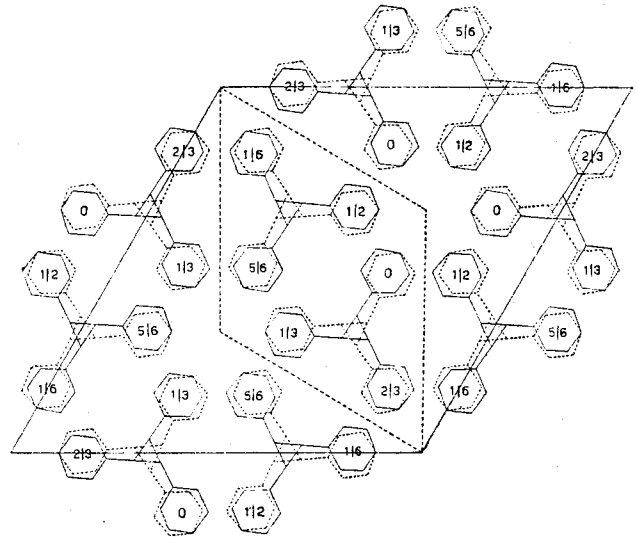


FIG. 1. Projection on a plane normal to the c-axis of the elementary unit cell of polystyrene.

6

NEW RESEARCHES IN THE FIELD OF OLEFINS*

by G. NATTA

(7 June 1955)
[*Proc. 4th World Petroleum Congress*, Section IV/C; Repr. 13 (1955)]

INTRODUCTION

In this communication we report the results obtained from our research work performed in the last few years on some organic syntheses, using olefins as raw material. In particular we refer to those results that could possibly find some interesting practical applications.

This communication consists of two parts: in the first part we describe the results obtained from our research work started a long time ago; e.g. on the reactions of olefins with carbon monoxide, synthesis of acids and esters, etc.

For brevity reasons, we summarize here only the most significant conclusions and their most important aspects for any possible practical application.

In the second part, we describe the most recent research on the polymerization of α-olefins. Investigations in this field have just begun, but have already given original results of scientific and practical interest.

In fact we have obtained a new class of polymers with an exceptional regularity of structure, and with unexpected properties: i.e. high melting temperatures, high degree of crystallinity, a helix-shaped structure of the molecules in the crystalline state, and, above all, interesting mechanical properties.

Even though these two parts are separated, they actually represent a single communication, since they both deal with catalytic syntheses and with the use of olefins as raw material.

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* Lecture held at the 4th World Petroleum Congress, Rome (Italy), on 7 June 1955.

G. NATTA

RESEARCH ON THE CARBONYLATION OF OLEFINS, HYDROFORMYLATION

(*with* R. ERCOLI)

The research on hydroformylation had already begun in this Institute in 1941, but the most interesting results were obtained during the last few years, after studying the kinetics of the reaction.

Many other reactions, which proved to be highly interesting from an industrial standpoint, had already demonstrated the importance of kinetic studies. We began this study in the field of hydroformylation with the aim of determining the type of the kinetic equations and the values of their constants, in order to provide information for the study of the size of industrial reactors, for the most suitable reaction times, and for the surfaces of thermal exchange necessary to obtain a determined reaction run. This kinetic study is also interesting because it allowed us to understand better the reaction mechanism and its developmen by adopting the most suitable conditions with the highest possible yields.

In some reactions of organic chemistry, which stoichiometrically are trimolecular or of higher order, it often happens that a different kinetic order takes place. It can be hardly foreseen and can cause reaction rates quite different from those expected in the usual homogeneous reactions. In the case of oxosynthesis, the first research work had been performed on the basis that the reaction, even if catalysed, occurred as a direct addition of carbon monoxide and of hydrogen to the olefin.

In 1945, in our first research work on the kinetics of oxosynthesis[1] with the use of metallic Co as catalyst, we had already observed that the reaction was of the first order with regard to the olefin, and that for high pressures and with equimolecular mixtures of CO and H_2 the reaction rate was independent of the total pressure. We had attributed this phenomenon to the saturation of the catalyst suspended in carbon monoxide and to the fact that the addition step of CO to the olefin was the determining step of the reaction.

More accurate studies,[2] made in 1952, on hydroformylation in the homogeneous liquid phase, with dissolved catalysts, demonstrated that even under these conditions, the reaction rate was independent of the pressure, between 100 and 400 atm with equimolecular mixtures of CO and H_2.

Moreover, it appeared that the reaction was nearly of the first order with respect to the concentration of the cobalt employed, and that the heat of activation was high. The reaction rate was doubled within a range of 7-8°C. This behaviour had been attributed to a reaction occurring at different steps: the first of these, which was the slowest, consisted of the reaction of the olefin with the catalyst, and kinetically it depended on their concentrations, while the subsequent steps, which were supposed to be very fast, did not influence the kinetics of the overall process, which, from a kinetic point of view, depends on the slowest step. The experimental results obtained were confirmed later by U. S. chemists.[3]

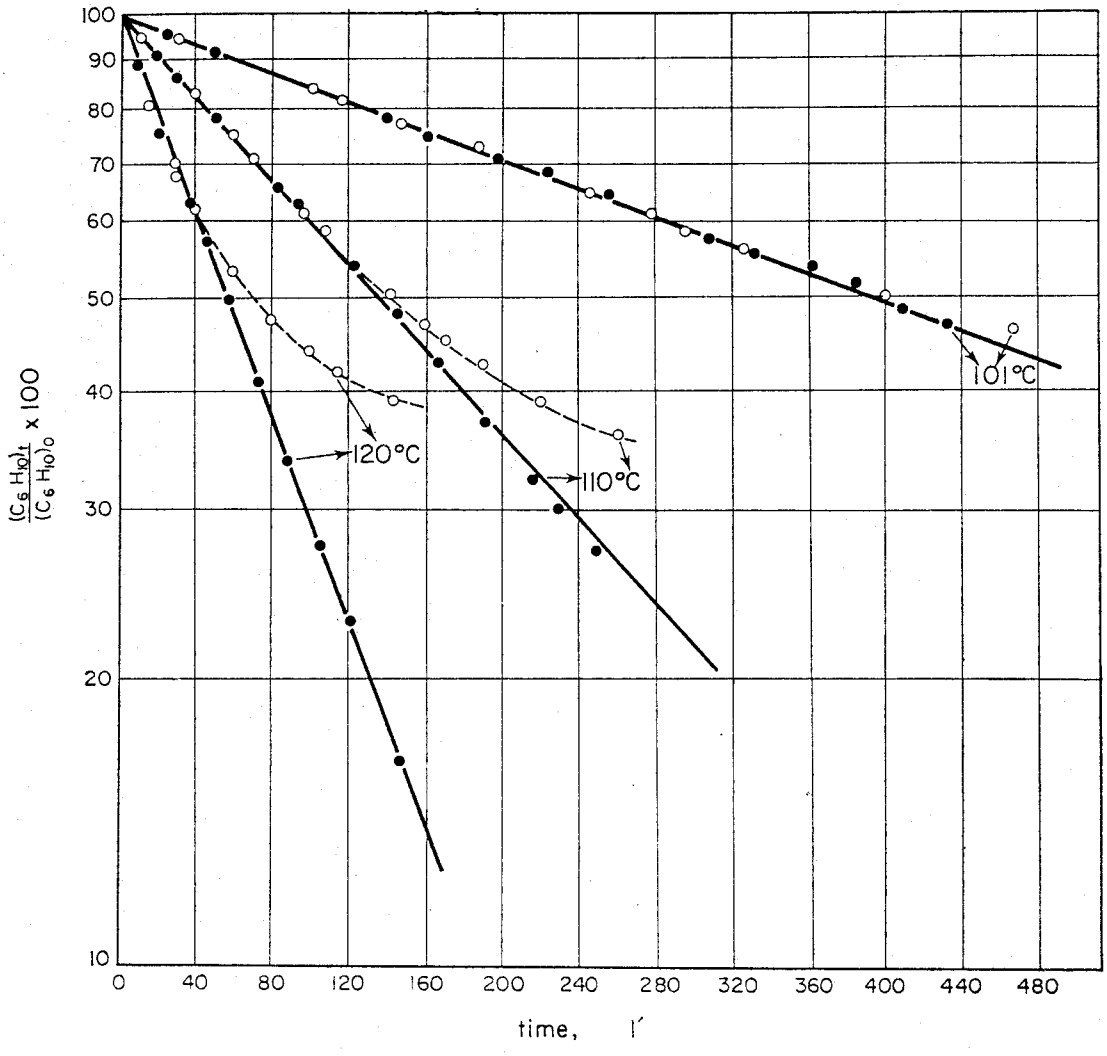


FIG. 1. Kinetic tests at constant volume (variable pressure) with $CO+H_2$ in equimolecular ratio. Above 30 atm the reaction rate is independent of the total pressure.

(Kinetics of hydroformylation:
C_6H_{10} in methylcyclohexane 42-44g%
$[Co(CO)_4]_2 = 2{\cdot}97$ g%
● 400-100 atm.
○ 65-15 atm.)

Our subsequent research done with mixtures of CO and H_2 in a stoichiometric ratio, allowed us to confirm that the reaction rate was independent of the total pressure, up to pressures of about 30 atm (Fig. 1). Some anomalies observed at lower pressures led us to accomplish kinetic studies at low pressures[4] with CO to H_2 ratios different from the stoichiometric one, that is, under conditions differing from those adopted in industry.

Experimental runs effected between 110 and 140°C, with the aid of dissolved cobalt carbonyl compounds, have emphasized the following items :

(a) The catalytic addition of CO and of H_2 to the olefinic double bond may also take place at exceptionally low pressures (4–10 atm) of CO.

(b) The hydroformylation rate, at a constant pressure, increases with the increase of the pressure of hydrogen.

(c) When the pressure of hydrogen is constant, the reaction rate increases with the increase of the partial pressure of CO until it reaches a maximum, which depends on the temperature, 8–12 atm, at 110–120°C. For each further increase of pressure of CO, the reaction rate decreases progressively.

(d) When the other conditions are equal, the range of pressures of CO, in which the reaction occurs more rapidly, corresponds to the range of pressures in which dicobaltoctacarbonyl and cobalt tricarbonyl co-exist in appreciable concentrations in the absence of hydrogen.

(e) The reaction is first order with regard to the olefin concentration.

(f) The reaction rate depends on the concentration of the dissolved cobalt in different amounts, according to the adopted pressure of CO ; for high pressures of CO, it tends to be proportional to the concentration of the dissolved cobalt.

(g) By operating with a H_2/CO ratio = 1, under a pressure ranging from 30 to 400 atm, the opposite effects of an equal increase of partial pressure of the two gases compensate one another and, therefore, the reaction rate is independent of the total pressure.

The above-mentioned items definitely confirm that the transfer process of carbon monoxide to the double bond does not occur by direct

reaction of CO with the olefinic compound, because in this case hydroformylation should be favoured kinetically by high pressures of CO.

Our most significant kinetic researches have been effected with a catalyst consisting of a pre-formed cobalt carbonyl; most probably, this is the reason that enabled us to observe these phenomena, which had not been noticed by former research workers.

When a cobalt salt is used as the catalyst, its transformation into a cobalt carbonyl compound is necessary, before the reaction begins. It can be observed from the longer induction period that this transformation is slow at low temperatures and under low pressures of CO. In the tests carried out under these conditions, it is possible that the reaction rate is influenced by the long induction periods.

Recently, Martin[5] by operating at 150°C with cobalt naphthenates, confirmed the results obtained by us with respect to the decrease of the pressure of CO above 25 atm.

In practice, using the pre-formed cobalt carbonyl and operating at low pressures of CO (partial pressure 10 atm), it is possible to

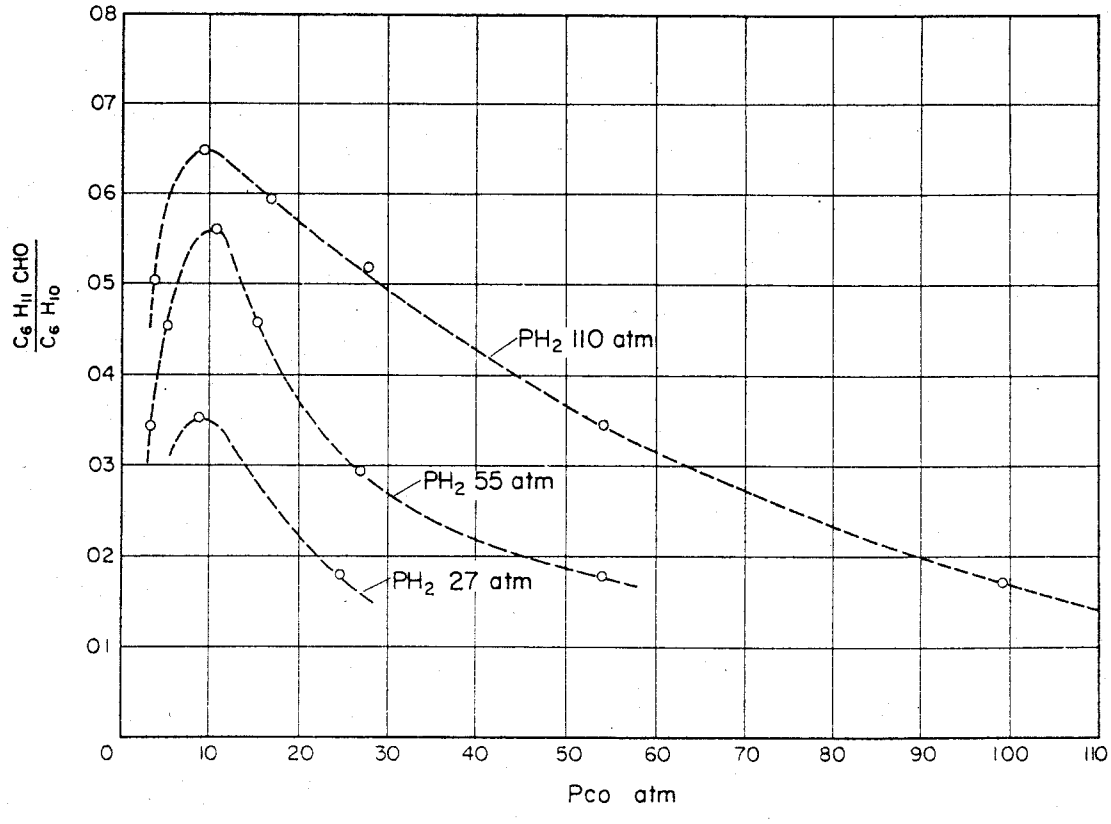


FIG. 2. Kinetic tests at constant pressure: conversion of cyclohexene into hexahydrobenzaldehyde vs. the pressure of carbon monoxide and of hydrogen

(*Kinetics of hydroformylation:*
$t = 110°C$; reaction time 68′; C_6H_{10} in toluene 33 g%;
$[Co(CO)_4]_2 = 1{\cdot}4$ g%.)

operate at temperatures of 100–120°C; at these temperatures, the secondary reactions are reduced, and reaction rates, which are higher than those obtained with equimolecular mixtures of CO and H_2 at a pressure of several hundred atmospheres, are obtained at rather low total pressures (30–40 atm).

For instance, under an overall pressure of 35 atm (8 atm of CO and 25 atm of H_2) the reaction rate at 110°C is almost double the rate at a total pressure of 110 atm, but with equimolecular mixtures of CO and H_2.

On the other hand by operating at a constant total pressure, it can be observed that, at 120 atm, the rate, with a ratio $H_2 : CO = 10 : 1$ is more than triple the rate obtained with the ratio 1 : 1. The curves in Fig. 2 clearly demonstrate the exceptionally favourable effect exerted by the use of low pressures of CO on the reaction rate.

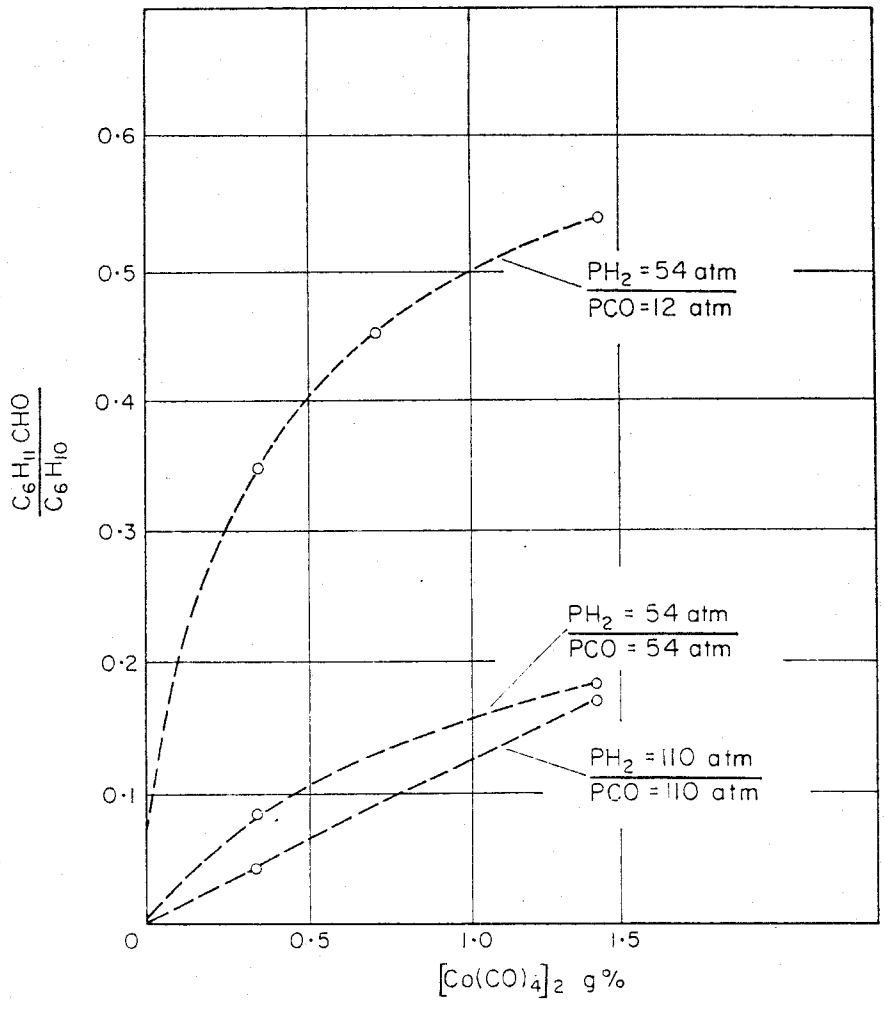


FIG. 3. Effect of the concentration of dissolved cobalt on the reaction rate at different pressures of carbon monoxide and of hydrogen.

(*Kinetics of hydroformylation:*
t = 110°C; reaction time 68′; C_6H_{10} in toluene 33 g%.)

It can be seen from Fig. 3, that the influence of the catalyst concentration on the reaction rate differs according to the pressures of carbon monoxide. As it was previously quoted, at high pressures (higher than 60 atm) the reaction rate is nearly proportional to the concentration of cobalt, while at low pressures it is almost proportional to its square root.

The addition mechanism of carbon monoxide and of hydrogen to the olefinic double bond has not yet been sufficiently clarified. The reaction is catalysed by dissolved cobalt, employed in the form of its addition compounds with carbon monoxide and possibly with hydrogen. Tetracobaltdodecacarbonyl $[CO(CO)_3]_4$ (called cobalt tricarbonyl), cobalt hydrocarbonyl $HCo(CO)_4$ and dicobaltoctacarbonyl $[Co(CO)_4]_2$ are well known nowadays; but very little is known[6] about the effect of the partial pressure of CO on equilibrium I, while nothing is known about equilibrium II.

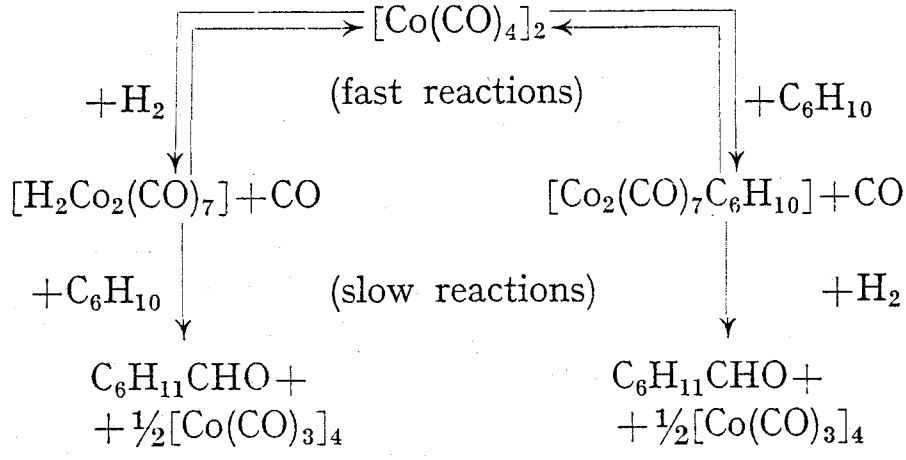
$$2[Co(CO)_4]_2 \rightleftharpoons [Co(CO)_3]_4 + 4CO \qquad \text{I.}$$

$$[Co(CO)_4]_2 + H_2 \rightleftharpoons 2HCo(CO)_4 \qquad \text{II.}$$

Oxosynthesis occurs with the highest rate at low pressures of carbon monoxide, that is when, in the absence of hydrogen, tricarbonyl and cobalt octacarbonyl coexist in appreciable amounts. Thus, it is decreased by too high concentrations of CO (high pressures).

These facts may be explained by assuming the existence of a competition phenomenon between carbon monoxide and either hydrogen or olefin. Oxosynthesis of cyclohexene could be represented, for instance, with scheme A :

[A]



or else, starting from cobalt hydrocarbonyl, according to scheme [B], admitting that the olefin is able to replace a CO molecule of the hydrocarbonyl.

[B] $$[Co(CO)_4]_2 + H_2 \rightleftarrows 2\,HCo(CO)_4$$

$$HCo(CO)_4 + C_6H_{10} \rightleftarrows [HCo(CO)_3 \cdot C_6H_{10}] + CO \qquad \text{III.}$$

$$[HCo(CO)_3 \cdot C_6H_{10}] + HCo(CO)_4 \longrightarrow$$

slow reaction

$$\longrightarrow C_6H_{11}CHO + \tfrac{1}{2}[Co(CO)_3]_4$$

Even if either scheme explains the kinetic aspects of the reaction, we preferred to study (with the co-operation of Dr. S. Castellano, of Montecatini, S. p. A.) the scheme indicated in [B], from a quantitative point of view.

When studying scheme [B], we considered the equilibriums I and II and applied the method of minimum squares for calculating the constants. By indicating with α the concentration of dicobalt octacarbonyl present in equilibrium under the reaction conditions, the kinetic expression corresponding to scheme [B] becomes :

$$\ln \frac{a}{a-x} = N.\,t.\,\alpha.\,\frac{P_{H_2}}{P_{CO}} \qquad \text{I.}$$

where $N(= K.k_{II}k_{III})$ is the product of the K, kinetic constant, multiplied by the constants of equilibriums II and III.

The agreement between the experimental points and those plotted from the curves obtained by calculation (Fig. 4) is satisfactory with regard to the tests carried out at 120°C; whereas, it is less certain with respect to those tests carried out at 110°C. Probably, our suppositions advanced in order to avoid extremely complicated mathematical calculations, that only one reaction rate was the determining one from a kinetic point of view (i.e. the slow rate) was not justified. This simplification leads to less representative theoretical previsions with regard to tests performed at lower temperatures.

Although our interpretation of the intermediate reaction mechanism is still in a preliminary stage, our kinetic knowledge allowed us to obtain the most suitable reaction conditions for hydroformylation, and for other reactions in which carbon monoxide reacts with catalysts like cobalt carbonyls.

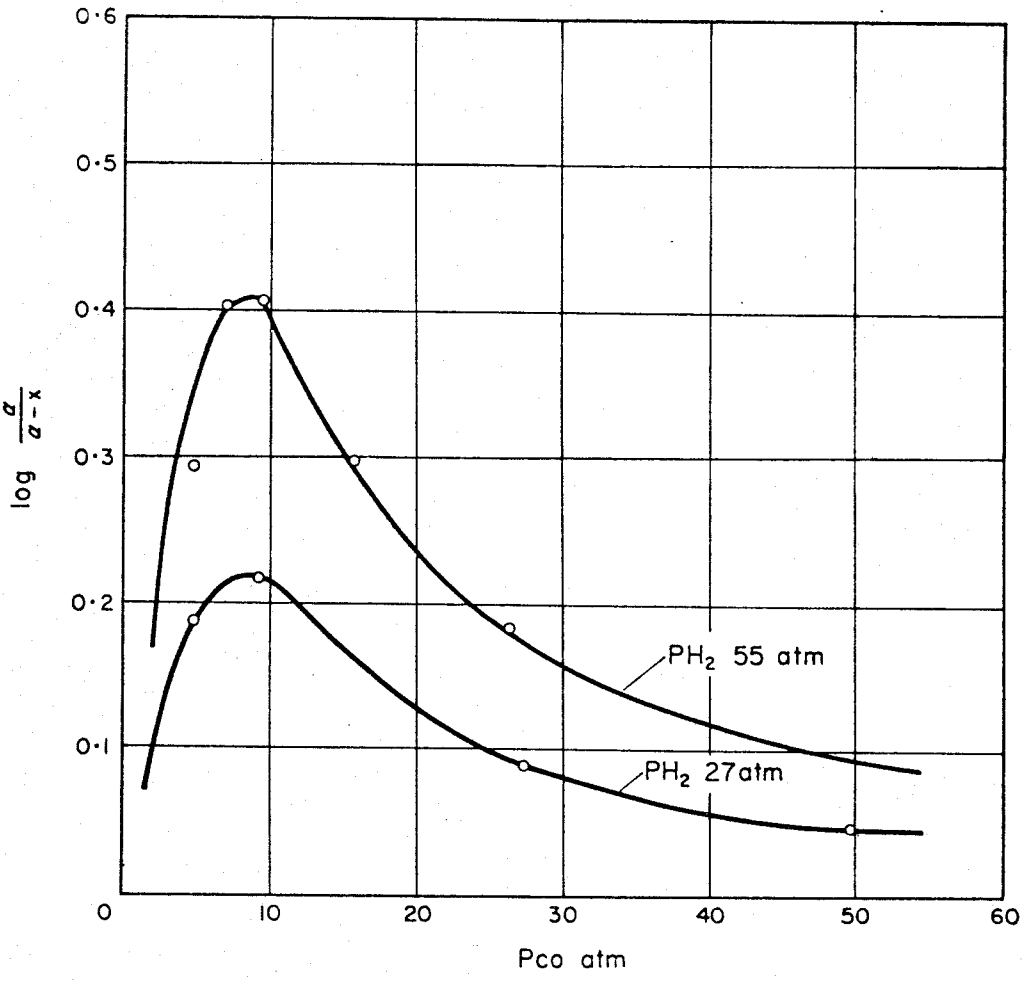


FIG. 4. Comparison between the kinetic results obtained at 120°C, and the curves calculated from the reaction mechanism [B].

(*Kinetics of hydroformylation:*
$t = 120°C$; reaction time 68' min; C_6H_{10} in toluene 33 g%;
$[Co(CO)_4]_2 = 0{\cdot}35$ g%
———— calculated curve
O experimental results.)

SYNTHESIS OF ACIDS AND THEIR ESTERS

(*with* P. PINO *and* R. ERCOLI)

The kinetic studies on oxosynthesis have also been applied to the direct synthesis of acids and of esters by the reaction of olefins with CO and with water and alcohols, respectively.

When operating under suitable conditions, we succeeded in increasing selectively the desired reaction rate, by the reduction of the formation of products derived from secondary reactions.[7]

The kinetic mechanism of the synthesis of esters is somehow analogous to that of the oxosynthesis.[8]

The synthesis of esters, however, occurs with fairly good rates, only at temperatures higher than those used for the oxosynthesis reaction. It follows that, when employing the same type of catalyst, one observes a modification of the value of the pressure of CO, which corresponds to the highest reaction rate.

This is due to the fact that the cobalt carbonyl complexes are stable at high temperatures only under high pressures of carbon monoxide.

At these temperatures, the dependence of the reaction rate on the pressure of carbon monoxide, even if clearly detectable, is less marked than in the oxosynthesis. In fact, when increasing the pressure of CO from 80 atm to 400 atm, one observes a progressive lowering of the rate of the synthesis of esters, and this is even more marked at higgher pressures. The formation of acetals, along with that of esters, is even more decreased by the increase of the pressure of carbon monoxide.

The synthesis of esters shows further analogies with the synthesis of aldehydes. Similarly to the latter, where the reaction rate is proportional to the pressure of hydrogen, in the synthesis of methyl ester, the reaction rate increases almost proportionally to the concentration of methanol (Fig. 5).

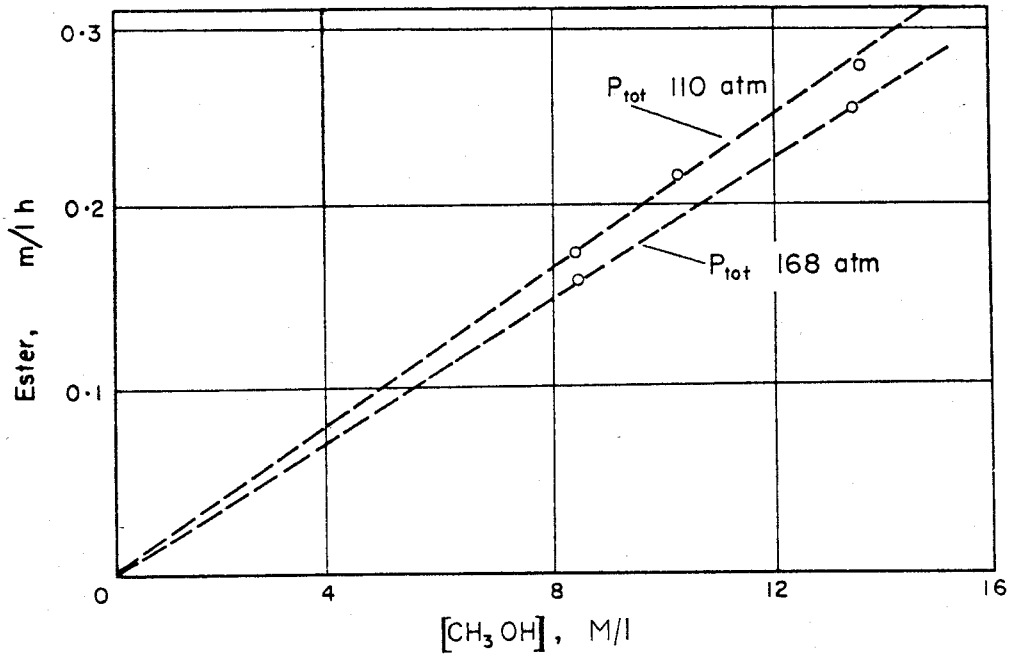


FIG. 5. Rate of formation of methyl hexahydrobenzoate vs. the concentration of methanol.

(*Kinetics of the synthesis of esters:*
$[Co(CO)_4]_2 = 3$ g%; $t = 165°C$; reaction time 260';
ester in m/l.h)

Generally, in the synthesis of esters, a great influence is exerted by the type of alcohols employed.

If one operates with a large excess of methanol in comparison with the olefin, then the reaction occurs with good yields and with little formation of secondary products, see Table 1 (synthesis of esters in the presence of an excess of methanol).

TABLE 1. CONVERSION OF CYCLOHEXENE INTO ALDEHYDE AND HEXAHYDROBENZOIC ESTER AT 165°C VS. THE MOLECULAR RATIO: ALCOHOL/OLEFIN $[Co(CO)_4]_2 = 4{\cdot}5$ g/cm³

CH_3OH (moles)	Cyclohexene (moles)		React. time (hr)	Max. p. (atm)	Alcohol/ olefin (moles)	Conversion into ester (%)	Conversion into aldehyde (%)
	Used	Recovered					
1·084	0·542	0·306	7·30	240	2	34	4·5
1·50	0·375	0·104	6·15	246	4	58·5	3·7
1·50	0·375	0·065	6·00	.107	4	62	13·0
1·87	0·234	0·026	5·30	242	8	74·5	4·2

In this case, according to the reactivity of the olefin employed, one can adopt reaction temperatures ranging from 170°C (cyclohexene) to 130°C (propylene) (Table 2).

TABLE 2. SYNTHESIS OF BUTYRRIC ESTERS STARTING FROM PROPYLENE, FROM CARBON MONOXIDE AND METHANOL AT 135°C, AT CONSTANT VOLUME. INITIAL PRESSURE: 250 ATM AT 25°C

CH_3OH moles used	moles CH_3OH / moles C_3H_6	$g[Co(Co)_4]_2$ in 100 g of solution $CH_3OH + C_3H_6$	Reaction time (hr)	moles butyric esters / initial moles C_3H_6
4·46	6	2·3	12	90
4·48	5	2·3	12	86
2·18	4·6	3·9	10	79

On the other hand, when employing other alcohols, in particular secondary alcohols, the presence of carbonyl cobalt complexes causes the partial dehydrogenation of alcohols, with the formation of the corresponding ketones and the transfer of hydrogen, which is used

in the hydroformylation of the olefin and in the synthesis of ketones starting from two moles of olefins, one of CO and one of H_2 :

$$2\,CH_2 = CH_2 + CO + H_2 \longrightarrow CO\begin{matrix}\diagup CH_2CH_3 \\ \diagdown CH_2CH_3\end{matrix}$$

Thus, simultaneous reactions occur, each of them depending on the other ; they help formation of ketones and of aldehydes, such as the dehydrogenation of primary and secondary alcohols, and the simultaneous addition of CO and H_2 to the olefins, in different stoichiometric ratios.

We point out that in this particular case, i.e. when considerable concentrations of molecular hydrogen are absent, the addition of CO and H_2 to low-molecular-weight olefins may be directed mainly to the formation of ketones.

However, the synthesis of esters by carboxylation of olefins is interesting only in the particular case of methyl esters.[9] Other procedures (e.g. synthesis of acids starting from olefins, from CO and from water followed by esterification, direct synthesis of methyl esters followed by their interesterification with higher alcohols and regeneration of methanol) seemed to be more suitable for the synthesis of esters of alcohols higher than the methyl ones.

Recent research carried out in this Institute allowed us also to effect the direct synthesis of acids to very high yields by considerably reducing side reactions.[10]

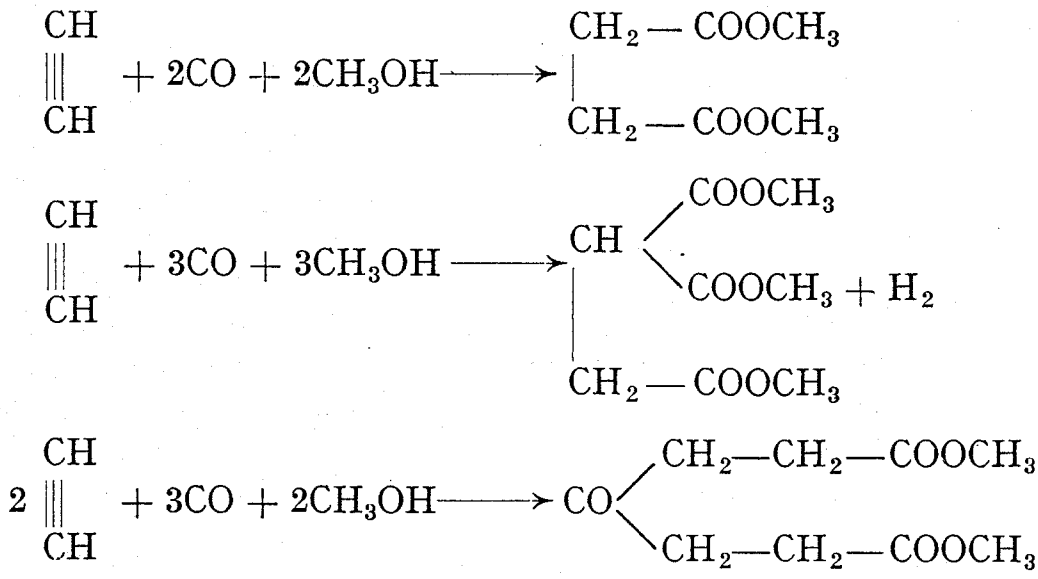
SYNTHESIS OF BICARBONYL DERIVATIVES, STARTING FROM ACETYLENE

(*with* P. PINO)

The great progress achieved by the processes of production of acetylene by the oxidation of natural gases at high temperature allows one to place the chemistry of acetylene in the wide field of petrolchemistry.

Our investigation in the field of acetylene reaction at high pressure with carbon monoxide gave results[11] of a certain practical interest.

Particular reaction conditions, and cobalt catalysts, instead of the nickel catalysts generally used by Reppe and co-workers,[12] allowed us to obtain by direct synthesis esters of bicarboxylic acids by the following reactions :



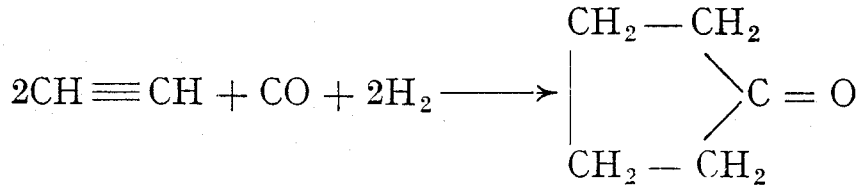
Recently, starting from acetylene, carbon monoxide and H_2O, it was possible to obtain succinic acid by a one step reaction, with yields higher than 80 per cent. This synthesis had already been performed at lower yields with the use of nickel catalysts.[13]

We must take into account that these syntheses can be achieved by using mixtures of acetylene and CO containing hydrogen and methane, thus avoiding the purification of acetylene obtained from methane.

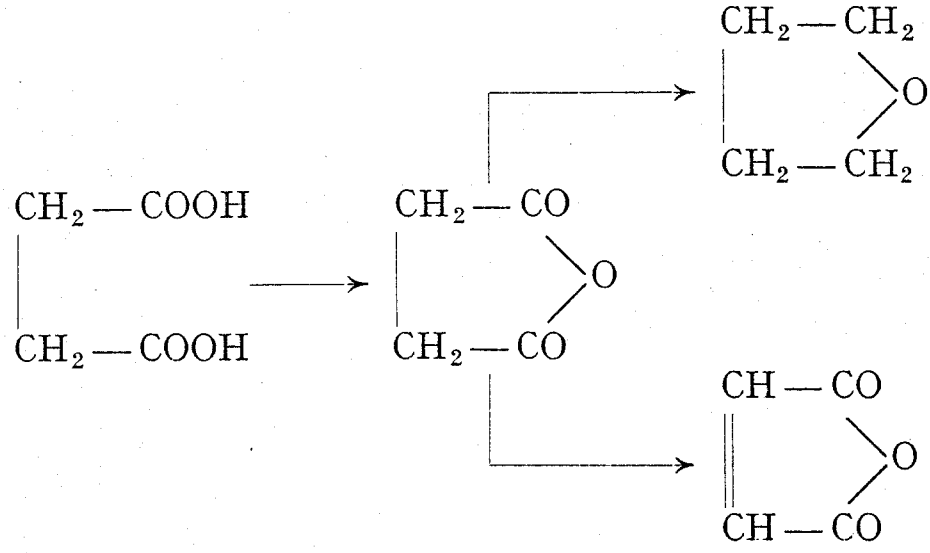
In fact, contrary to the synthesis of aldehydes and of esters from olefins, the synthesis of esters or of acids from acetylene, alcohols and water, respectively, takes place with a reaction rate higher than that of the carbonyl compounds obtained from acetylene, CO and hydrogen.

The oxosynthesis on acetylene is in fact a rather slow and very complicated reaction which yields high-boiling products.[14]

Only under particular conditions can the oxosynthesis cause the synthesis of cyclopentanone, though at rather low yields, following the scheme :



The direct synthetic processes studied by us might allow succinic acid to be obtained very cheaply, and to open new fields of application for this product, e.g. production of polyesters, of tetrahydrofuran and of maleic anhydride:



these last products being obtained by hydrogenation and by oxidation of succinic acid.

SYNTHESIS AND CHARACTERIZATION OF THE NEW POLY-α-OLEFINS WITH AN EXCEPTIONAL REGULARITY OF STRUCTURE

General Considerations on Poly-α-olefins

The polymerization of $CH_2 = CHR$ monomers, which should probably yield long chains, of the type

$$-CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-$$

in practice, by ordinary polymerization processes, yields polymers whose regularity of structure may be imperfect for different reasons. These are some of the better known ones:

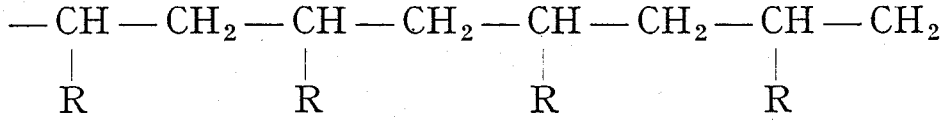
1. The presence of local head-to-head or tail-to-tail enchainments instead of only head-to-tail ones between the monomeric units. Chains of the following type are formed:

$$-CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-\underset{\displaystyle R}{\underset{|}{CH}}-CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-CH_2-CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-$$

2. The formation of abnormal branchings due either to chain transfer phenomena (frequent in polymerizations hindered by free radicals) or to dissociation phenomena of the intermediate polymerization products and their copolymerization with the monomer (frequent in polymerization processes involving a cationic mechanism). However, it results that many synthetic macromolecules, instead of being formed, as it was previously thought, by linear chains of unidimensional structure, actually consist of very branched molecules. The properties that such branchings may give to the product are sometimes appreciable and sometimes undesirable.

For instance I.C.I. polyethylene consists of strongly and differently branched polymers of ethylene ; its melting temperature and its degree of crystallinity is lower than that of the polymethylenes[15] and polyethylenes obtained by the Ziegler-type processes;[16] these polymers in fact are absolutely linear and free from branchings.

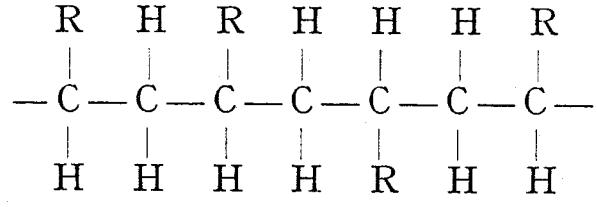
3. Moreover, vinyl polymers, even if they are formed by linear macromolecules with a complete head-to-tail enchainment, may be irregular, due to the presence in the chain, of asymmetric carbon atoms which alternate themselves with methylenic groups :



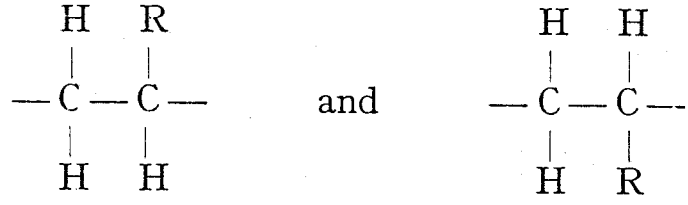
In the main chains of these ordinary polymers, the asymmetric carbon atoms with a particular steric configuration alternate in a disordered way with the carbon atoms, having a different steric configuration ; this causes irregularity along the main chains of macromolecules and hinders their crystallization.*

* From the literature it results that only polymers of alkylvinyl ether (C. E. SCHILDKNECHT *et al.*, *Ind. Eng. Chem.* **40**, 2104 (1948)) and of some substituted styrenes (A. NYQUIST and E. KROPA, Brit. patent 574,141 (7 Dec. 1943)) which were obtained previously, possessed traces of partial crystallinity. One might have supposed that they would contain asymmetric carbon atoms of a certain steric configuration, disposed with a definite regularity along the main chains of the macromolecules. These polymers, whose structure had not yet been established, did not find interesting practical applications primarily because of their difficult preparation. The necessity to establish a practical nomenclature for distinguishing the oriented polymers from the non-crystallizable ones was at that time overlooked.

According to Flory[17] a vinyl polymer containing asymmetric carbon atoms, such as



may be considered as a copolymer of two different polymeric units:



where the asymmetric carbon atom in one of them has the *l* configuration, and in the other the *d* configuration.

If these monomeric units, which contain an asymmetric carbon atom either with a *l* or a *d* configuration, repeat themselves statistically along the polymeric chain, as generally happens in all the known vinyl polymers, the polymer may be considered as a copolymer of two structural units; consequently, if the R substituent is much bigger than the H atom, the polymer is essentially amorphous and does not show a point of first order transition.

The polymerization of α-olefins of the aliphatic series has been the object of a great number of investigations by the most important petrochemical industries, as it results from the great number of patents filed on this subject.

The first attempts generally were concerned with the production of low polymers, which proved to be interesting as fuels and as lubricants. Only later on, after the success had been achieved with high polymers of ethylene, used as plastics and by the polymers and copolymers of isobutylene used as elastomers, did the petrochemical industries devote a great deal of their research to the polymerization of α-olefins for the production of high-molecular-weight polymers.

Linear α-olefins higher than ethylene could not be successfully used for the production of very high polymers by the previously known polymerization processes. The highest polymers of propene and of butene-1, obtained at low temperatures with the aid of known catalysts such as aluminium chloride and boron fluoride, were more or

less viscous liquid products, having hardly any practical interest. When examined by an I.R. spectrophotometer, they would show a very branched structure with branchings of different length.

The use of solid catalysts, containing polyvalent heavy metal oxides, has recently allowed the production of high-molecular-weight polymers, though only in the case of the polymerization of ethylene.

Patents on this subject have been filed by the Standard Oil of Indiana[18] and by the Phillips Petroleum Co.[19] Our research, effected by the use of the same catalysts, allowed us to observe that the ethylene polymers thus obtained were highly crystalline, as revealed by X-ray examination; consequently, they had a linear structure and were practically free from branchings. They were different from the polyethylene produced by the I.C.I. methods. Very high-molecular-weight linear polymers of ethylene were recently produced by simple methods at low pressures and temperatures by Ziegler; their properties have already been described at the last Hannover Trade Fair.

The Phillips and the Standard Oil of Indiana patents describe the production of polymers higher than ethylene; but the products obtained still had rather low molecular weight (lower than 20,000).

Our research on the production of propylene polymers with the aid of catalysts described in those patents, have up to now only resulted in low yields of almost completely amorphous polymers, having irregular structures. Only when employing technical propylene, which contains some percent units of ethylene, the mixture of the polymers obtained has small amounts of a solid crystalline product that, as revealed by X-ray examination, consists of polyethylene.

SYNTHESIS AND CHARACTERIZATION OF CRYSTALLINE POLYMERS OF α-OLEFINS

(*with* P. PINO, G. MAZZANTI, *and* P. CORRADINI)

According to the data found in the literature, it is impossible to obtain very high-molecular-weight solid polymers, which might be suitably employed as plastics, if one starts from linear α-olefins higher than ethylene. Possibly this could be attributed to the lack of structural regularity of the polymers obtained.

Our research study made with the aid of solid catalysts containing ions of small diameter, enabled us to effect a more regular polymeri-

zation with the obtainment of high or extremely high-molecular-weight polymers, whose molecular weight could be varied at will by some thousands or even hundred of thousands, consisting of chains with a regular structure and with a head-to-tail enchainment.

The surface of the solid catalyst employed enables the determination of a particular configuration, which has its influence on the steric configuration of the polymer, with respect to the monomer molecules, adsorbed on its surface near an active centre. However, if one does not adopt particular methods for the preparation of the catalysts, the polymers obtained are not for the most part homogeneous, but consist of mixtures of products showing very different physical properties.

In general, in a polymerization run, one finds crystalline and amorphous polymers. Their separation can be performed easily because their solubility, independently of their molecular weights, is different as is demonstrated by their properties shown in Table 3.

TABLE 3

Polymer	*M.W.*	*Structure*	*Solubility*
Polystyrene	1,000,000	crystalline	insoluble in methyl ethylketone
Polystyrene	1,000,000	amorphous non-crystallizable	soluble in methyl-ethylketone
Polystyrene	10,000	crystalline	insoluble in acetone
Polystyrene	10,000	amorphous non-crystallizable	soluble in acetone
Polypropylene	30,000	crystalline	insoluble in heptane
Polypropylene	30,000	amorphous non-crystallizable	soluble in heptane
Polypropylene	10,000	crystalline	insoluble in ether
Polypropylene	10,000	amorphous	soluble in ether

These crystalline polymers are particularly interesting because they are new and because they possess interesting and unforeseen properties.

The structure of the new crystalline high polymers of α-olefins has been determined by X-ray examination of the oriented fibres in these polymers.

The identity period of the elementary unit cell along the fibre axis of different poly-α-olefins was measured by us, as indicated in Table 4.

TABLE 4

Polymer	*Identity period along the chain axis (Å)*	*Melting point by X-rays (°C)*	*Density by X-rays*	*Density determined at 20°C*
Polypropylene	6·50±0·05	160	0·94	0·92
Poly-α-butene	6·70±0·1	128	0·96	0·91
Poly-α-pentene	6·60±0·1	75	—	0·87
Polystyrene	6·65±0·05	230	1·12	1·08

X-ray densities have been calculated for polystyrene and for polybutene on the basis of a hexagonal unit cell (space group = $R3c$ or $R\bar{3}c$) ; for polystyrene : $a = 21{\cdot}9$ Å ; for polybutene : $a = 17{\cdot}3$ Å. The unit cell contains 6 chain segments, each of them containing 3 monomeric units.

Because of lack of sufficient data, the determination of the exact unit cell and the X-ray density of propylene were calculated by interpreting the X-ray equatorial reflections on the basis of an oblique unit cell with $a = 6{\cdot}56$ Å, $b = 5{\cdot}46$ Å, $\gamma = 106°30'$, by taking into account the identity period along the fibre axis, $c = 6{\cdot}5$ Å.

From the above considerations, it appears that in all these cases, the identity period along the fibre axis is 6·5–6·7 Å.

By comparing the X-ray data with the density data it can be observed that each segment of the main chain, contained in the elementary unit cell, corresponds to 3 monomeric units (—CH_2——CHR—). It follows that a regular succession having alternately *d* and *l* atoms must be excluded. Among all the possible regular successions of *d* and *l* asymmetric carbon atoms that may yield a crystalline polymer, only the succession in which all the asymmetric carbon atoms have the same steric configuration can justify the X-ray data.

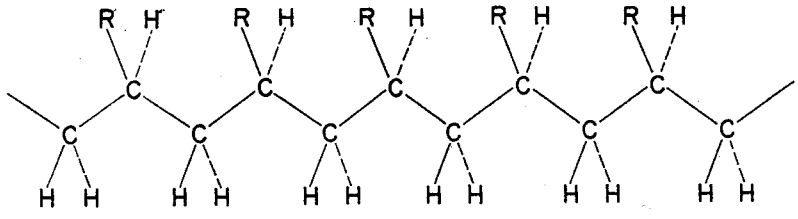


FIG. 6. Model of the main chain of an isotactic molecule stretched on the plane of the paper.

In Fig. 6 we show the model of the main chain arbitrarily stretched on the plane of the paper. The R substituents and the hydrogen atoms bound to the tertiary carbon atoms are, respectively, all above and all below the plane of the paper.

In this case, the steady existence of a paraffinic chain completely stretched on a plane, appears to be very improbable, due to the steric hindrances of the R substituents. In the crystalline state, the main chain must also assume a non-planar configuration.

The X-ray examination revealed that this configuration has a spiral shape. The hypothesis of a screw configuration of the main chain in the crystalline state agrees with the value of the identity period along the same chain (6·5-6·7 Å), which is shorter than the length of the planar structure when completely stretched (7·62 Å for three monomeric units).

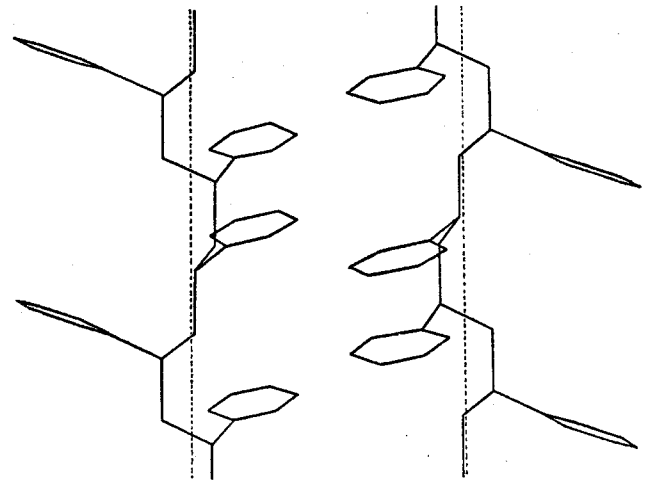


FIG. 7. Projection on a plane parallel to the *c*-axis of macromolecular chains of crystalline isotactic polystyrene.

In Fig. 7 we have drawn the chain structure of polystyrene, which we could determine more accurately.

Considering the projection of the elementary unit cell on the plane normal to the *c* axis (see Fig. 1 of paper 5), it is possible to observe that each left-handed helix is surrounded by three right-handed helices and vice-versa.

Such a structure provides these polymers with properties that were previously unknown in polyhydrocarbons. In fact, these high-molecular-weight products are, at ordinary temperatures, crystalline solid products which differ greatly from those elastomers, obtained from

isobutene. These elastomers, at ordinary temperatures, are crystallizable only under pressure and show a linear screw chain, though with a very different identity period.

The same order of crystallinity is also found in low-molecular-weight polymers. For example, we obtained low-molecular-weight polypropylenes (m.w. 2500) and polystyrenes (m.w. 1200) which show the same crystalline structure as polymers having much higher molecular weights.

In order to avoid possible misunderstandings, in the interpretation of the new regularly-structured polymers, one has to abandon the nomenclature used for the low-molecular-weight compounds containing asymmetric carbon atoms, based on the optical activity of these compounds.*

In a communication presented at the Accademia Nazionale dei Lincei on 11 Dec. 1954,[20] in which for the first time we described this type of polyhydrocarbon, we proposed to call those polymers having successive carbon atoms of the same steric configuration "isotactic", a word coined from the Greek : *ἴσος* (same), *τάττω* (to place in order).

MECHANICAL PROPERTIES OF THE ISOTACTIC POLYMERS

(*with* F. DANUSSO, G. LUTZU, *and* G. MORAGLIO)

The greatest differences which exist between the properties of isotactic and non-isotactic polymers are observed in their visco-elastic behaviour.

Linear, non-isotactic polymers may be considered as liquids of very high viscosity, which is higher the higher their molecular weight. For molecular weights higher than 20,000, these products are elastic solids, but they are deformed easily and permanently by viscous flow.

* Regularly-structured polymers, obtained from optically inactive monomers, did not show any optical activity, even if each molecule contained a succession of carbon atoms of the same steric configuration. Each macromolecule, consisting of asymmetric atoms with the same orientation, could only show a weak optical activity. In fact, the optical activity of the asymmetric carbon atoms, contained in one half of the chain, is eliminated by the internal condensation of the second half, except for the influence of the end groups. An optically inactive polymer is generally obtained, because the weak optical activity, attributed to each molecule, is completely annulled by external compensation of couples of enantiomorphous molecules.

Linear paraffinic polyhydrocarbons show a very low temperature of second order transition (about -35°C for linear non-isotactic polypropylene). Head-to-tail non-isotactic linear polystyrene has a temperature of second order transition of about +90°C, which practically coincides with that of ordinary polystyrenes. It is observed, even if less markedly, at the same temperature in isotactic polystyrenes that are not well crystallized.

All the crystallized isotactic polystyrenes show a temperature of first order transition of about 230°C.

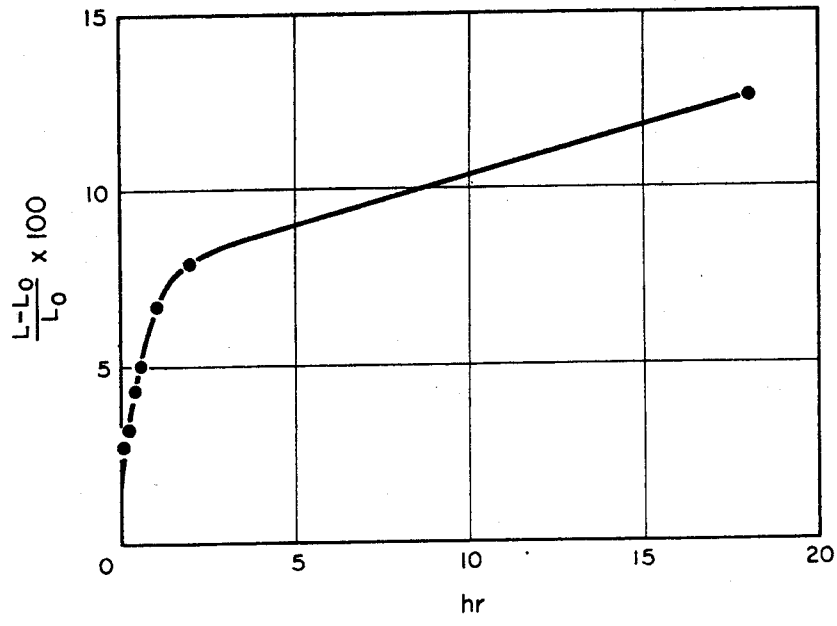


FIG. 8. Curve of the constant deformation under stretching (15 g/cm) of a linear non-isotactic polypropylene (m.w. about 20,000).

In Fig. 8 we show the flow curves of a non-isotactic polypropylene having a molecular weight of about 20,000, for which one can observe its viscous flows at ordinary temperature (+23°C) and under very low stresses.

The isotactic polymers, on the contrary, show very different mechanical properties, as is shown in Fig. 9, for a crude polypropylene with an average molecular weight of about 30,000. Tensile strength increases with the increase of molecular weight and of crystallinity. The isotactic polymers of very low molecular weight crystallize more easily, forming bigger crystals, but since they are the product of short molecules they are fragile and show very low values of elongation at break.

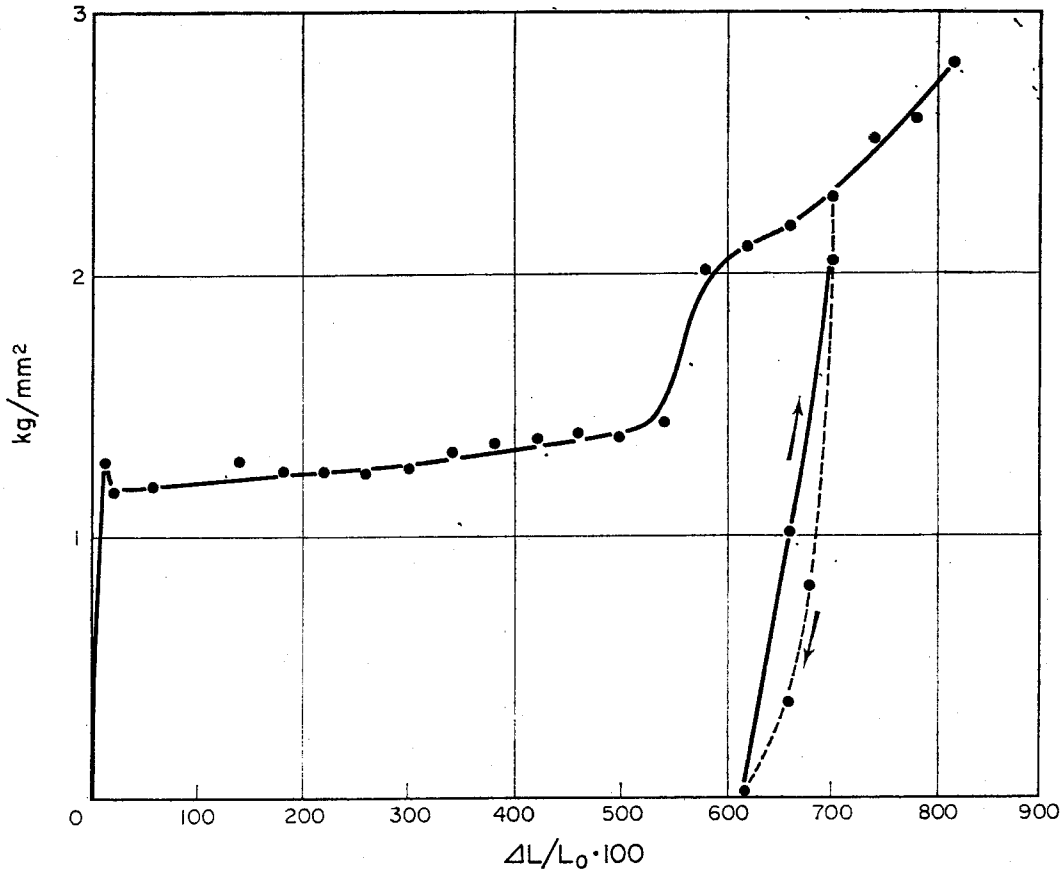


FIG. 9. Stress–strain diagram of an isotactic polypropylene with a rather low average molecular weight (m.w. 30,000).

Polypropylenes having a molecular weight of 40,000–50,000 may be extended at higher temperatures than those of the first order transition. On cold stretching one obtains oriented products with a high tenacity (Fig. 10).

The high tenacity of some extruded samples is a consequence of the stretching which takes place during and after the extrusion. As opposed to the best known crystalline polymers (e.g. nylon, terephthalate of glycol, obtained by condensation processes, which in general do not show very high molecular weights), polypropylenes and in particular polypropylenes having very high molecular weights (above 100,000), show, above the temperature of first order transition, a wide range of temperatures, at which they behave as plastic and elastic materials of high viscosity.

Therefore very high-molecular-weight polymers (for instance those having a m.w. higher than 200,000) can only be extruded with great difficulty and only at temperatures much above the crystallographic melting.

The highest tensile strengths have been observed in samples with the highest molecular weight. In a sample of molecular weight higher

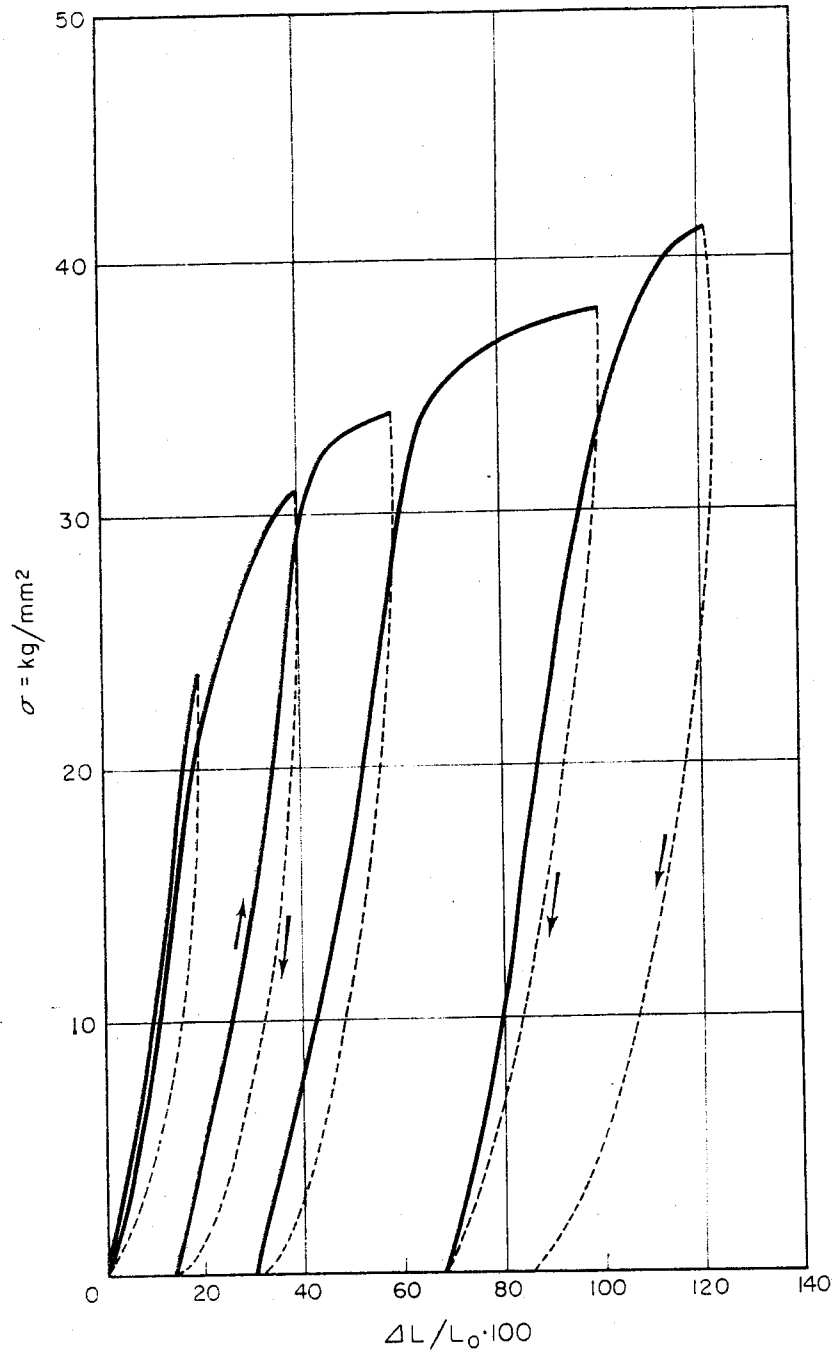


FIG. 10. Stress-strain diagram in successive stages under increasing stress of an isotactic polypropylene fibre having a molecular weight higher than 200,000, oriented by previous partial stretching.

than 200,000, extruded and subsequently subjected to a preliminary stretching up to a stress corresponding to 60 kg/mm² referred to the actual section, we observe (Fig. 11) a very high elasticity (reversible deformation of about 20 per cent) and a tensile strength of more than 75 kg/mm² with an elongation at break point of about 30 per cent. These last data are related to the section obtained after the recovering of elasticity subsequent to the preceding stretching.

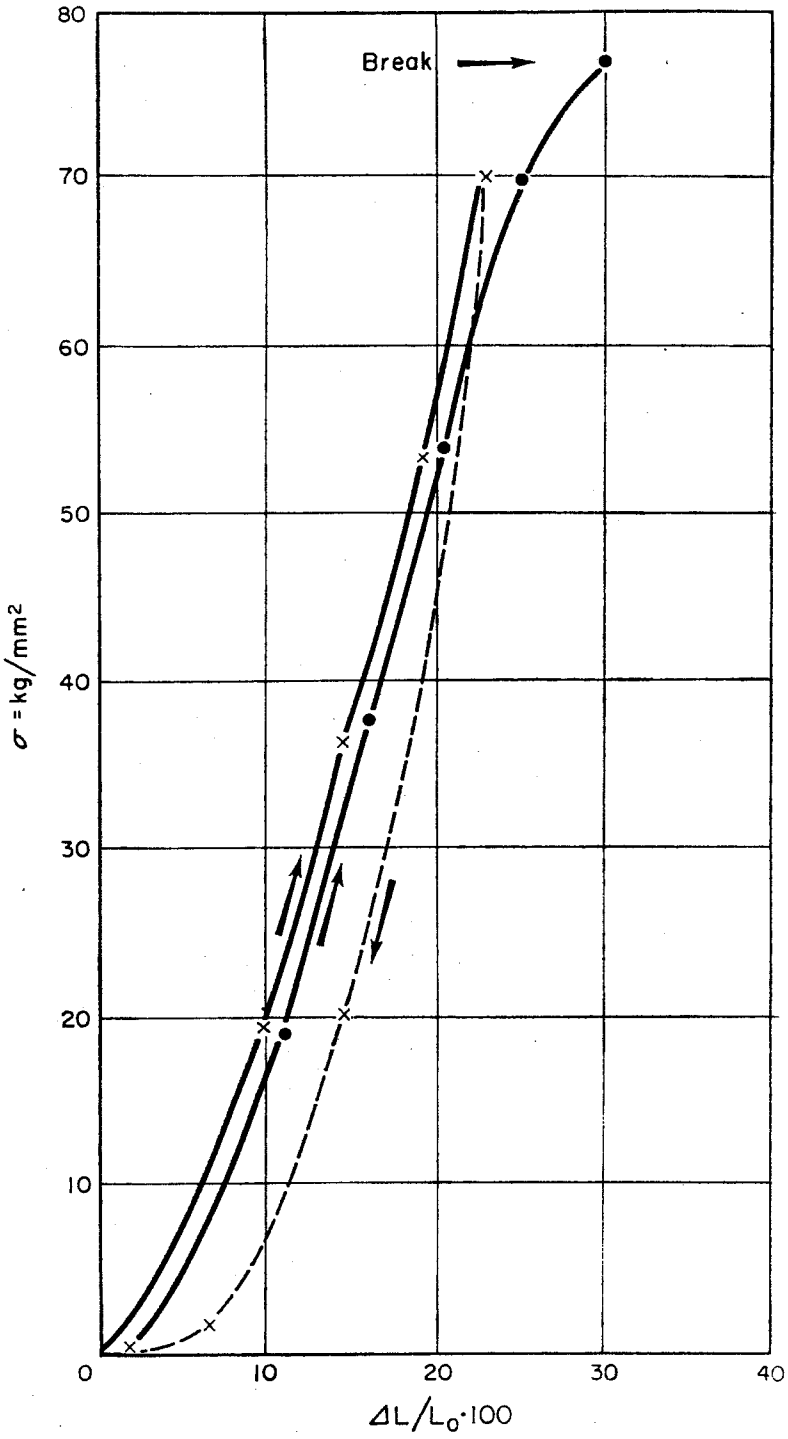


FIG. 11. Stress–strain diagram of an isotactic polypropylene fibre, stretched at its maximum, having a molecular weight higher than 200,000.

Elongations at break depend on the previous orientation of the material in the preliminary stretching step.

Pressed sheets of prevailingly isotactic polypropylene, which have not been subjected to orientation during moulding effected at 200–220°C, show very high elongations at break up to

700–900 per cent. Other samples of molecular weights of 120,000–150,000 show tensile strengths of 4–5 kg/mm² with regard to the initial section, and 30–50 kg/mm² with regard to the final section (Fig. 12). They show a hardness Shore of about 100.

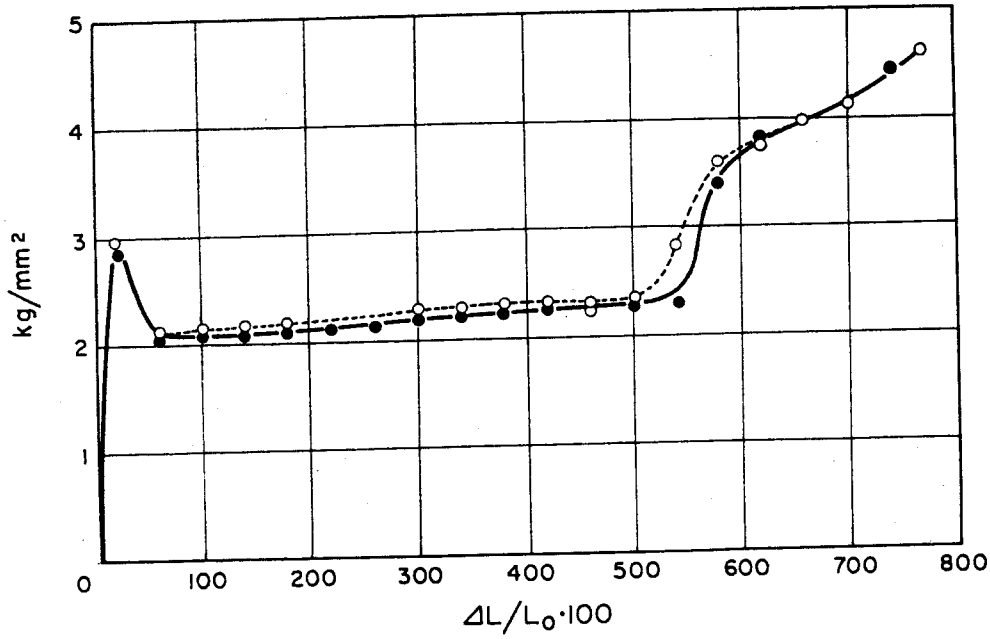


FIG. 12. Stress-strain diagram of a prevailingly isotactic polypropylene sheet, having an average molecular weight of 120,000–140,000, moulded at 200°C. Rate of strain: 50 mm/1'; test tube: ASTMC.

The idea of employing some partially or totally isotactic polymers as construction materials seems highly interesting. In the oriented state, they can adsorb considerable amounts of energy as work of elastic deformation and with a rather low hysteresis.

Some types of polypropylenes show, from numerous standpoints, thermal properties higher than those of polyethylenes.

Polybutene shows a low temperature of the first order transition (125–130°C); that is why some samples with the same molecular weight can be moulded and extruded at lower temperatures than isotactic polypropylene.

Isotactic polystyrene is of particular interest: in the crystalline state, it has a melting temperature, determined by X-rays coincident with its transition temperature and measured by dilatometric means, of about 230°C. We prepared polystyrenes having a desired molecular weight ranging from 1000 to several millions. At temperatures above 230°C they became amorphous and very viscous. Low-molecular-weight isotactic polystyrenes (m.w. 1000–2000), on the contrary, melt at a slightly lower temperature, yielding mobile liquids.

Our research demonstrated that the behaviour in solution of isotactic macromolecules of polystyrene is not very different from that of non-isotactic polystyrene: it follows that the average molecular weights may be evaluated by the usual viscosimetric methods.

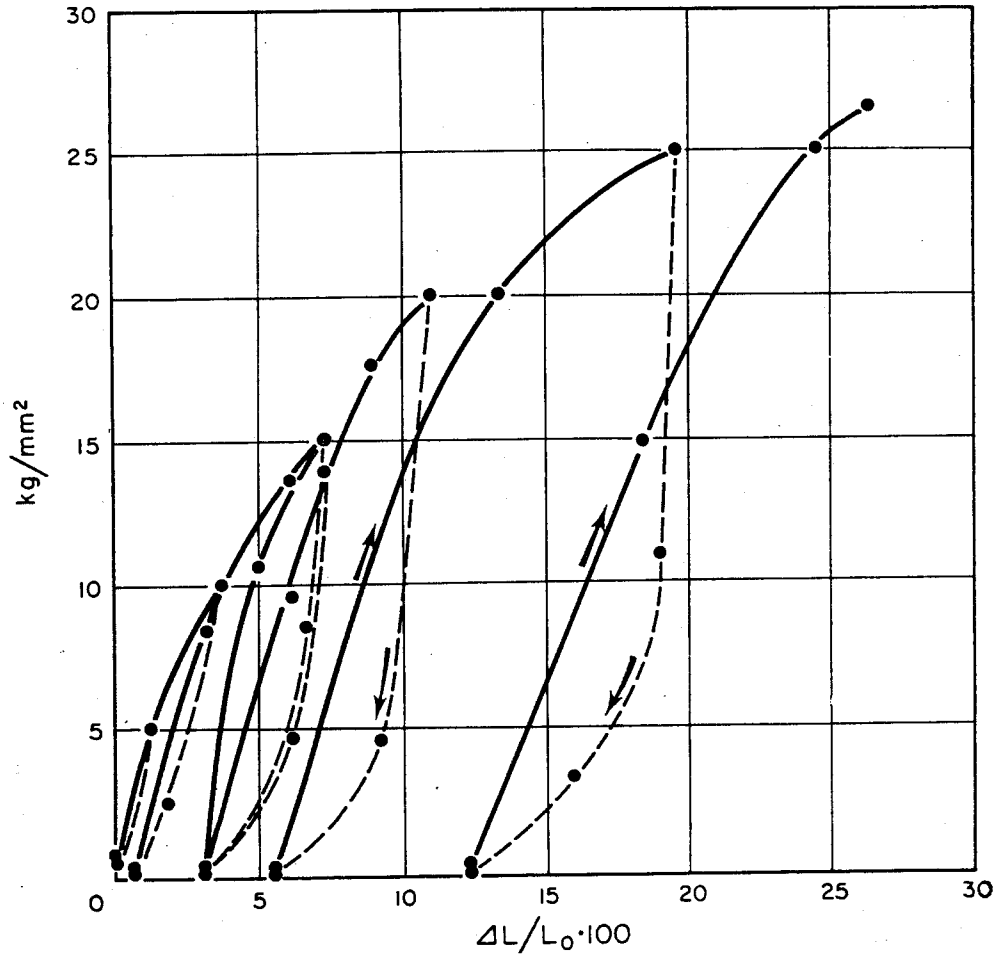


FIG. 13. Stress-strain diagram in successive stages under increasing stress of an extruded sample of polybutene, having an average molecular weight of 33,000.

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7

SYNTHESIS AND STRUCTURE OF SOME CRYSTALLINE POLYHYDROCARBONS CONTAINING ASYMMETRIC CARBON ATOMS IN THE MAIN CHAIN

by G. NATTA, P. PINO and G. MAZZANTI

(22 July 1955)
[*Chimica e Industria* **37**, 927 (1955)]

ABSTRACT

The production of isotactic polymers from monomers containing a vinyl group may be effected by the use of very different conditions.

Isotactic poly-α-olefins may be obtained with catalysts of the same type as those used by Ziegler for the polymerization of ethylene at low temperature and low pressure. Low-molecular-weight isotactic polypropylene has been isolated among the propylene polymerizates with the use of catalysts based on metal oxides.

In the case of vinyl ethers, it is possible to obtain isotactic polymers with catalysts of boron fluoride type.

With regard to the chemical behaviour of isotactic polymers, we have studied their depolymerization, isomerization, chlorination and oxidation.

High-molecular-weight isotactic polymers maintain their characteristic regularity of structure, even during prolonged heat treatments with strong catalysts of isomerization, such as aluminium halides.

A very fast depolymerization of isotactic polymers occurs in the reactions taking place by a radical mechanism (oxidation with oxygen in the presence of peroxides, chlorination with elementary chlorine, etc.) whereas the depolymerization either thermal or in the presence of ionic catalysts is slower.

Chlorination of the isotactic polymers causes a gradual decrease of their crystallinity, which completely disappears in the case of polypropylene and of polybutenes for a chlorine content higher than 30 per cent.

8

ISOTACTIC POLYMERS*

by G. NATTA

(28 July 1955)
[*Makromol. Chemie* **16**, 213 (1955)]
[*Chimica e Industria* **37**, 888 (1955)]

DESCRIPTION OF ISOTACTIC POLYMERS

Some crystalline polymers of α-olefins were described in a communication presented by the author at the Accademia Nazionale dei Lincei on 11 December 1954, and in subsequent publications.[1] The molecules of these polymers show a very high regularity of structure and a strictly head-to-tail enchainment of the monomeric units and, at least for long portions of the main chain, they contain carbon atoms with the same steric configuration. These polymers are in general easily crystallizable and have high melting points; in the crystalline state, their molecules have a helix-shaped structure, characterized by an identity period along the chain axis of 6·5–6·6 Å, corresponding to three monomeric units. The author proposed to the I.U.P.A.C. Commission on Macromolecules that all the polymers having this regularity of structure should be called "isotactic".

The structure of isotactic polymers has been determined by studying interferences with electrons and X-rays.[2]

The side and end views of an isotactic polymer chain (poly-α-butene) are represented in Fig. 1.

This chain has one of the various configurations foreseen by Bunn[3] for paraffinic chains, taking into account the valence angles and the steric hindrances to the free rotation of the C—C bond.

* Lecture presented at the Symposium of Macromolecular Chemistry, Zurich, on 28 July 1955.

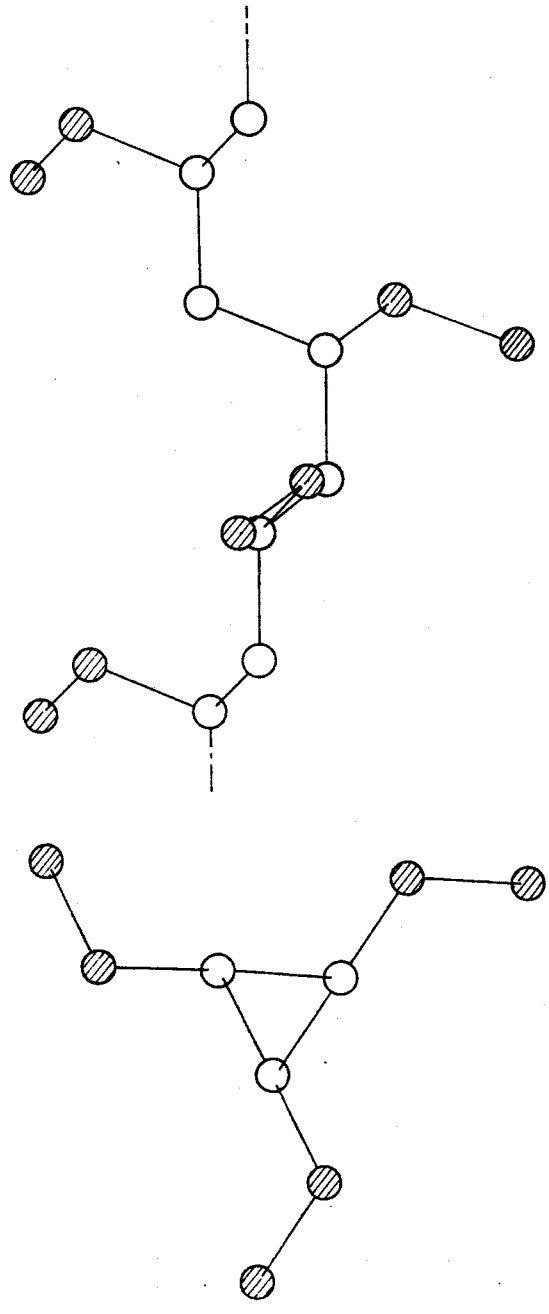


FIG. 1. Side and end views of the chain of isotactic crystalline poly-α-butylene. The atoms of the side chain are shaded.

The main chain of crystalline polymers is formed by sequences, each consisting of 4 carbon atoms, contained in a plane with a *trans*-enchainment. The bonds linking the terminal carbon atoms of each group to the preceding or following carbon atom are rotated by $+120°$ and $-120°$, respectively, in comparison with the position they would have, had the whole chain been planar. Bunn attributed a ternary symmetry to such a chain, and an identity period (6·2 Å) which is slightly lower than that observed by us.

This chain configuration is not stable in the paraffinic chains of linear unbranched hydrocarbons, in spite of the presence of lines that can be attributed to an "oblique" enchainment, observed by us in the photograms of very high-molecular-weight (more than 200,000) polymethylenes and polyethylenes, which had been subjected to many and intensely cold mechanical deformations.[4]

In the solid state, this structure is stabilized by the presence of asymmetric carbon atoms with the same steric configuration, linked to bulky substituents (CH_3, C_2H_5, etc.). In fact only with this structure, the shortest distances between the carbon atoms of the R groups of the same molecule do not become shorter than about 4 Å without causing deformations of the bonds or of the valency angles. A planar structure of the chain, such as that of polyethylene, would cause a very compact packing, which is not admissible for the R groups, or excessive deformations of the valence angles.

The structure of the chain of polystyrene was more accurately determined by us.[5] Figure 1 of paper 5 shows the projection of the elementary unit cell on a plane normal to the *c*-axis. It should be borne in mind that two types of helices (one right- and one left-handed) are possible in adjacent positions in the crystalline lattice.

The structures of polystyrene and polybutene, as revealed by X-ray examination, correspond to hexagonal unit cells (space-group $R3c$ or $R\bar{3}c$) with $a = 21{\cdot}9$ Å for polystyrene, and $a = 17{\cdot}3$ Å for polybutene. The unit cell contains 6 chain segments, each of these containing three monomeric units. Up to now we do not possess sufficient data to determine the exact unit cell of polypropylene. The X-ray density of this polymer has been calculated by interpreting the X-ray equatorial reflections on the basis of an oblique unit cell with $a = 6{\cdot}56$ Å, $b = 5{\cdot}46$ Å, $\gamma = 106°30'$ and identity period along the fibre axis $c = 6{\cdot}5$ Å.

The identity period along the fibre axis for all the isotactic polymers examined is 6·4–6·6 Å, and is independent of the symmetry of the crystals.

By comparing the X-ray and the density data, it can be deduced that, for all the polymers examined, each portion of the main chain, corresponding to an identity period *c* of the elementary unit cell, contains three monomeric units (—CH_2—CHR—) ; therefore any regular succession of asymmetric atoms having alternately different steric configurations *(l* and *d)* must be excluded. Among all the possible regular successions of asymmetric carbon atoms *d* and *l* that can lead

to a crystalline polymer, the only succession that can justify the X-ray data, for all the crystalline poly-α-olefins examined, is that in which all the asymmetric carbon atoms have the same steric configuration.

Had the main chain been stretched on a plane, the R substituents linked to the tertiary carbon atoms would all be on one side, for instance all above (and the hydrogen atoms respectively below) this plane.

In our case, the existence of a stable configuration of a paraffinic chain completely stretched on a plane is impossible, owing to the steric hindrance of the R substituent groups. In the crystalline state the main chain must therefore assume a non-planar configuration.

Such a structure gives the polymers properties that were previously unknown in polyhydrocarbons.[6] In fact, these high-molecular-weight products are, at ordinary temperatures, hard crystalline solids; therefore their properties are very different from those of the polymers obtained from isobutene by the known methods. At ordinary temperatures these latter polymers are crystallizable only under stretching conditions and, in this state, the linear chain assumes a helix shape. The identity period (18·6 Å), however, is very different.

High crystallinity has also been observed in low-molecular-weight isotactic polymers. For example, we obtained polypropylenes with a molecular weight of about 2500 and polystyrenes with a molecular weight of about 1200; they show the same crystalline structure as polymers with a molecular weight of several hundreds of thousands.

TABLE 1

Isotactic polymer	*Identity period (Å)*	*Melting point (°C)*	*Experimental density*
Polypropylene	6·50 ± 0·05	158–170	0·92
Poly-1-butene	6·42 ± 0·05	125–130	0·91
Poly-1-pentene	6·60 ± 0·15	75–80	0·87
Polystyrene	6·65 ± 0·05	230	1·08

Table 1 shows the identity periods, determined by us, of the elementary unit cells along the fibre axis of various polymers of α-olefins.

It must be borne in mind that the helix structure, described above, is characteristic of the crystalline solid state. In the liquid state, the molecules can exhibit many other configurations. Even if these, also in the molten state, exhibit a structure different from those

of the non-isotactic molecules, it could be foreseen that the difference in the physical properties would be far less in the liquid state than in the solid state. This has been confirmed experimentally.

In a paper presented at the Congress of Organic Chemistry in Zurich[7] we discussed some characteristics of the isotactic polymers, which, above all, could interest the organic chemist : say, the nature of stereoisomery phenomena, their influence on optical properties, the chemical properties, the oxidability, the depolymerizability and their behaviour to reactants which act through an ionic or radical mechanism.

I will only summarize here some of the most important results. Isotactic polymers appeared very resistant to isomerization processes that modify the configurations of the single tertiary carbon atoms, also in the presence of catalysts acting through an ionic mechanism. Prolonged heat-treatment either at 300 – 350°C in the absence of catalysts, or at lower temperatures in the presence of various reactants acting through a free radical mechanism, can produce a very marked depolymerization of the macromolecules. The low polymers (with a molecular weight of the order of thousands or tens of thousands) thus obtained by depolymerization of isotactic polymers are still isotactic and crystallizable.

METHODS FOR THE SYNTHESIS OF ISOTACTIC POLYMERS

We have identified isotactic polymers for the first time, by fractionating mixtures of heterogeneous propylene polymers consisting of an insoluble crystalline part (about 40—60 per cent) and an amorphous part soluble in aliphatic hydrocarbons. We have prepared these polymers for the first time by polymerization of propylene with the aid of catalysts of the type discovered and applied by Ziegler in his brilliant polymerization process of ethylene at low pressure.[8] In the case of ethylene, these catalysts give linear polymers[4] that differ considerably in their physical properties from the more or less branched polymers, obtained by the traditional polymerization processes acting through a free radical mechanism.

We subsequently improved these catalysts and obtained some highly selective ones that permitted us to obtain yields higher than 90 per cent of crystalline isotactic poly-α-olefins. Later on, we prepared isotactic polymers from other monomers and with the aid of catalysts of a different type.

We could demonstrate also that the crystalline polymers of vinyl ethers prepared by Schildknecht and studied by Mark[9] exhibit an isotactic structure, as revealed by the electron-ray examination of thin lamina of crystalline polyvinylisobutyl ether, prepared in our Institute using boron trifluoride as catalyst, and also by the comparison between these spectra and those of the isotactic polymers of 5-methyl-hexene.

Although vinylisobutyl ether has a low symmetry (probably pseudohexagonal rhombic), and poly-5-methyl-hexene-1 has a hexagonal symmetry, both positions and intensities of the main diffractions are very similar. This is due to the fact that the chains exhibit the same configuration (determined by the Fourier transform) and the same identity period of 6·5–6·6 Å along the chain axis *c*.[10]

Then we prepared isotactic poly-α-olefins with the aid of catalysts different from the Ziegler-type ones. We isolated small quantities of high-molecular-weight isotactic polymers by fractionating propylene polymers which were prepared without using metallo-organic reactants, but with the use of certain catalysts consisting of polyvalent metallic oxides.

With regard to the formation of isotactic polymers, we believe that it is not necessarily conditioned by a single type of chemical polymerization mechanism. In fact, in the above-mentioned synthesis of isotactic polyvinyl ethers, one can observe a typical case in which catalysts are usually considered as cationic. We believe that in the case of the synthesis of poly-α-olefins with the aid of Ziegler-type catalysts, depending on the cases either a "stepwise addition", typical of certain metallo-organic syntheses, or else a polymerization process, to which one can attribute a mechanism similar to the one observable in the Ziegler polymerization of ethylene [8, 11] can occur.

In the 1954 Symposium on Macromolecular Chemistry held in Turin and in Milan, we described our kinetic studies on the polymerization of ethylene with aluminium triethyl.[12] We considered only the low polymers of ethylene, and further studied the growing and splitting processes of the polyethylene chains; we found that the splitting of the chains can occur simultaneously, but to a different degree, depending on temperature and pressure, both by dissociation of the metallo-organic compound and by chain transfer with the monomer. Both processes imply the regeneration of the initiator.

If one compares this polymerization mechanism with the better known types of cationic catalysis, one should admit, first of all, that

the forces linking the growing chains to the initiator are weaker in the case of cationic catalysis which requires lower temperatures in order to obtain very high polymers.

If a polymerization with transfer of the negative charge to the carbon atom and of the positive charge to the metal is attributed to the carbon–metal bond of some metallo-organic compounds of metals more electronegative than hydrogen, and if we further consider the ability of certain metallo-organic compounds to dissociate into hydride and olefin, we are then able to find some correlation between the polymerization processes carried out with the aid of the Ziegler catalysts and the ionic catalysis. We therefore attribute an anionic type of mechanism to them.

It should be borne in mind that, in the case of heterogeneous catalysis, the existence of definite compounds (such as metallo-organic compounds) is not necessary. But it is enough that metal-alkyl bonds are formed in the chemisorption processes.

In the case of the synthesis of isotactic polymers, it has been observed that, whereas with the Ziegler-type catalysts this can occur at temperatures above room temperature, in the case of cationic polymerization (polyvinyl ethers) it is necessary to operate at very low temperatures. Otherwise the easy dissociability of the compound between initiator and growing chain causes isomerization and chain transfer processes, which hinder the formation of high polymers with a regular structure.

Great importance can be attributed to the diameter of the ion, since, in the case of cationic catalysis, the formation of polymers with a very regular structure has been observed only when the ions have a relatively small diameter.

Schildknecht points out that the production of crystalline polymers is obtained only when the catalyst is not dissolved and the polymer grows on the interface between catalyst and monomer solution. In our case the presence of a solid catalyst seems to have a determining importance to render the catalytic process heterogeneous.

We have observed that, depending on the operating conditions and with the aid of catalysts containing the same chemical components, it is possible to obtain either crystalline or amorphous polymers. It was recently possible to obtain a quantity of isotactic polymers, which, by weight, corresponds to many thousands of times the weight of the initiator. This has confirmed that the catalysis leading to the formation of isotactic polymers is heterogeneous.

The formation of isotactic polymers not only requires a strict head-to-tail enchainment, but also a particular chain propagation mechanism. When a new monomeric unit is introduced by opening the double bond and consequent formation of an asymmetric carbon atom, the latter must assume the same steric configuration as the asymmetric carbon atom already present near the growing end of the chain. This occurs preferably when using heterogeneous catalysts having such a composition that one must assume that each active centre (to which a growing chain is bound) is part of a surface in which the atoms are arranged according to particular geometric configurations with respect to the active centre. We believe that such configurations impose a forced orientation of the —CHR group upon the monomer molecules, in the chemisorbed state, in relation to the active centre and to the growing chain.

Assuming that the chemisorption phenomenon is connected with an absorption heat of the same sign and is not very different from the polymerization heat, it would follow that the phenomenon of chain growth would include two almost simultaneous steps : an endothermic one of monomer desorption from the surface on which it was chemisorbed, and an exothermic one of addition to the polymeric chain. The low overall thermal capacity of these two steps when considered together, could facilitate the regularity of growth, avoiding isomerization phenomena during the chain growth.

The elementary growth reaction clears the surface upon which the reacted monomer molecule was chemisorbed. When such a surface has a certain geometric configuration, it is likely that every new chemisorbed monomer molecule is oriented in a fixed position with respect to the active centre. This is also the identical position of the preceding molecule. The phenomenon of chain growth can be compared with the growth of a plant which springs up on a soil, formed by the catalyst surface, and is fed through the root, formed by the bond linking the chain to the atoms of the surface of the solid catalyst. The chain growth reaction consists of successive additions, and the production of high molecular weight polymers is possible if the dissociation and chain transfer processes are much slower.

The high regularity of structure of the chain must be attributed to the impossibility (due to steric factors) of the occurrence of chain transfer phenomena different from those occurring by effect of the monomer and of chain rupture, which are due to the interaction of different chains or of free radicals.

The physical nature of the more selective catalysts for the synthesis of isotactic polymers seems to confirm this hypothesis. We intend to study it further by means of accurate kinetic studies and, in spite of its remarkable experimental difficulties, by means of an electron-ray study of the catalysts.*

CHARACTERIZATION AND PROPERTIES OF ISOTACTIC POLYMERS

The polymerization methods for the production of isotactic polymers, which we had initially used in the first half of 1954, were not

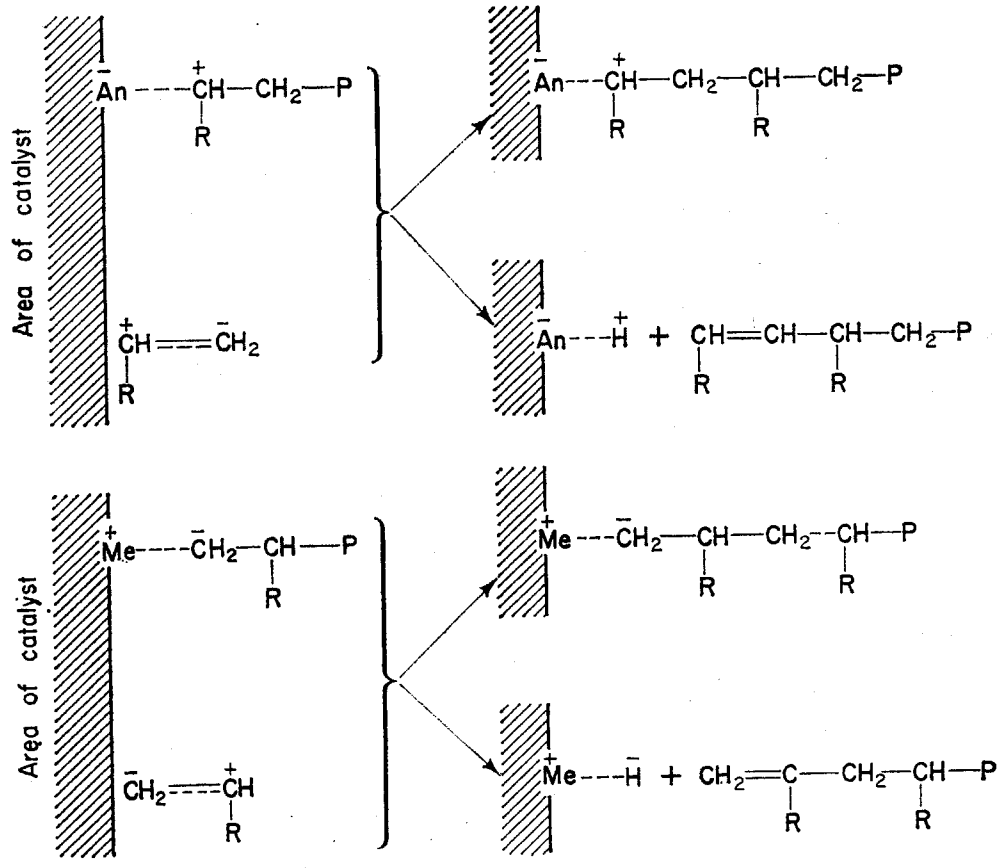


FIG. 2. Schematic drawing of the polymerization of vinyl monomers with formation of isotactic polymers.

* The infrared spectra of polypropylenes with a medium molecular weight, obtained by fractionating partially isotactic raw polypropylenes, obtained with the aid of catalysts containing metal alkyl compounds, have demonstrated that most double bonds are of the vinylidenic type. This confirms the hypothesis of an anionic mechanism of catalysis.

completely selective and therefore gave mixtures of both isotactic and non-isotactic polymers. Only later on completely selective catalysts were found for the rapid, high yield synthesis of raw polymers (more than 90 per cent isotactic). Selective catalysts have also been found for the synthesis of non-isotactic head-to-tail high polymers of the same monomers.[13]

Separation by solvent extraction permitted the separation of isotactic from non-isotactic polymers in the first mixed polymers. The separation was followed by X-ray and infrared examinations.

Figure 3 shows the infrared spectra (determined with the cooperation of E. Mantica and M. Peraldo) of isotactic polystyrene both in the solid crystalline state and in the molten state. The latter is very similar to the spectrum of polystyrene produced by the known polymerization methods, initiated by free radicals.

Figure 4 shows X-ray spectra registered with a Geiger counter (with a copper anticathode) of a raw polypropylene, and of the various extracts with ether and heptane solvents and of the residue.[2]

The ether amorphous extract of the product indicated in the figure has a molecular weight of some 20,000 and has a very intense band corresponding to about 5·3 Å.

After vulcanization, effected by introducing about 1 per cent sulphur by sulphochlorination, this product exhibits elastomeric properties; if stretched and examined by X-rays normal to the stretching direction it gives photograms in which the band of the amorphous product (5·3 Å) is more intense along the photogram equator.

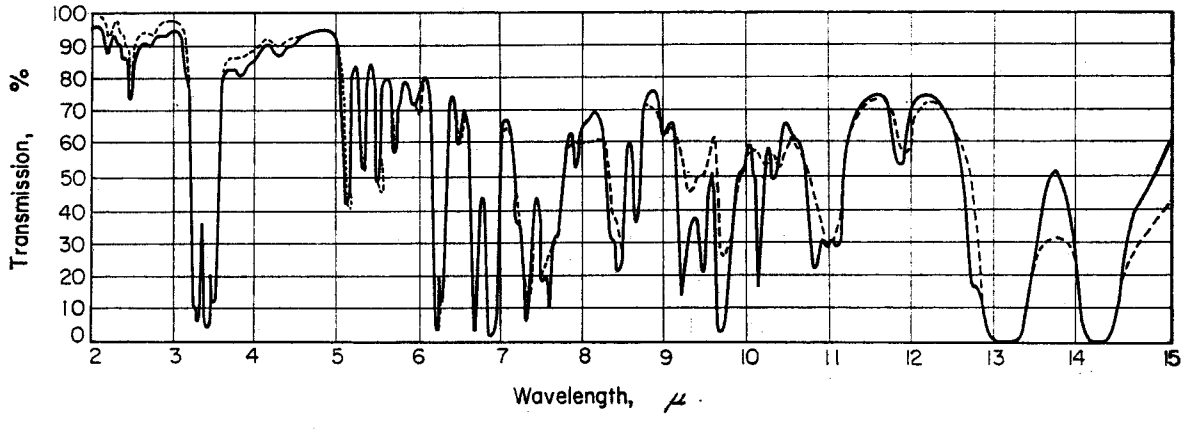


FIG. 3. I. R. spectrum of isotactic polystyrene in the crystalline solid state (full line) and in the molten state (dotted line).

This reflection, therefore, depends on the distance of the chain and indicates a chain arrangement parallel to the direction of stretching.

When comparing linear polymers of different monomers, it has been observed that the photograms of amorphous products exhibit their maxima in correspondence with distances increasing with the number and the size of the side chains.

TABLE A

Amorphous polymers	*Amorphous maximum in X-ray spectra attributed to the distance between the chains*
Linear polyethylenes and polymethylenes	4·5 Å
Polyisoprene	4·9 Å
Polypropylene	5·3 Å
Polyisobutylene	6·3 Å

The residues to the extraction with low-boiling hydrocarbons of raw poly-α-olefins are very crystalline.

High yields of crystalline polymers with an average molecular weight, which can vary, depending on the operating conditions, from some thousands to many hundreds of thousands (poly-α-olefins) and even millions (polystyrene) can be obtained very easily.

A perfect crystallinity has been observed in low-(some thousands) molecular-weight polymers, which, however, do not exhibit the mechanical properties of the high-molecular-weight products. In all the high-(above 100,000) molecular-weight polymers, a small amorphous part is always present and can be observed by a rising of the lower region of the spectra corresponding to the above-mentioned maximum (for instance, 5·3 Å for propylene). This is not necessarily due to the heterogeneous composition of the polymers; in fact, in the crystallizable polymers of extremely high-molecular-weight substances, the long molecules generally form part of several different crystals, arranged in regions of random substance. This phenomenon, which occurs when the crystals are much smaller than the lengths of the molecules, was studied by us particularly in linear polymethylenes and polyethylenes.[4]

If certain isotactic polymers that have extremely high melting points in the crystalline state (e.g. crystalline polystyrene, which

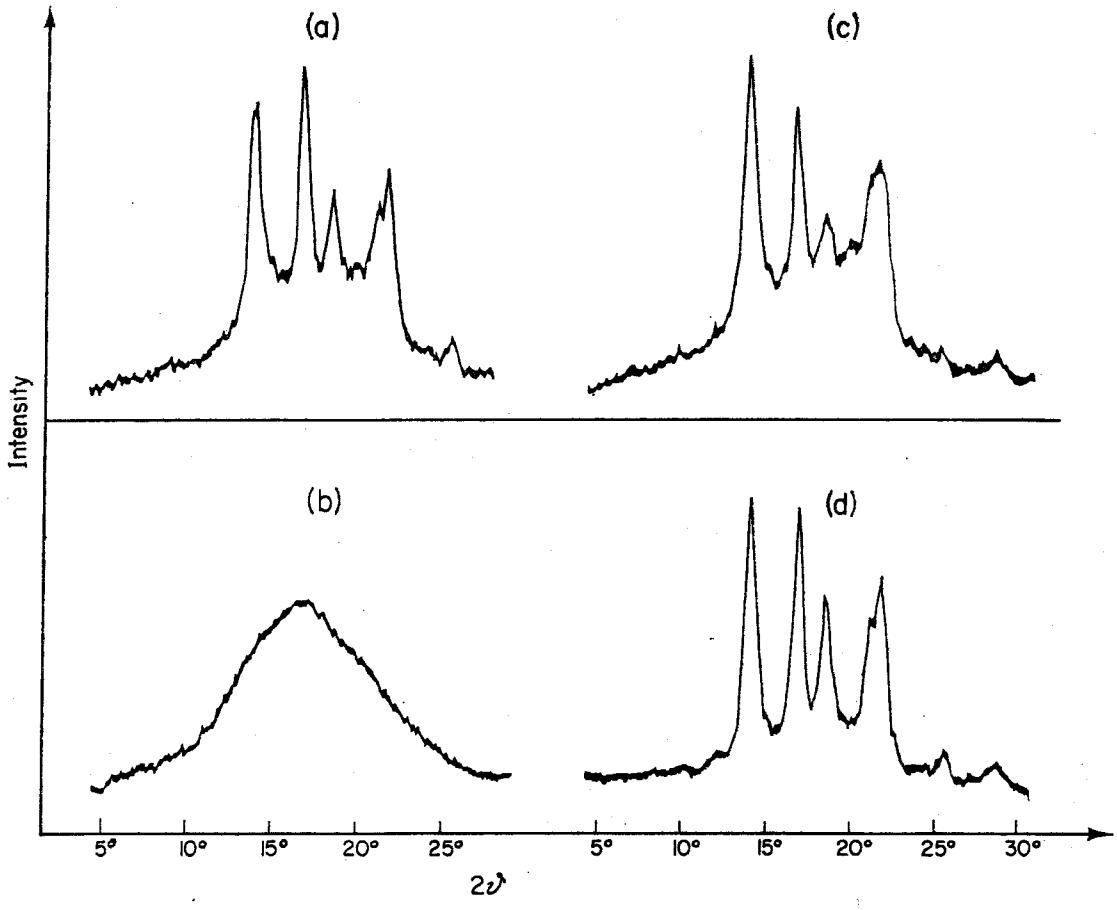


FIG. 4. X-ray spectra registered with a Geiger counter
(a) Crude polypropylene (mixture of isotactic and non-isotactic polymers)
(b) Ether extractable fraction of crude polypropylene (non-isotactic amorphous polymer)
(c) Heptane extractable fraction (product containing isotactic polymer)
(d) Residue (isotactic polymer)

melts at 230°C) are heated up to a temperature slightly above the melting temperature and rapidly hardened, one obtains X-ray photograms that show a completely amorphous structure. They exhibit maxima in the same positions as those of amorphous non-isotactic polymers, but they differ from them because they become crystalline by annealing at a temperature below the melting point of crystalline polymer (Fig. 5).

The polymers moulded at temperatures slightly lower than that of complete melting have a felt-type orientation : the *c*-axis of the crystals is parallel to the plane of the layers (Fig. 6).

The high-molecular-weight isotactic polymers melt within a very limited range of temperatures (Fig. 7). Their melting has been controlled both by X-rays and by dilatometric means.[6]

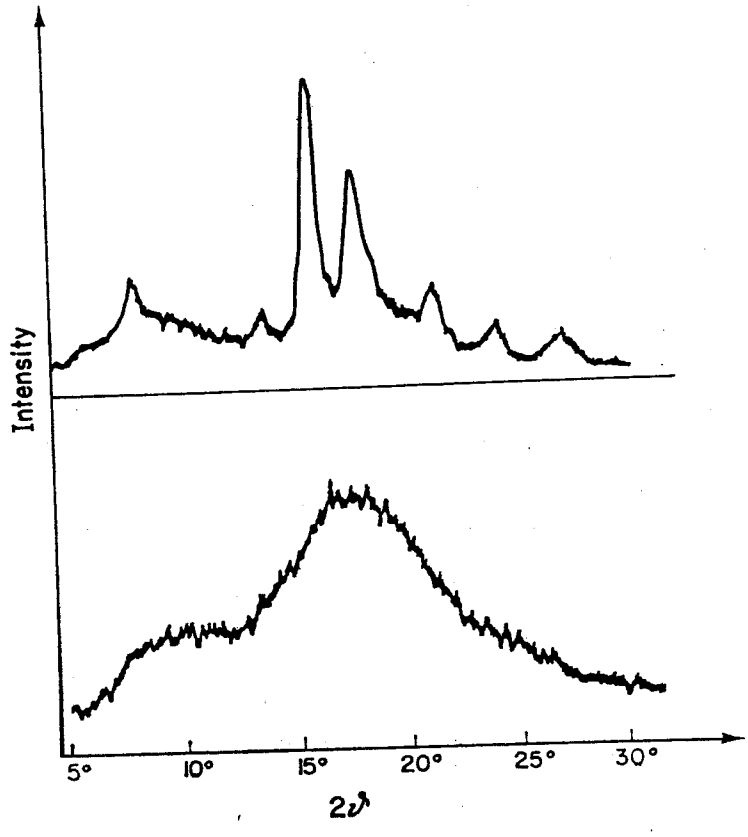


FIG. 5. Geiger counter recording of the spectra of crystalline isotactic polystyrene and of the molten and quenched (amorphous) product of the same material.

Isotactic polymers with a molecular weight lower than 10,000 show slightly lower melting temperatures ; but the melting point does not vary further on for molecular weights above some tens of thousands. It is interesting to compare the properties of linear isotactic polymers of α-olefins with the properties of linear non-isotactic polymers. Figure 8 shows the dilatometric curve of non-isotactic polystyrene (showing a temperature of the second order transition of about 85°C) compared with that of isotactic polystyrene with a temperature of the first order transition (melting) of 230°C.

Solubilities of isotactic and of non-isotactic polymers are considerably different (Table 2).

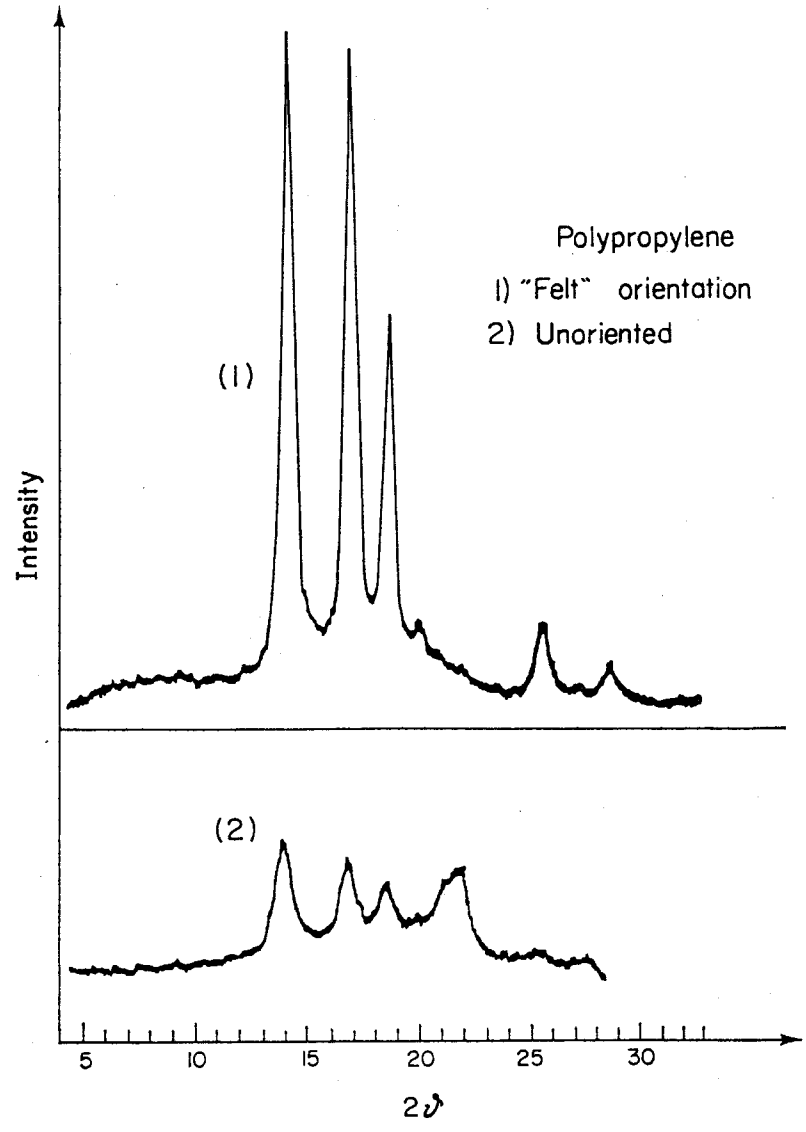


FIG. 6. X-ray spectrum registered with a Geiger counter of a lamina of isotactic polypropylene with a felt orientation (1), compared with the spectrum of a non-oriented lamina (2)

The elastomeric behaviour of "amorphous" polypropylene is clearly indicated by the stress–strain hysteresis curves (Fig. 9). The sample had already been subjected to previous stretching up to a tension of 0·8 kg/mm². The polymer examined had a molecular weight of 10,000, and was cured, after sulphochlorination, up to a rate of 1·5 per cent S.

Figure 11 of paper 6 shows the mechanical behaviour of a prevailingly isotactic crude polypropylene of high molecular weight.

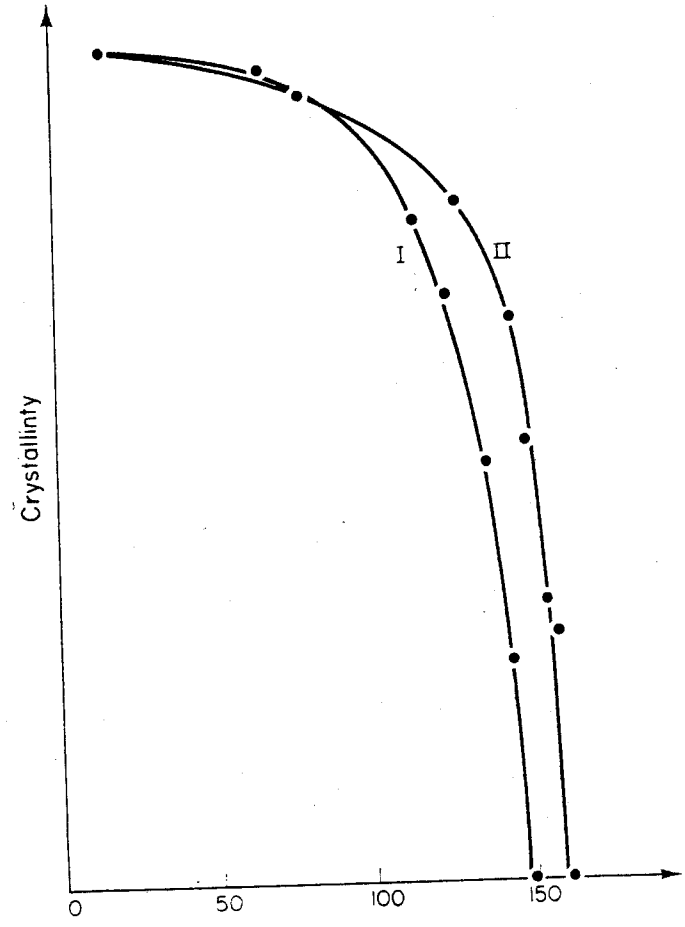


FIG. 7. Variation of the crystallinity vs. temperature of two samples of polypropylene having different molecular weights.
(I) M.W. = 2500 ; (II) M.W. = 100,000.

TABLE 2. COMPARISON BETWEEN THE SOLUBILITY OF ISOTACTIC AND NON-ISOTACTIC LINEAR POLYMERS WITH A HEAD-TO-TAIL ENCHAINMENT

Polymer	*M.W.*	*Structure*	*Solubility*
Polystyrene	1,000,000	crystalline	insoluble in methylethyl-ketone
Polystyrene	1,000,000	non-crystallizable amorphous	soluble in methylethyl-ketone
Polystyrene	10,000	crystalline	insoluble in acetone
Polystyrene	10,000	non-crystallizable amorphous	soluble in acetone
Polypropylene	30,000	crystalline	insoluble in heptane
Polypropylene	30,000	non-crystallizable amorphous	soluble in heptane
Polypropylene	10,000	crystalline	insoluble in ether
Polypropylene	10,000	amorphous	soluble in ether

It is very difficult to characterize amorphous polymers with a head-to-tail structure, which are obtained with the aid of certain catalysts. The properties of such amorphous polymers had been attributed to the presence of a statistical distribution of the asymmetric carbon atoms having the two steric configurations *l* and *d*. If this were true, all linear amorphous polymers with a head-to-tail enchainment and the same average molecular weight would have the same properties unless the distribution curves of their molecular weights were different. The difficulties we encountered in obtaining reproducible data of viscosity and of temperature of the second order transition lead us to believe that the chains of the

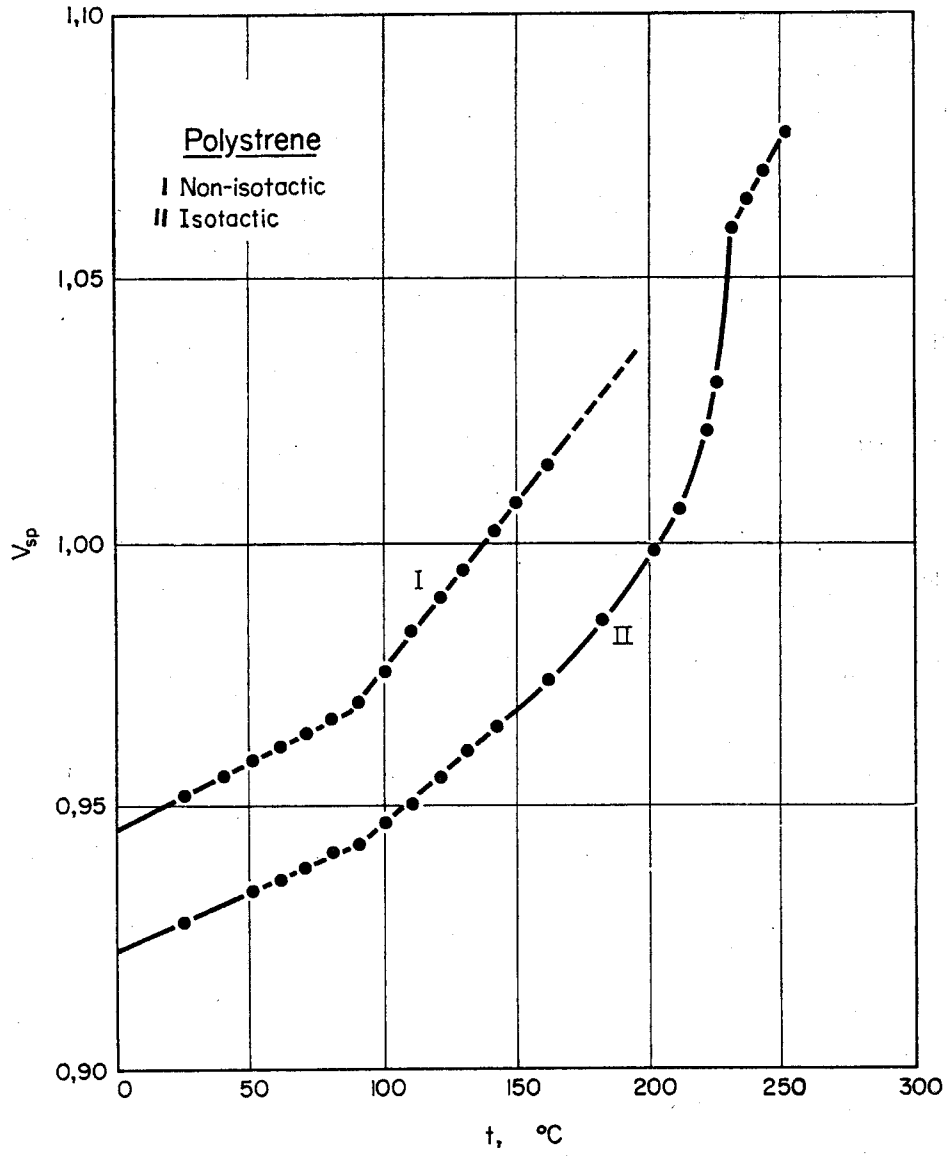


FIG. 8. Dilatometric curves of isotactic and non-isotactic polystyrenes.

amorphous polymers we produced together with isotactic polymers, are formed by successions of sequences of chain portions such as $r(CH_2—CHR—d)$, $s(CH_2—CHR—l)$, each of these containing asymmetric carbon atoms that are all either right- or left-handed, where r and s are any whole number ranging from one to some tens.

Molecular weights of isotactic polymers were calculated by viscosimetric methods. Our research work demonstrated that in the case of fractionated samples of polystyrene, isotactic and non-isotactic macromolecules in solution in practice behave identically (Fig. 10).

SYNDIOTACTIC POLYMERS

It may be interesting now to compare the isotactic polymers containing long sequences of tertiary atoms with the same steric configuration, with another type of crystalline polymer recently discovered by us.[14]

We intend to call these polymers "syndiotactic". They are crystalline and have tertiary carbon atoms in the main chain. They differ, however, in that they contain asymmetric atoms in regular sequences consisting of alternatively right- and left-handed atoms.[15]

We encountered great difficulties in synthesizing crystalline vinyl polymers having this structure. Up to now we have succeeded in doing so only by a controlled butadiene polymerization which leads to the formation of polymers with a 1,2-enchainment.

It is known that butadiene can polymerize in different ways, giving either linear or branched chains and, under certain conditions, even bridge bonds.

Three types of enchainment are possible in the linear chains of polydiolefins, that is to say : *trans*-1,4, *cis*-1,4 and 1,2. The *trans*-1,4 enchainment is known in guttapercha and the *cis*-1,4 one in natural rubber, but polymers containing only the 1,2 enchainment were unknown up to now.

The previously known synthetic polybutadienes contain monomeric units with all three possible types of enchainment.

By using selective catalysts acting through a particular anionic mechanism, it was possible for us to polymerize butadiene, with the obtainment of polymers that contain almost exclusively the 1,2 enchainment. We also obtained crystalline *trans*-1,4 butadiene polymers

by using heterogeneous catalysts. It was more difficult, however, to prepare polybutadiene with a prevalently *cis*-1,4 enchainment. We will give a detailed account of the preparation of these polymers in another paper.

The infrared spectra (determined with the co-operation of E. Mantica and D. Morero) of two types of polybutadienes very rich in 1,2 units are shown in Figs. 11 and 12. The first type (Fig. 11) contains

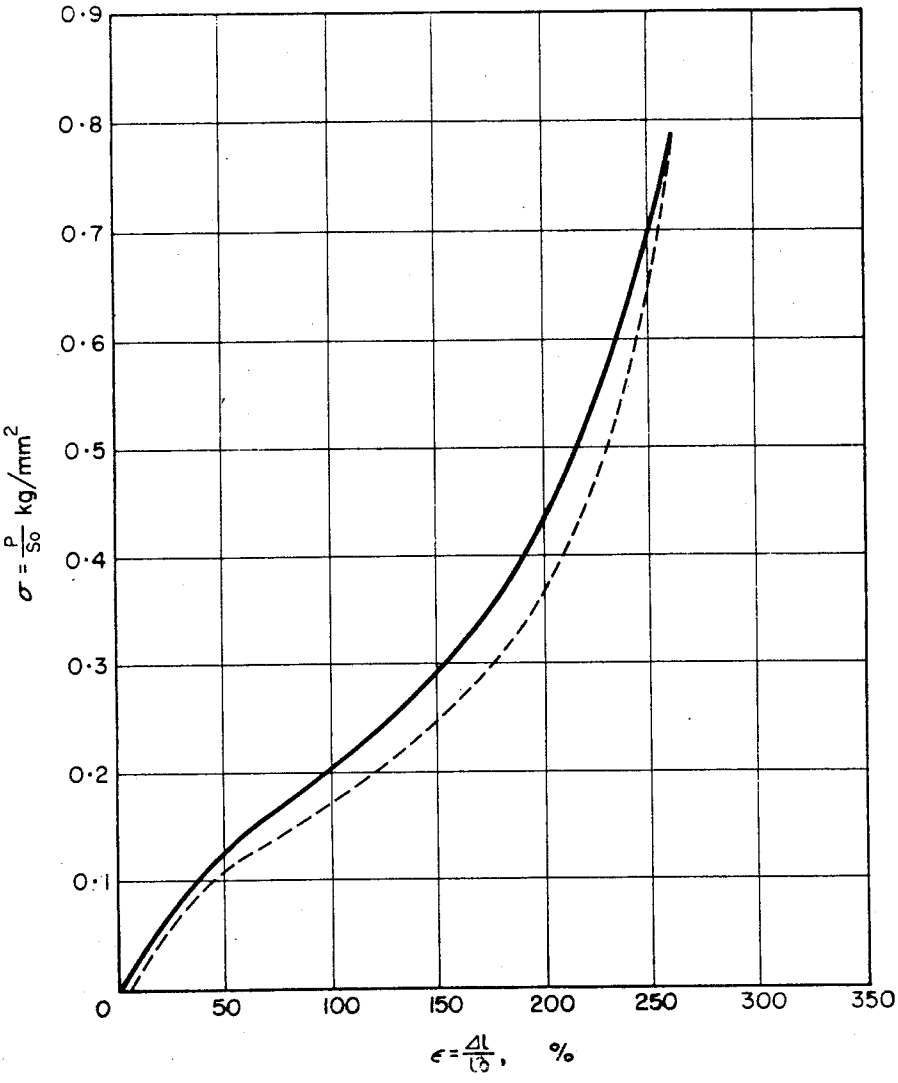


FIG. 9. Stress–strain diagram of an amorphous polypropylene sample vulcanized after sulphochlorination.

very few *trans*-1,4 units; the second (Fig. 12) very few *cis*-1,4 units. Both give excellent X-ray spectra with the same reflections, which, therefore, must be attributed to the 1,2 enchainment. The small amounts of 1,4 monomeric units lie in the amorphous parts. Figure 13 shows the I.R. spectrum of a *trans*-1,4 polybutadiene. The crystalline structure of this polymer, which is dimorphous like guttapercha, and melts at about 130°C, will be discussed in another paper.

The properties of 1,2-polybutadiene are very different from those of the known polymers of butadiene. 1,2-polybutadiene melts at about 155°C, and yields oriented fibres showing physical properties very similar to those of isotactic polymers.

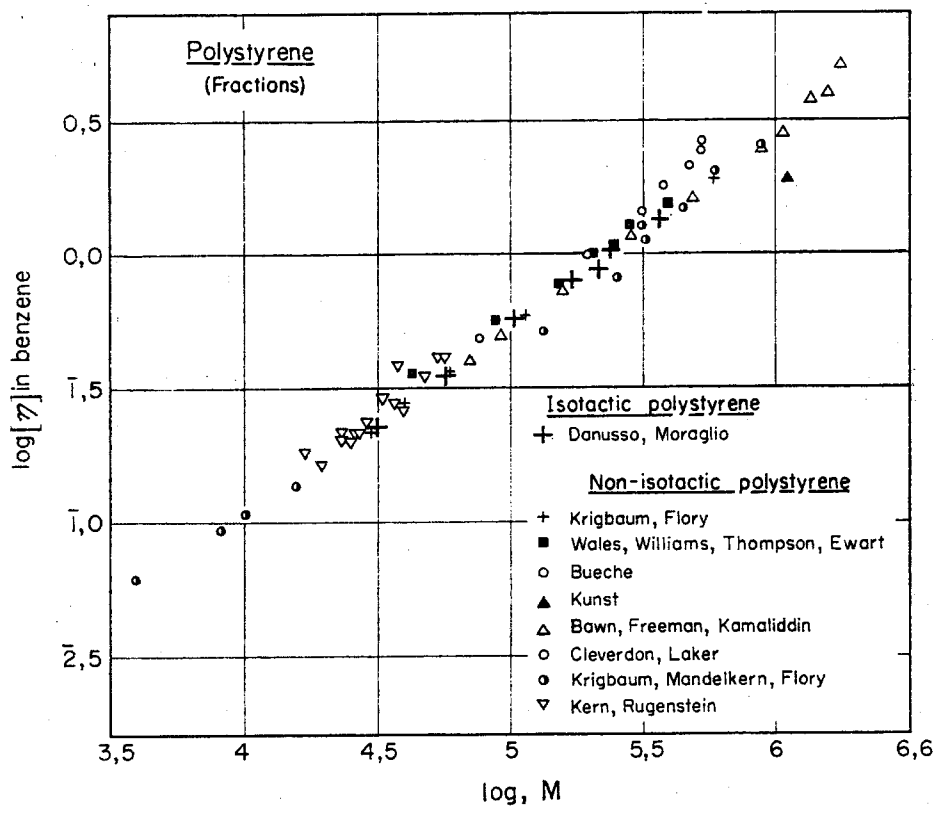


FIG. 10. Comparison between the properties of isotactic and non-isotactic polystyrenes in solution.

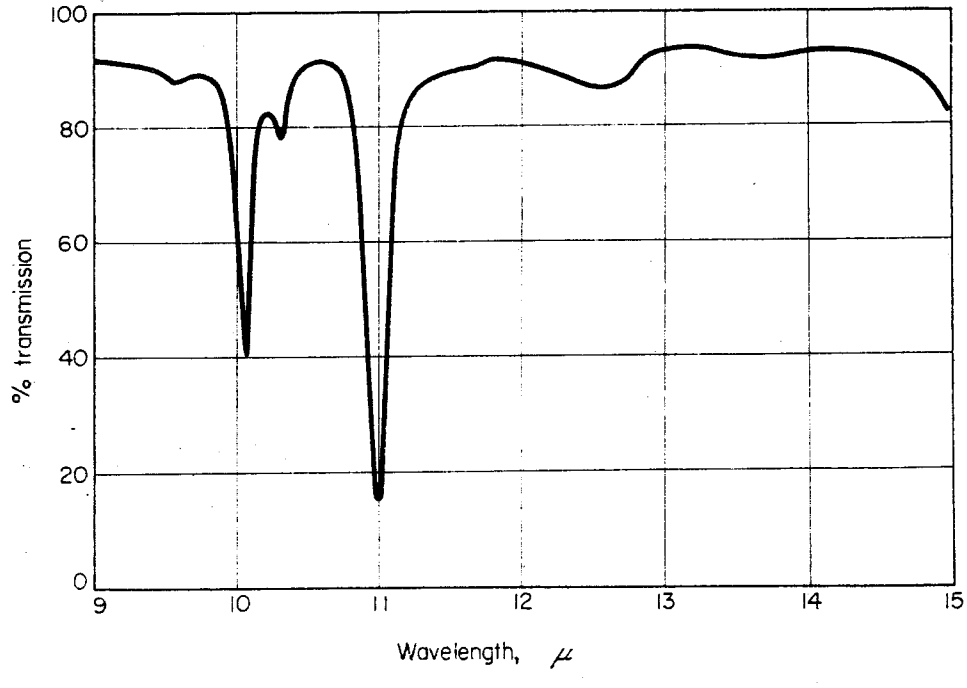


FIG. 11. I.R. spectrum of polybutadiene containing 90 per cent of 1,2 and less than 10 per cent of *trans*-1,4 monomeric units.

In contrast to the isotactic polymers, 1,2-polybutadiene exhibits an almost planar main chain with an identity period of 5·14 Å corresponding to two monomeric units.

Table 3 shows some data obtained from X-ray and electron diffraction spectra of syndiotactic polymers. Figure 14 shows the pro-

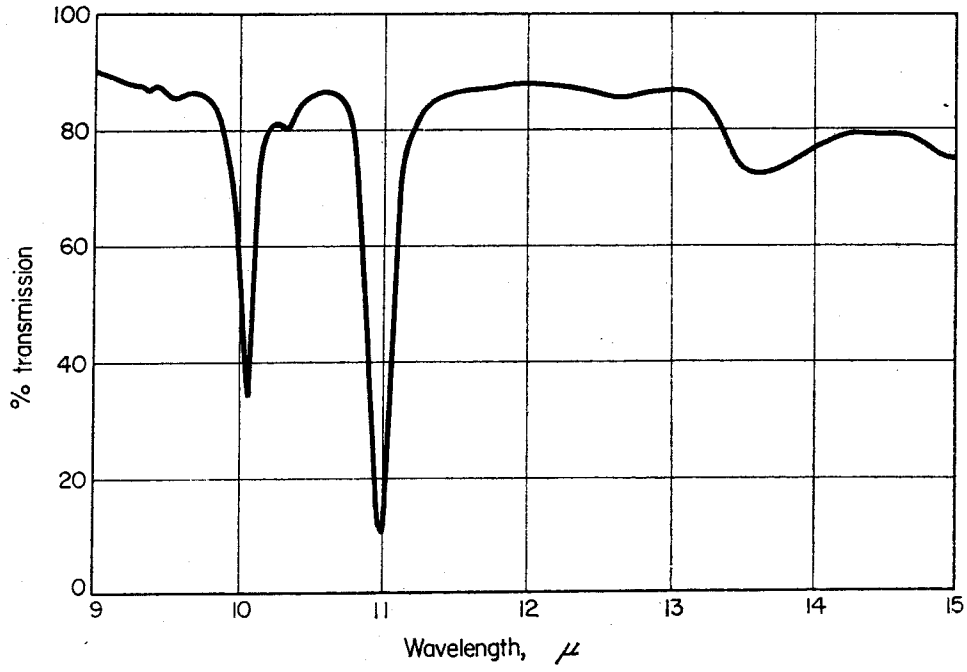


FIG. 12. I.R. spectrum of polybutadiene containing 90 per cent of 1,2 and less than 10 per cent of *trans*- and *cis*-1,4 monomeric units.

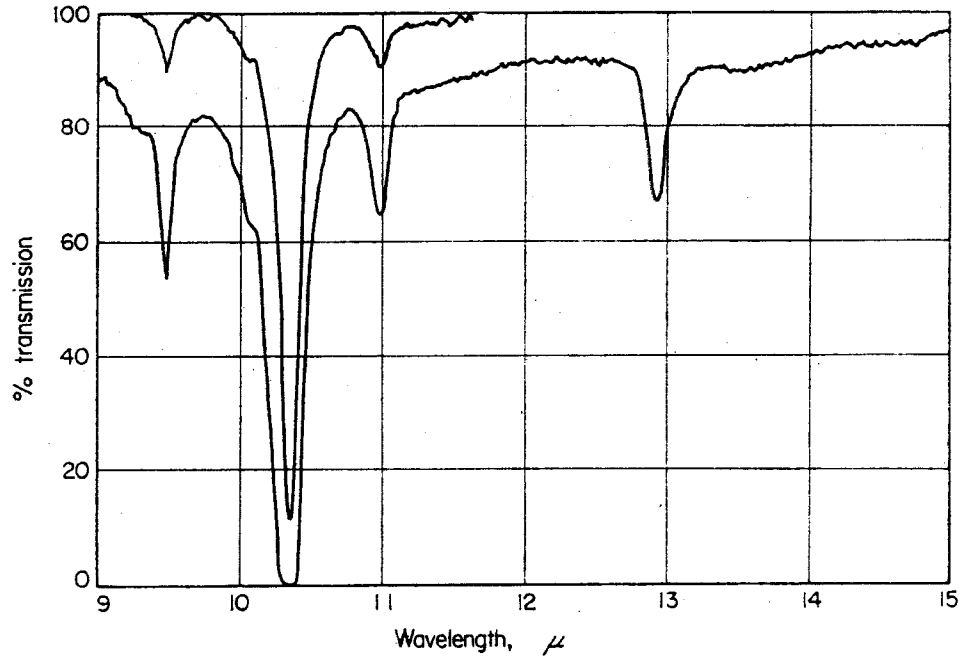


FIG. 13. I.R. spectrum of polybutadiene almost entirely *trans*-1,4.

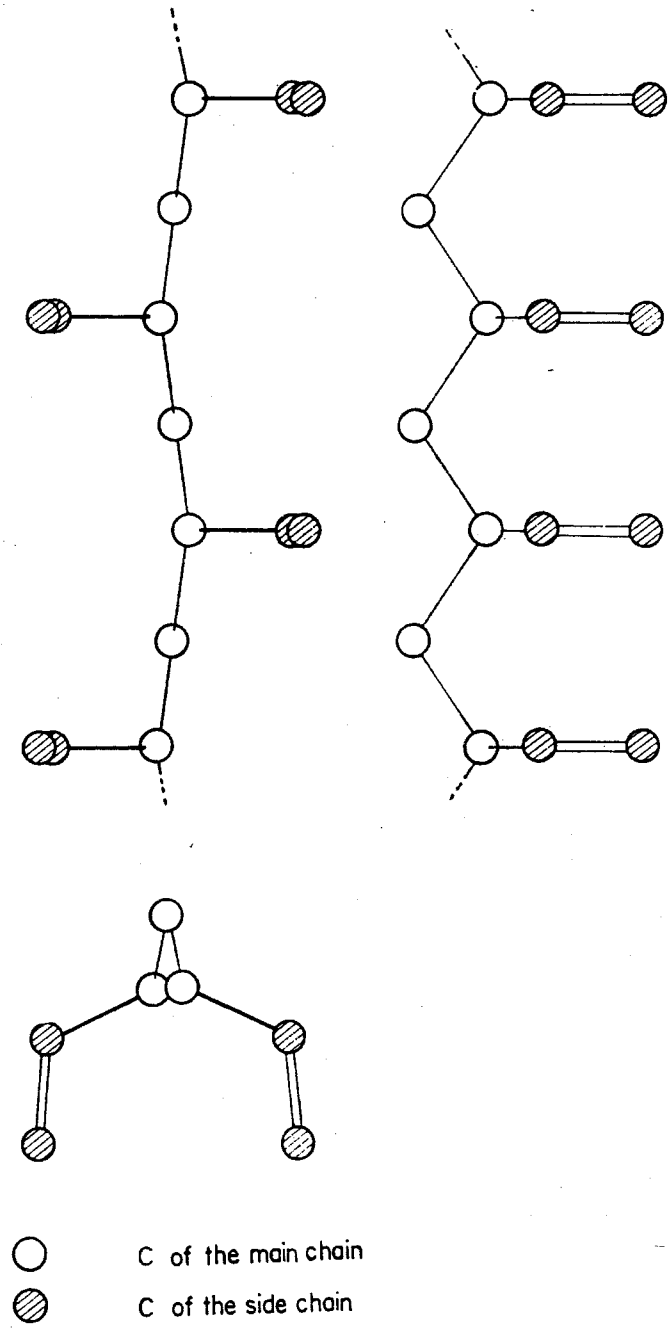


FIG. 14. Side and end views of the chain of crystalline 1,2 polybutadiene on three perpendicular planes.

jection on three perpendicular planes of the 1,2-polybutadiene chain in the crystalline state. Figure 15 shows the projection of the structure of the elementary unit cell.

The polymers of some vinyl monomers (for example, vinyl chloride), which are generally amorphous, obtained by a free radical mechanism, sometimes exhibit X-ray diffraction bands in the oriented state, which can be attributed to a similar structure (Table 3).

TABLE 3

Polymers having syndiotactic structure	*Cristallyne polibutadiene (1,2 enchainment)*	*Movil (Polyvinyl chloride in stretched threads)*
Lattice constants :		
a	0·98 Å	10·65 Å ± 0·1
b	6·60	5·32 ± 0·1
c	5·14	5·1
Calculated density	0·96	1·44
Experimental density	0·92	1·40
Minimum packing between atoms of adjacent molecules :		
CH_2, CH_2	4·0 Å	—
CH, CH	4·0	—
Cl, Cl	—	4·4 Å
Cl, CH_2	—	3·9

We believe that the discovery of these new polymerization methods opens a new chapter of stereoisomerism, which should be of considerable practical and theoretical interest. Stereoisomerism phenomena are assuming a great importance in the field of macromolecules. They determine differences in the physical properties of certain types of stereoisomers, which are more evident than in the usual lowmolecular-weight compounds.

A vast new field of research, which is now only just beginning, is opened to chemists. Our research on block and grafted polymers, and on copolymers, permits one to foresee very important developments. The interest of the new isotactic and syndiotactic polymers is not only theoretical. In the oriented state, polypropylene has a very high ultimate tensile strength (Fig. 11 of paper 6), that is of the same order as steel, but it has a specific gravity of only one-eighth that of steel. The elastically absorbable energy of tensile deformation is, for equal weight, some tens of times higher for the oriented polypropylene than for steel.

Textile fibres obtained from certain isotactic polymers have the same tensile strength as nylon, but are more elastic.

The great availability and the very low cost of the raw materials used for producing certain isotactic polymers, the very high yields obtained from polymerization processes, which we can carry out

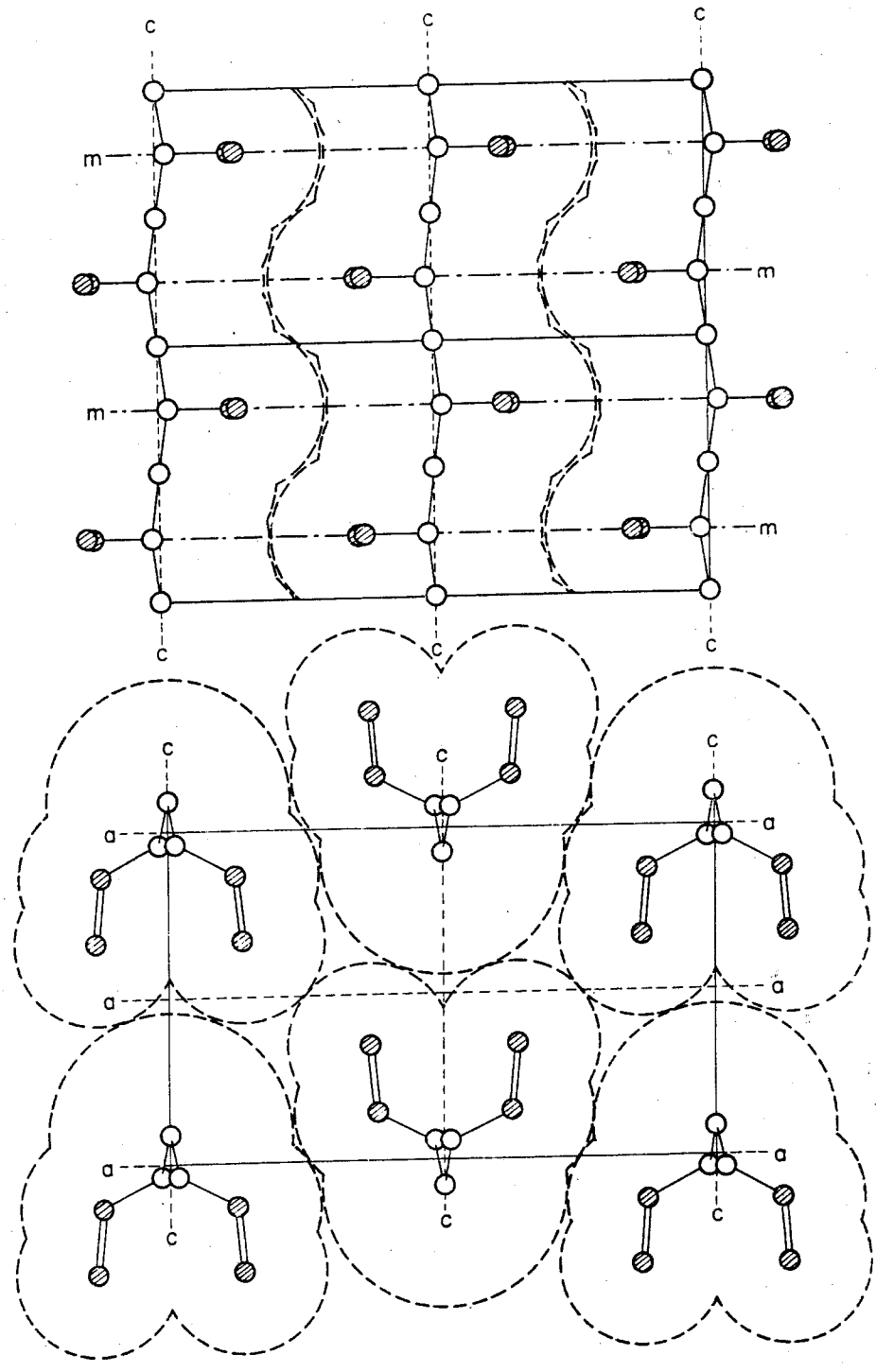


FIG. 15. Projection on the planes (001) and (010) of the structure o 1,2 polybutadiene

even at ordinary pressures, and the excellent mechanical properties of the polymers are a series of factors favouring a rapid development of the industrial production of these new polymers.

In my opinion, the discovery of isotactic polymers can be an important step in the progress of the industry of plastics, of synthetic textiles and of construction materials.

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9

CRYSTALLINE POLYMERS OF BUTADIENE AND STRUCTURE OF 1,2-POLYBUTADIENE

by G. NATTA and P. CORRADINI

(12 Nov. 1955)

[*Rend. Accad. Naz. Lincei* (8) **19**, 229 (1955)]

As one of us pointed out at the Symposium on Macromolecular Chemistry in Zurich,[1] the systematic study of X-ray and electron-ray spectra of butadiene-1,3 polymers, obtained by different anionic polymerization processes, allowed us to identify two types of highly crystalline polymers.

The processes of selective catalysis that permitted the preparation for the first time of these new polymers will be described in another paper, written with the co-operation of L. Porri.

Trans-1,4 Polybutadiene. The infrared spectrographic research performed by E. Mantica and D. Morero in this Institute permitted us to establish that one of the two types of crystalline polymers obtained with heterogeneous catalysts has *trans*-1,4 monomeric units. By means of X-rays it is shown to be dimorphous. This polymer has a crystalline modification stable at room temperature, but it is transformed, at a temperature above 60°C, into another crystalline modification.

This last form melts at 130°C as revealed by X-rays for polymers having a molecular weight of the order of 100,000.

The type which is stable at room temperature shows a periodicity of 4·9 Å along the chain axis. The packing of the molecules normal to the chain axis is hexagonal with $a = 4{\cdot}54$ Å. The modification which is stable at a higher temperature seems to be connected with a spiralization of the chain.

The structures of the two crystalline modifications of *trans*-1,4-polybutadiene and the results obtained from a structural study of other crystalline polydiolefins will be described by us in another communication.

1,2-Polybutadiene. The other type of crystalline polymer of butadiene-1,3 has, in contrast, 1,2 monomeric units. As a matter of fact, the samples, in which the enchainment was observed, revealed, by infrared examination, the presence of vinyl double bonds (more than 90 per cent and of *cis* and *trans* double bonds less than 10 per cent).

In this communication we are going to describe only the crystalline structure of this last polymer.

The products examined are a white powder that can be easily moulded. By X-ray examination (radiation of a copper anticathode) these products give spectra, registered with a Geiger counter, like the one shown in Fig. 1, with maxima for lattice distances of 6·60, 5·59, 4·20, 3·80 Å. They markedly differ from the spectrum of isotactic poly-α-butene.[2] In the spectrum performed on extruded stretched threads, the first three maxima mentioned above, and those of others, fall on the equator (Fig. 2), whereas the maximum at 3·80 Å falls on the first layer. Periodicity along the fibre axis is of 5·1±0·1 Å.

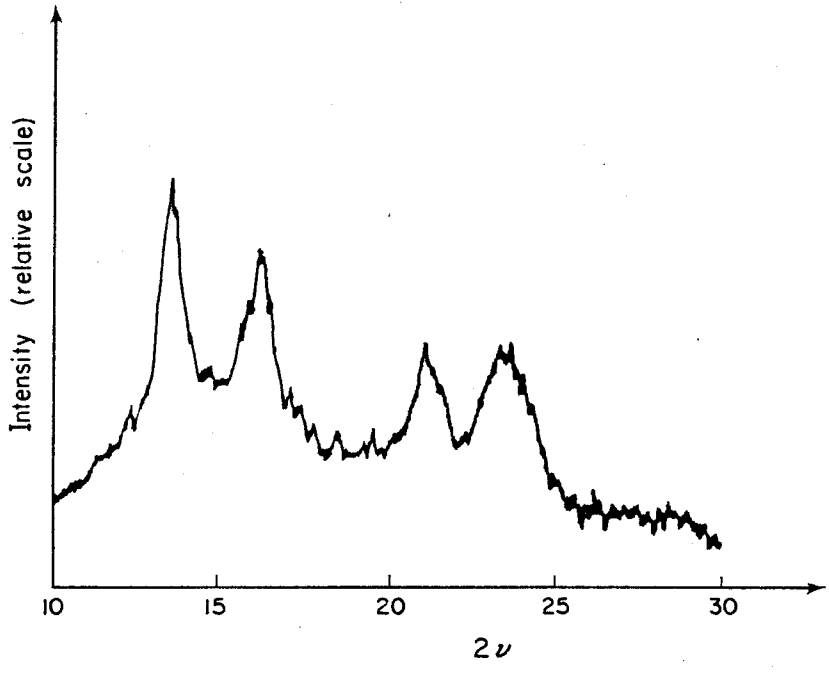


FIG. 1. X-ray spectrum registered with a Geiger counter of 1,2-polybutadiene (Cu$K\alpha$).

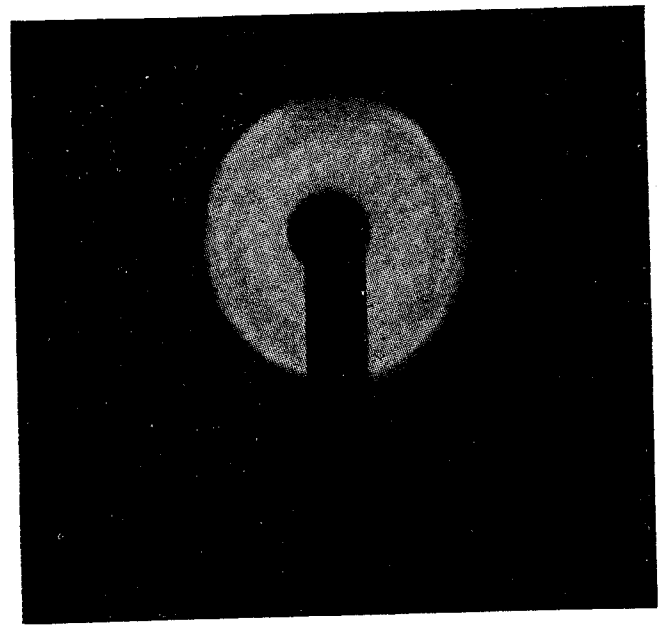


FIG. 2. Fiber spectrum of 1,2-polybutadiene.

By performing a powder spectrum of the product by means of an apparatus that permits operation at different temperatures, as already described by us,[3] interferences disappear; this means that the product melts completely at 154°C.

An interval of melting temperature, as can be seen from Fig. 3, is normal in the case of high polymers, and can be attributed only in part to amorphous regions due to the presence of monomeric units of different configurations.

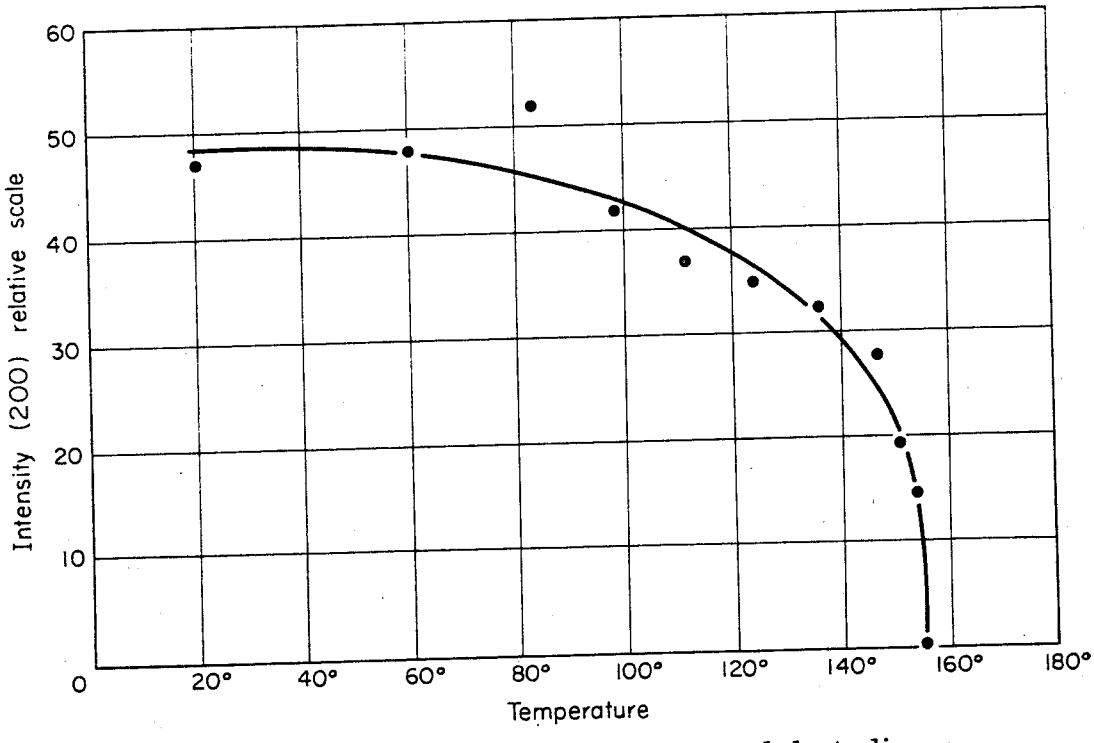


FIG. 3. X-ray melting curve of 1,2-polybutadiene.

EXAMINATION OF THE ELECTRONIC DIFFRACTIONS

Very thin laminae of the polymer (about 100 Å thick), in which all the molecules are arranged with the fibre-axis perpendicular to the lamina, have been obtained by the evaporation of films of benzene solutions of the polymer stretched on water. These laminae, gathered on copper wire gauzes, have been examined with the co-operation of I. W. Bassi, by an electron diffraction camera (Finch Electron Diffraction Camera). Figures 4 and 5 show two typical spectra obtained by the incidence of beams perpendicular ($\delta = 90°$) and oblique ($\delta = 30°$) to the lamina, respectively. Table 1 shows the diameters $2r$ of the various reflections observed on the film.

TABLE 1. $R\lambda = 5{\cdot}435 \times 10^{-8}$ cm²

Equator		*1st layer*	
2r(mm)	*Intensity*	*2r (mm)*	*Intensity*
8·3	s	14·3	s
9·9	s	19·9	w
12·9	s	28·2	w
16·9	ms	2nd layer	
19·2	mw	23·2	mw
21·4	m	27·3	mw
25·8	m	28·6	vw
29·5	w	30·7	w
30·7	w	32·9	mw

s, strong ;
ms, medium strong ;
w, weak ;
mw, medium weak ;
vw, very weak ;
m, medium.

The equatorial reflections (Fig. 6) can be interpreted on the basis of a rectangular plane lattice having axes $a = 10{\cdot}98 \pm 0{\cdot}10$ Å and $b = 6{\cdot}60 \pm 0{\cdot}05$ Å.

For indexing the reflections of the upper layers, we adopted the type of construction represented in Fig. 6. Segments OP_{hk} proportional to all the possible values 1: $d(hk0)$ are placed, starting from O, on the line OP. The same thing is done on the parallel lines $O'P'$, $O''P''$ drawn at successive proportional distances of $1/c$. In an orthorhombic

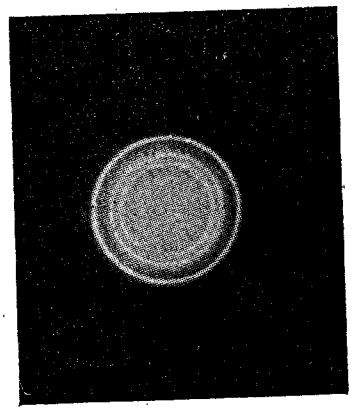


FIG. 4. Spectrum obtained by an electron diffraction camera of a lamina of 1,2-polybutadiene (normal incidence).

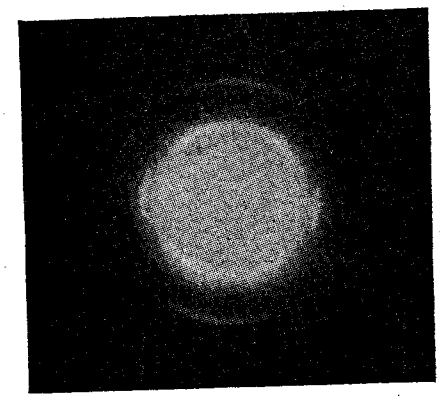


FIG. 5. Spectrum obtained by an electron diffraction camera of a lamina of 1,2-polybutadiene (oblique incidence).

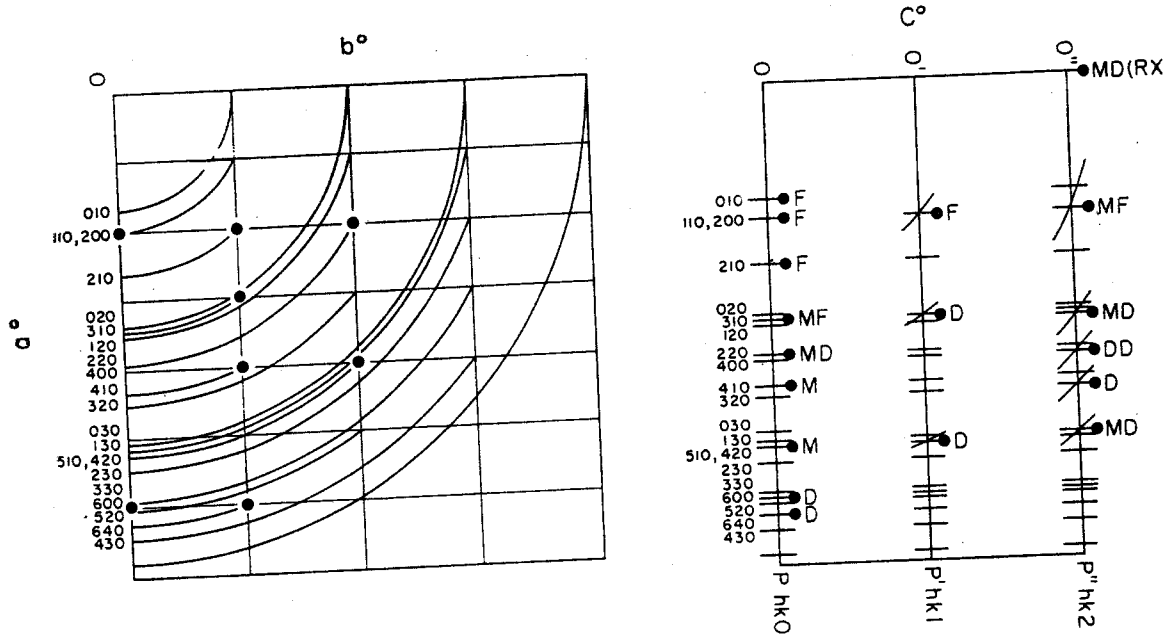


FIG. 6. Reconstruction of the reciprocal lattice of 1,2-polybutadiene.

lattice, circles having a radius proportional to 1: $d(hkl)$ with centre in the interesect O for $l = 1$, the line $O'P'$ for $l = 2$, the line $O''P''$ in points P'_{hk1} or P''_{hk2} furnish the indexes of reflections.

The best reconstruction of the reciprocal lattice has been obtained by assuming an elementary unit cell with constants $a = 10{\cdot}98$ Å, $b = 6{\cdot}60$ Å, $c = 5{\cdot}14$ Å.

Supposing that 4 monomers are contained in the unit cell, the calculated density is found to be $0{\cdot}963$; this is much higher than the experimental one ($0{\cdot}92$), which was observed for most microcrystalline substances.

The lack of $0kl$ reflections for $l = 2n+1$ and $h0l$ for $h = 2n+1$, even if the statistics do not prove this rigorously (because either these weak reflections could be absent or because of considerations based on the possibility of packing), lead us to consider *Pacm* as the most probable space-group.

DETERMINATION OF THE STRUCTURE

We have chosen to call C_1 the carbon atoms of the CH_2 groups and C_2 the carbon atoms of the CH groups of the main chain ; while C_3 and C_4 are the carbon atoms of the CH and CH_2 group, respectively, of the vinyl side chain.

In general the weakness of the $hk0$ reflections with $h = 2n+1$ permits us to state that the C_1 and C_2 atoms of the chain are projected along c near $x = 0$, $y = 0$ and $x = \frac{1}{2}$, $y = 0$.

The periodicity of 5·1 Å along the fibre axis is in agreement with that which is foreseeable for a zigzag rigid linear paraffinic chain, if one assumes that the identity period corresponds to a portion of the main chain containing 4 carbon atoms.

Since this identity period corresponds to two monomeric units, one must conclude that the vinyl atoms are alternated in different positions, such as those foreseeable by supposing that they are bound to asymmetric atoms with right- and left-handed configurations, respectively. A distribution of this type was proposed for the interpretation of the broad spectrum given by polyvinyl chloride, though this spectrum shows a much lower degree of order.[4]

From the space-group *Pacm*, it can be deduced that the molecule contains a symmetry plane with a translation of $\frac{1}{2}$ along c. The paraffinic main chain, supposed to be planar, must, therefore, be placed in the plane $(0, y, z)$. After having established a certain chain pattern, satisfying the conditions mentioned above, it is necessary to calculate the structure factors, by only varying one parameter along b, in order to establish the position of the molecule in the unit cell.

In order to determine the orientation of the vinyl atoms, we took as a basis the exceptional intensity of the reflection (201); this should have indicated that vinyl atoms were alternated in right to left positions. They were dephased by 1/2 along c with respect to the adjacent molecules (see Fig. 7) and also to the basis of the intensity, which is also an exception of the independent (310) reflection. This must be

considered according to what was mentioned above ($h=3$), in regard to the chain atoms, and, therefore, probably to the disposition in the phase of the vinyl atoms (Fig. 7).

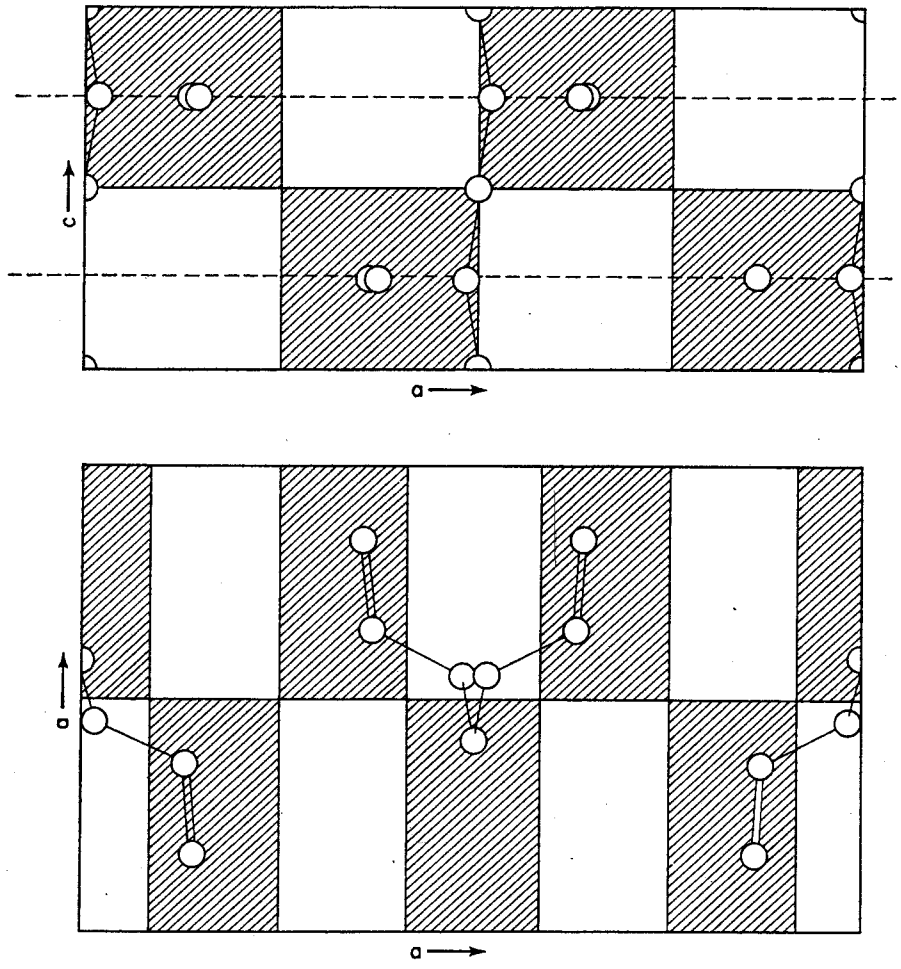


FIG. 7. Graphs of the structure factors of the (201) and (310) reflections of 1,2-polybutadiene.

When one calculates the structure, the assumed distances between the carbon atoms and the valency angles are those usually accepted. The pattern having the paraffinic chain parallel and planar to (0, *y*, *z*) gave the best agreement between the experimental intensities and the structure factors, as reported in Table 2. The following are the values for the coordinates:

	x	*y*	*z*
C_1	0	0·896	0
C_2	0	0·030	0·250
C_3	0·117	0·164	0·250
C_4	0·117	0·364	0·250

TABLE 2. COMPARISON AMONG THE VALUES OF nF^2 (F = STRUCTURE FACTOR CALCULATED USING ATOMIC X-RAY FACTORS) FOR THE STRUCTURES: I (WITH A PLANAR MAIN CHAIN) AND II (WITH A CHAIN SLIGHTLY DIFFERENT FROM PLANARITY)

Indexes	nF^2		*Exp. int.*	*Indexes*	nF^2		*Exp. int.*
	(I)	*(II)*			*(I)*	*(II)*	
010	64	90	s	401	1	1	—
110, 200	136	87	s	411	1	3	—
210	116	116	s	321	0	2	—
020	5	6	—	131	2	3	—
310	50	67	ms	421	0	3	—
120	12	1	—	511	8	24	w
220	26	42	mw	231	0	0	—
400	0	0	—	331	3	3	—
410	65	46	m	002	20	20	mw (X-rays)
320	4	2	—	012	0	1	—
030	1	4	—	112, 202	72	59	ms
130	0	0	—	212	0	0	—
420, 510	96	58	m	022	0	1	—
230	1	3	—	312	0	3	—
330	6	6	—	122	23	30	mw
600	12	49	w	222	4	2	—
520	3	4	—	402	25	22	vw
610	34	27	w	412	1	0	—
111, 201	96	131	s	322	21	24	w
211	0	2	—	032	5	2	—
311	39	19	w	132, 422	52	52	mw
121	0	0	—	512	3	1	—
221	7	4	—	232	8	2	—

This model, like any other model in which the paraffinic chain is planar, leads to a strong packing between the C_1 and C_4 carbon atoms (3·9 Å), in addition to a packing of the C_4 atoms of the same chain among themselves. This is excessive with respect to the packings (about 4·2 Å) among other carbon atoms.

When we examined other structures, allowing the same space-group, small displacements were deriving from the preceding structure. A better agreement and a better packing of the molecules among themselves has been found for a model not very different from the preceding one, in which the paraffinic chain is slightly different from planarity (Fig. 15 of paper 8). The coordinates are:

	x	y	z
C_1	0	0·916	0
C_2	0·014	0·050	0·250
C_3	0·136	0·143	0·250
C_4	0·143	0·342	0·250

Table 2 shows a comparison between the experimental intensities and the calculated nF^2 values for the two structural models.

The van der Waals' contacts for the last model are considered to be all equal to or higher than 4 Å (Table 3).

TABLE 3. VAN DER WAALS' CONTACTS

C_4–C_4 (different chains)	4·0 Å
C_4–C_4 (same chain)	4·0 Å
C_4–C_1 (different chains)	4·3–4·4 Å
C_3–C_3 (different chains)	4·0 Å
C_3–C_1 (different chains)	4·2 Å

The calculation of the structure factors favours, even if only slightly, this last hypothesis, but only more accurate and improved structural studies (which are possible if better X-ray fibre photograms can be obtained) would confirm it. This, however, can be accepted from an energetic point of view. In fact, the increase of potential energy, caused by a displacement of a polyethylene chain by the same angle (10°) from planarity, is very low (about 200 cal/bond) and it is probably compensated for by the lowering of the potential energy connected with the lower packing of the C_4–C_4 atoms in the same chain.

The C—C—C angle of the main chain is 113°, which is in agreement with other values reported up to now:[5] polyethylene 111°, polypropylene and polyisobutene 114°, polystyrene 116°.

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   G. NATTA and P. CORRADINI, *Rend. Accad. Naz. Lincei* (8) **18,** 19 (1955).

10

THE CHAIN STRUCTURE OF CRYSTALLINE POLYVINYLISOBUTYL ETHER

by G. NATTA, I. W. BASSI and P. CORRADINI

(2 Dec. 1955)
[*Makromol. Chemie* **18–19**, 455 (1955)]

ABSTRACT

The chain structure of polyvinylisobutyl ether prepared by cationic catalysis according to Schildknecht *et al.* is discussed in this paper.

The X-ray data are interpreted with the aid of molecular Fourier transforms. It was possible to conclude that the polymer in the crystalline state is isotactic, that is : all the tertiary carbon atoms have the same steric configuration, with a ternary helix-type symmetry of the chain (of the Bunn's $(AB)_3$ type). It has been observed that a complete analogy exists between the molecular structure of crystalline polyvinylisobutyl ether and that of isotactic poly-5-methyl-hexene-1. The latter was prepared by anionic catalysis.

11

SYNTHESIS AND PROPERTIES OF CRYSTALLINE HIGH POLYMERS OF BRANCHED α-OLEFINS

by G. NATTA, P. PINO, G. MAZZANTI, P. CORRADINI and U. GIANNINI

(10 Dec. 1955)
[*Rend. Accad. Naz. Lincei* (8) **19**, 397 (1955)]

ABSTRACT

The polymerization of 3-methyl-1-butene, 4-methyl-1-pentene, 4-methyl-1-hexene and 5-methyl-1-hexene was performed with the aid of stereospecific catalysts which consisted of titanium halides and triethylaluminium. The various mixtures of polymers possessing a wide order of stereoregularity were fractionated, yielding highly crystalline fractions, insoluble in ether and, in the case of poly-3-methyl-1-butene, insoluble in boiling heptane.

The highly crystalline fractions have very high melting points, e.g. more than 100°C higher than those of polymers of linear α-olefins having either the same molecular weight or the same chain length; furthermore, their solubility and density are lower than those of the polymers of linear α-olefins having the same chain length.

A preliminary investigation of the structure of the crystalline fractions strongly suggests that these polymers have an isotactic structure. The principal chains of the macromolecules in the solid state possess helical conformations with a different number of monomeric units for each turn of the helix.

The polymer of the racemic 4-methyl-1-hexene is highly crystalline, in spite of the fact that, in the monomer, there exists asymmetric carbon atoms of two possible absolute configurations. Two tentative interpretations for the above experimental fact are proposed.

12

CRYSTALLINE STRUCTURE OF SOME ISOTACTIC POLY-α-OLEFINS

by G. NATTA, P. CORRADINI and I. W. BASSI

(10 Dec. 1955)
[*Rend. Accad. Naz. Lincei* (8) **19**, 404 (1955)]

ABSTRACT

The X-ray examination of some crystalline polymers of α-olefins, and more precisely of butene-1, 3-methylbutene-1, 4-methylpentene-1, 4-methylhexene-1 and 5-methylhexene, revealed that these polymers, independently of their identity periods and number of monomeric units contained in them, possess, in their crystalline state, structurally equivalent monomeric units. These are head-to-tail sequences of monomeric units containing carbon atoms with the same steric configuration ; thus they are isotactic.

It has been proposed that the isotacticity determines the helix-type configuration of the chains in the crystals and that the configuration of the chains does not always correspond to the ternary symmetry structure as observed, for instance, for polystyrene, but that the helix may be more flattened and broad with a high identity period and a different number of monomeric units per pitch, according to the shape and size of the side groups. Helices may consist of 4 monomeric units per pitch as in poly-3-methylbutene-1 (identity period 6·85 Å), or of 3·5 monomeric units per pitch (corresponding to an identity period of 13·8–14 Å comprising 7 monomeric units and two pitches of the helix) as in the examined poly-4-methylalkenes, instead of 3 monomeric units per pitch, like in polypropylene, in the modification I of polybutene-1 and in polystyrene (identity period 6·45–6·65 Å). It also results in 3 monomeric units in poly-5-methylhexene-1.

Therefore, it is probable that a methyl branching in the side chains of the isotactic polymers causes a deformation of the main chain; this deformation is most marked if the methyl group is near the main chain, less marked if the methyl group is spaced by one methylene group, and absent if the main chain is greatly spaced.

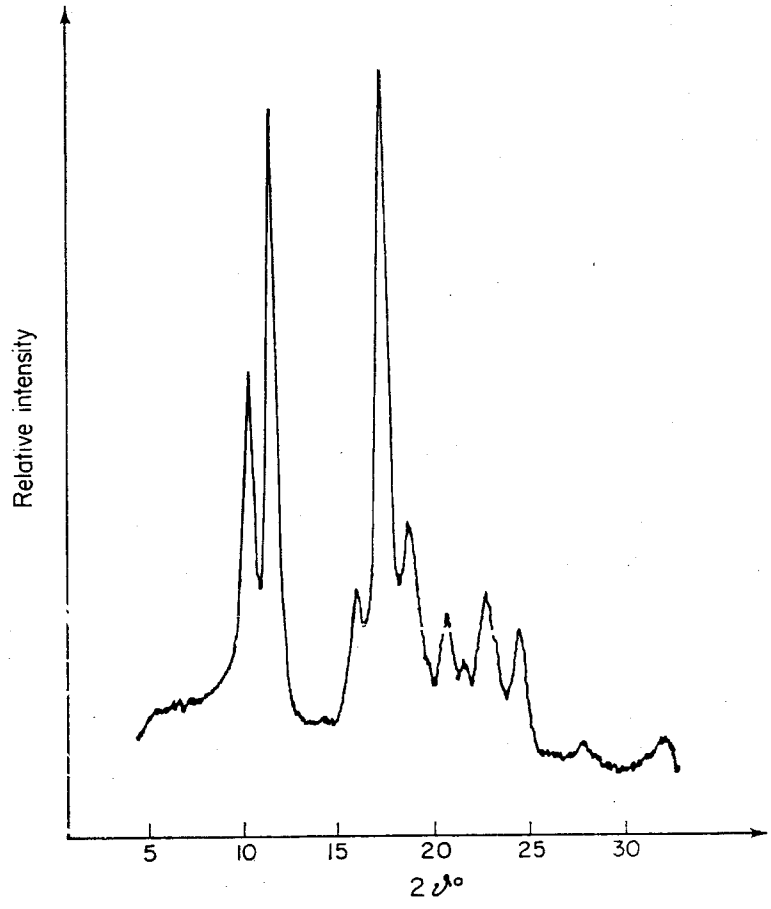


FIG. 1. X-ray spectrum registered with a Geiger counter (Cu$K\alpha$) of poly-3-methylbutene, left as residue to the heptane extraction.

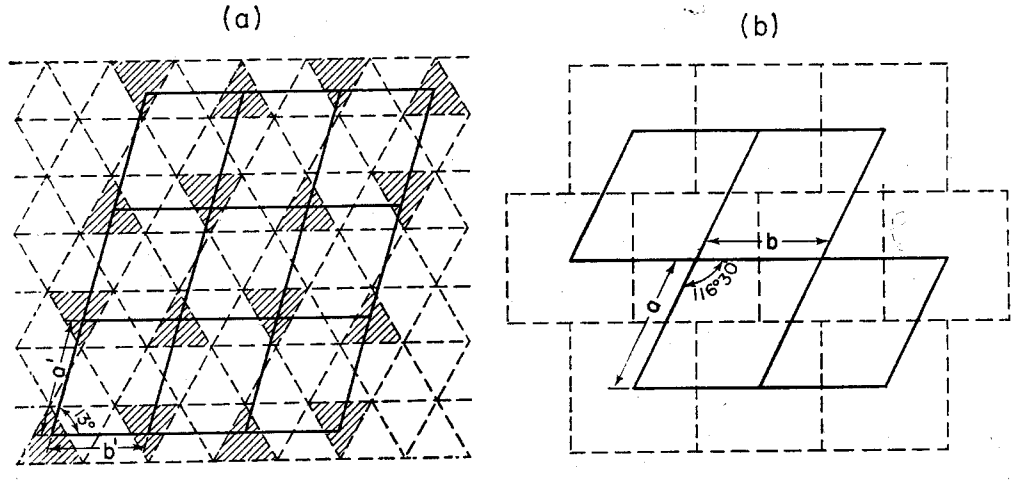


FIG. 2. Derivation of the projection on the 001 plane of a possible subcell of (a) prolypropylene and (b) poly-3-methylbutene-1.

13

THE GEOMETRIC SHAPE OF SPIRALIZED CHAINS OF ISOTACTIC POLYMERS

by P. CORRADINI and I. PASQUON

(10 Dec. 1955)
[*Rend. Accad. Naz. Lincei* (8) **19**, 453 (1955)]

ABSTRACT

The following analytical relationships have been deduced between the identity period d along the axis of the helix-type chain of the isotactic polymers of α-olefins, the σ_1 and σ_2 angles formed by planes which are determined by four successive bonds, the Φ valence angle, the length r of the C—C bond, and the Θ angle between the end views of the two atoms following one another on the same helix:

$$d = \frac{2\, r \sin^2 \Phi/2 \, \sin(\sigma_2 + \sigma_1)/2}{\sin \Theta/2}$$

$$2 \cos \Theta = 2 \cos \sigma_1 \cos \sigma_2 + 2 \cos \Phi \sin \sigma_1 \sin \sigma_2 - \\ - \sin^2 \Phi \, (1 + \cos \sigma_1)\,(1 + \cos \sigma_2)$$

Supposing that σ_1 and σ_2 are equally different from the values ($\sigma_1 = 60°$ and $\sigma_2 = 180°$) occurring in the case in which the principle of the maximum displacement of the bonds is valid (staggered bonds), it is possible, when knowing the type of helix, to calculate d when Φ varies.

These calculations were completed for some of the isotactic polymers of α-olefins.

The helix conformation of poly-4-methylpentene-1 (7 monomers on a period corresponding to 2 helix pitches) has been confirmed by a comparison between experimental intensities formed by an X-ray fibre spectrum and the calculated intensities. For this purpose, a formula has been deduced in order to calculate the distributed intensity diffracted on various layers from a helicoidal polymeric chain.

14

VISCOSITY NUMBER AND MOLECULAR WEIGHT OF FRACTIONATED ISOTACTIC POLYSTYRENE

by G. NATTA, F. DANUSSO and G. MORAGLIO

(15 Dec. 1955)
[*Makromol. Chemie* **20**, 37 (1956)]

ABSTRACT

Viscosities and osmotic pressures of benzene and toluene solutions of isotactic polystyrene fractions were measured. The relationship between intrinsic viscosity and molecular weight was found to be not substantially different from that determined by other authors for fractions of amorphous polystyrenes. Thus conventional viscosimetric methods can be used with isotactic polystyrene for the determination of molecular weights.

15

STEREOSPECIFIC POLYMERIZATION OF α-OLEFINS

by G. NATTA, P. PINO, E. MANTICA, F. DANUSSO, G. MAZZANTI and M. PERALDO

(12 Jan. 1956)
[*Chimica e Industria* **38**, 124 (1956)]

In previous papers we have described a number of crystalline polymers of α-olefins with an isotactic structure, without discussing the mechanism of formation.[1]

For a monomer of the $CH_2 = CHR$ type, to lead to the formation of isotactic macromolecules, a polymerization process must be carried out with a mechanism, which exhibits a particular selectivity not only in determining a regular head-to-tail enchainment of the monomeric units in the main chain of the polymer, but also that each new added unit is arranged in a predetermined steric pattern as to the mutual orientation of the R group and the terminal monomeric unit of the growing chain.

As it will be described in more detail in a subsequent paper, the simplest scheme of formation of isotactic polymers is represented by the polymerization processes of the ionic type. The ionic couple, consisting of the polymeric chain and the inorganic metallo-organic ion of the opposite sign, is added to the monomer molecule in a *trans*-position. The monomer should always be in the same relative position with the same orientation[2] to the terminal monomeric units at the end of the growing chain.

Due to their particular characteristics, we shall indicate the processes which lead to the formation of isotactic polymers as "stereospecific" processes of polymerization, and we shall indicate as "stereospecific catalysts" the catalysts used in the above processes.

A radical polymerization mechanism of vinyl monomers in the homogeneous phase, as it is usually represented, cannot be stereospecific, because, in this case, the end of the growing molecule and the monomer molecule do not appear to be connected with a fixed relative position in space.

Stereospecificity, however, is possible in the ionic heterogeneous catalyses, in which the growing chain is chemically bound to the solid catalyst, which chemi-adsorbs the monomer. In this case, both the position of the chain in relation to the ion fixed on the surface and the position of the chemi-adsorbed monomer in relation to the growing chain are predetermined. The assumption of an intermediate phase of chemisorption of the monomer, even if accompanied by a disappearence of the planar structure of the monomer in a phase previous to the chain growth phase does not modify the previously held concepts.

The catalysts previously known for polymerizing α-olefins were not stereospecific. We have only recently found that different types of catalysts can exist with a certain "stereospecificity" for the polymerization of α-olefins.[3] With some of these, almost exclusively isotactic polymers are obtained, while with others, even when operating under similar temperature and pressure conditions and with the same monomer, isotactic polymers accompanied by greater or lesser quantities of non-isotactic polymers are obtained. This is proved by the data indicated in Table 1, which shows the percentage of isotactic polymers obtained from different monomers with the aid of different catalysts.

The polymers obtained with catalysts based on CrO_3 differ appreciably, however, from those obtained with catalysts based on titanium halides: in particular, their molecular weights are much lower.

A higher stereospecificity is observed in catalysts obtained from titanium halides and alkyl aluminium compounds. It varies appreciably depending on the type of titanium halide and on the aluminium alkyl compound used, and in some cases, on the molecular ratio between the aluminium and titanium compounds adopted in the preparation of the catalyst. This will be described in more detail in subsequent papers.

The highest stereospecificity is observed when using as catalysts halides of titanium (and of other hardly reducible transition metals) having a valency lower than maximum, and which are microcrystalline and insoluble in the solvent used.

TABLE 1. PERCENTAGE OF ISOTACTIC POLYMER[a] OBTAINED IN POLYMERIZATION RUNS CARRIED OUT UNDER SIMILAR CONDITIONS AT TEMPERATURES BETWEEN 80°C AND 90°C

Monomer	% *isotactic polymer*[a]			
	$TiCl_4$–$Al(C_2H_5)_3$[b]	$TiCl_3$–$Al(C_2H_5)_3$[c]	CrO_3 *on* SiO_2–Al_2O_3[d]	CrO_3 *on* SiO_2–Al_2O_3 *in the presence of* $Al(C_2H_5)_3$[e]
propylene	35–45	85–95	1–2	—
n-butene-1	30–40	60–70	1–3	15–17
3-methylbutene-1	60–70	85–95	—	—
pentene-1	1–3	30–40	—	—

[a] The highly crystalline substantially isotactic fraction, which can be separated from the non-isotactic fractions by extraction with solvents, has been considered as the isotactic polymer. In particular, in the case of polypropylene and poly-3-methyl butene-1 the boiling heptane non-extractable fraction, in the case of polybutene-1 the ether non-extractable fraction, in the case of polypentene-1 the ethyl acetate non-extractable fraction have been considered as isotactic polymers.

[b] Catalyst prepared by adding 0·04 moles of $TiCl_4$ in 50 cm^3 of n-heptane to a solution of 0·10 moles of $Al(C_2H_5)_3$ in 400 cm^3 of heptane.

[c] Catalyst prepared from 0·04 moles of $TiCl_3$ and 0·10 moles of $Al(C_2H_5)_3$.

[d] Catalyst prepared according to the Phillips patent[4] by impregnating a silicon–aluminium support with an aqueous 0·8 N solution of chromium anhydride and subsequently activated with dry air at temperatures between 500° and 600°C. The data refer to 24-hr runs carried out at a temperature of 90°C, in an autoclave in which solvent (n-heptane), catalyst and monomer were introduced (ponderal ratio monomer/solvent = 0·32).

[e] Ponderal ratio SiO_2–Al_2O_3/$Al(C_2H_5)_3$ = 8·3.

In the study of the mechanism of the polymerization of α-olefins with the aid of catalysts obtained from titanium halides and aluminium alkyl compounds, the following experimental findings have a particular significance.

1. Aluminium alkyl and titanium alkyl compounds alone are not stereospecific catalysts. The titanium alkyls, which are obtained by the action of magnesium alkyl halides on titanium tetrachloride,[5] or which can be assumed to be formed by the exchange of lead tetraethyl and titanium tetrachloride, do not yield, under the experimental conditions adopted, appreciable quantities of isotactic polymers.

2. All the best stereospecific catalysts discovered up to now for the production of isotactic polymers are solids.

3. The catalysts obtained from maximum valency titanium halides reacted with aluminium alkyl compounds contain aluminium, halides, alkyl groups and titanium with a valency which is lower than maximum.

4. These polymers show the presence of organic groups which during

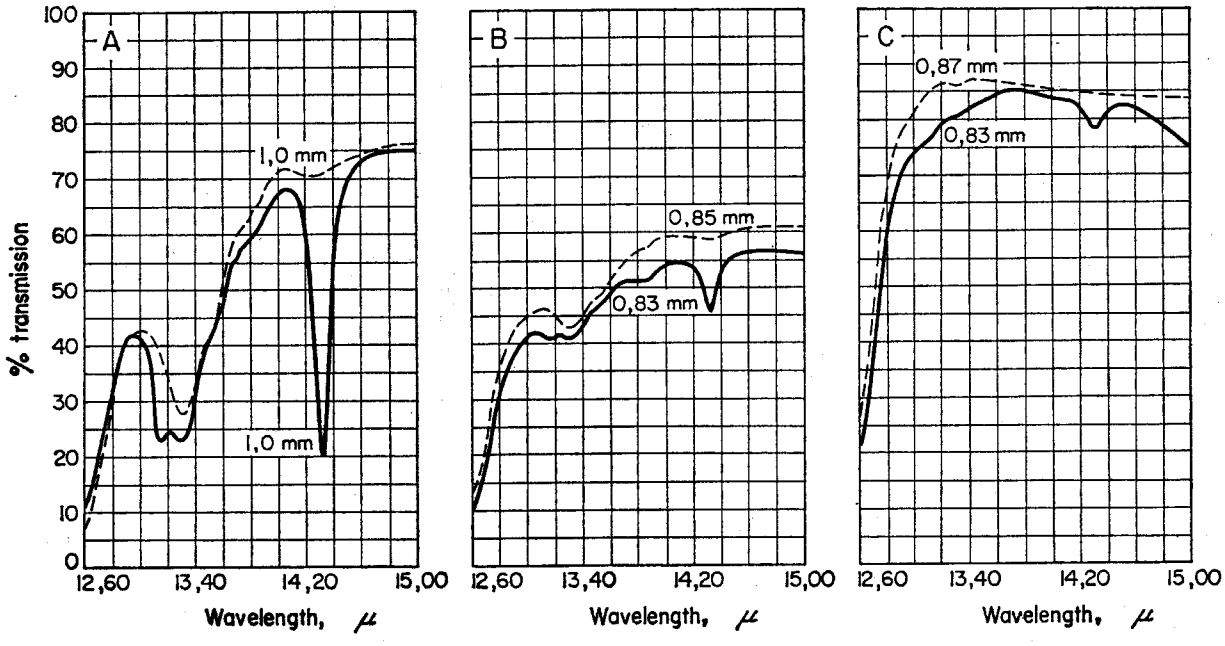


FIG. 1. Spectra of various fractions of polypropylene.

A. Ether extract
——— Product obtained in the presence of aluminium-triphenyl
— — — — Product obtained in the presence of aluminium-tripropyl

B. Heptane extract
——— Product obtained in the presence of aluminium-triphenyl
— — — — Product obtained in the presence of aluminium-tripropyl

C. Residue
——— Product obtained in the presence of aluminium-triphenyl
— — — — Product obtained in the presence of aluminium tripropyl

the preparation of the catalysts were linked to the aluminium in the aluminium alkyl compounds. For example, in the polymer obtained by polymerizing propylene with the aid of catalysts prepared from triphenyl aluminium, we established the presence of phenyl groups linked to the tertiary carbon atoms as shown by the absorption bands at 13·16 μ and 14·33 μ given by the different fractions of the polymer (Fig. 1).

A comparison between the number of molecules present, calculated by viscosimetric measurements, and the number of phenyl groups present, determined approximately by the absorption bands at 14·33 μ on laminae of a known thickness, has demonstrated that, in the polymerizate, the ratios between the number of macromolecules and the number of phenyl groups present is higher than 1 (from 3 to 8 for the different fractions obtained by extraction of the polymers formed in a 4–5 hr polymerization of propylene at 90°C).

5. The infrared spectra of both amorphous and crystalline polypropylenes (the latter with a medium molecular weight) indicate the presence of double bonds, which, for the most part, are terminal vinylidenic double bonds. Figure 2 shows the absorption bands at 11·27 μ*

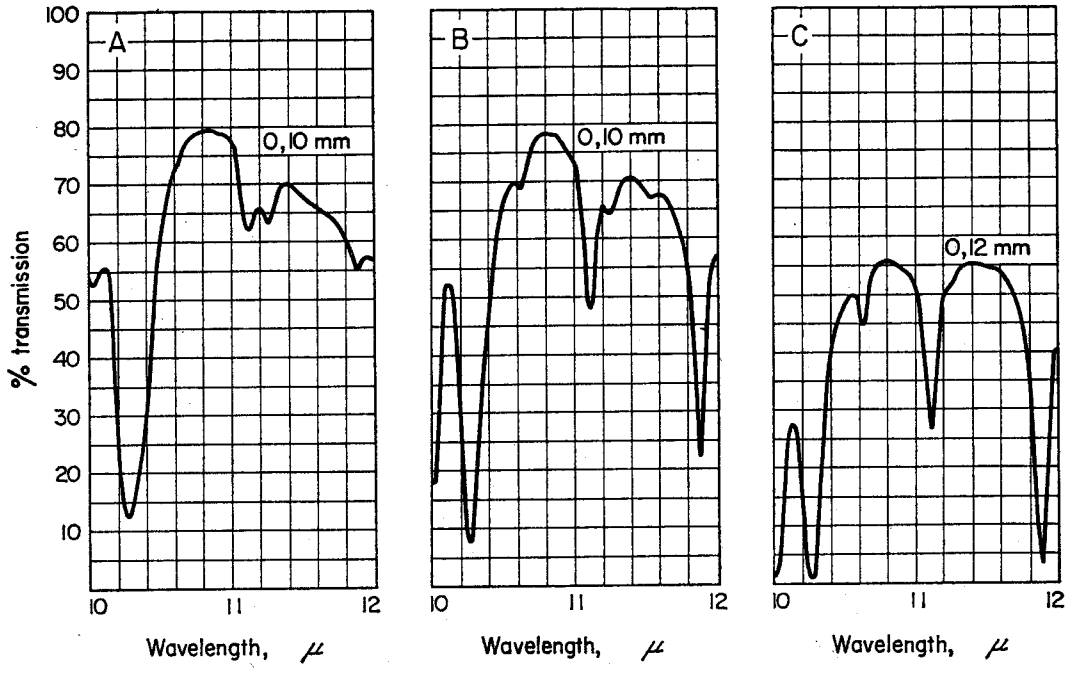


FIG. 2. Infrared spectra of various fractions of polypropylene.
A. Ether extract
B. Heptane extract
C. Residue

* Vibration region of the deformation of the hydrogen outside the plane of the $>C=C<^{H}_{H}$ group.

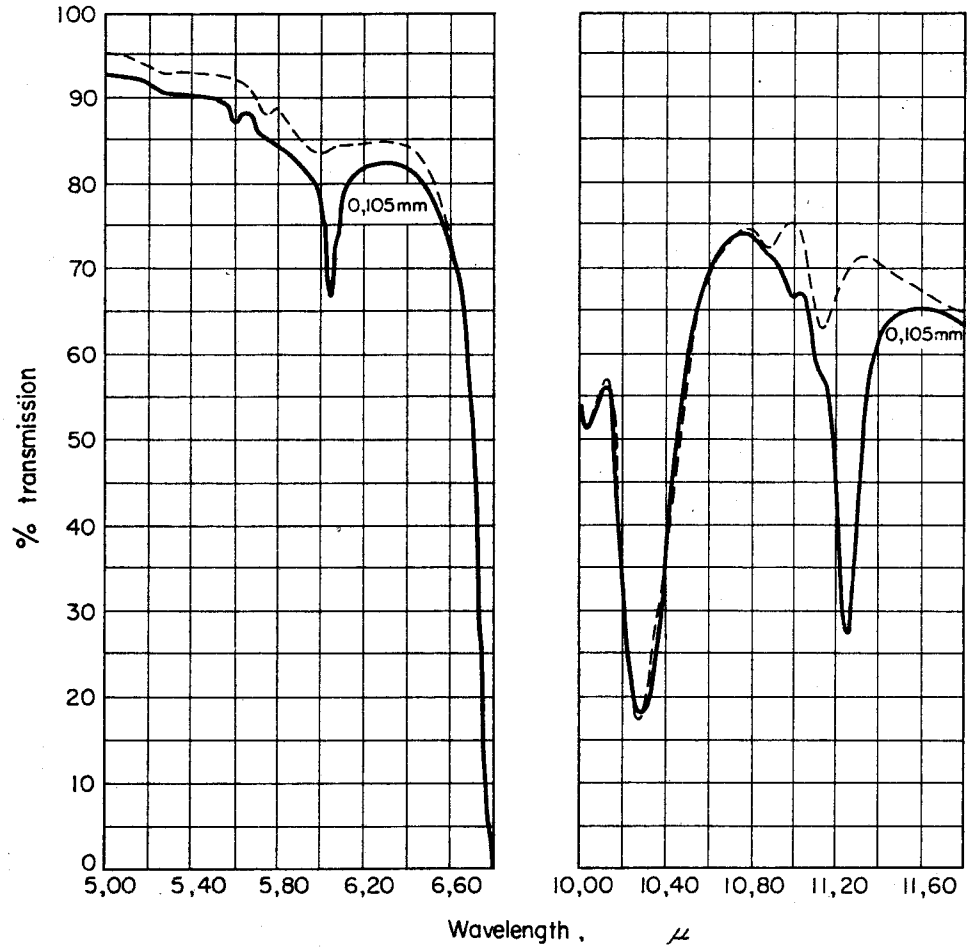


FIG. 3. Infrared spectra of low-molecular-weight polypropylenes (oily fractions) before _____ and after — — — — — hydrogenation

for various fractions of polypropylene. For the oily low-molecular-weight fractions, Fig. 3 shows the bands at 11·27 μ and 6·05 μ, as well as the valency vibration of the $\rangle C=C\langle$ group* and the same spectrum regions for the hydrogenated product.

If one assumes that each molecule contains a double bond of the vinylidenic type, an approximate calculation of the molecular weight, based on the concentration of the double bonds present, leads to values of the same order as those deduced from viscosimetric measurements.

The following interesting deductions can be argued from these experimental findings.

(a) With the use of catalysts prepared by reacting titanium compounds with organic aluminium compounds, the polymerization starts by the insertion of a monomer molecule between a metal atom of the catalyst and an atom of the alkyl or aryl groups originally linked

* The position of the band further proves the presence of vinylidenic double bonds.

to the aluminium. It can be assumed that the reaction with other monomeric units procedes analogously with the participation of the new couple consisting of the catalyst, and the alkyl or alkyl-aryl group thus formed.

(b) The presence of vinylidenic end groups (demonstrated by the isopropyl groups formed by hydrogenation of the polymer) and of benzylidenic type groups: C_6H_5—CH in the polymer obtained with the aid of catalysts prepared from aluminium triphenyl and $TiCl_4$, demonstrate that, in the chain growth reaction, a monomer with a vinylidenic end group of the $CH_2=CHR$ type is inserted with the CH_2 group turned towards the metal atom and the CHR group turned towards the growing chain.

(c) The viscosimetric molecular weight of the polymer obtained in the presence of catalysts prepared from $Al(C_6H_5)_3$ and $TiCl_4$ is in fairly good agreement with that calculated on the basis of the number of vinylidenic double bonds present, assuming that each molecule contains one double bond. This molecular weight, moreover, is much lower than the molecular weight calculated on the basis of the number of phenyl groups present. Thus, in accordance with the kinetic data which will be published in other papers, it is demonstrated that chain termination reactions occur without involving the deactivation of the catalyst. For the termination reaction to occur with the formation of a double bond in the molecule and the regeneration of the catalyst, it must be assumed that it includes a separation of the hydride ion (H^-) from the growing molecule. This hydride ion can be transferred to another monomer molecule or to the catalyst, depending on the transfer obtained. A chain termination reaction will occur corresponding either to a chain transfer with the monomer or to the formation of an unstable hydride, which can be added successively to the monomer molecule. Thus there will be a catalytic process in both cases.

On the basis of these data, we can confirm the hypothesis previously formulated by one of us,[6] that the stereospecific polymerization of α-olefins with catalysts based on titanium halides and aluminium-alkyl compounds is of the anionic type. This can be schematically represented in the manner indicated below, assuming that in the case of propylene and of a catalyst prepared from $TiCl_4$ and $Al(C_6H_5)_3$ a complex is formed, which, for the sake of simplicity, is indicated by $X_nMe—C_6H_5$, where X_n represents the other groups bound to the metal in the catalyst. For the metallo-organic bond we have

1. Initiation

$$\left[X_nMe-C_6H_5 \longleftrightarrow \overset{(+)\,(-)}{X_nMe\ C_6H_5}\right] + CH_2=CH-CH_3 \rightarrow \left[X_nMe-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C_6H_5 \longleftrightarrow \overset{(+)\,(-)}{X_nMe\ CH_2}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C_6H_5\right]$$

2 Propagation

$$\left[X_nMe-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C_6H_5 \longleftrightarrow \overset{(+)\,(-)}{X_nMe\ CH_2}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C_6H_5\right] + n\,CH_3-CH=CH_2 \rightarrow$$

$$\rightarrow\left[X_nMe-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-(CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}})_n-C_6H_5 \longleftrightarrow X_nMe\overset{(+)\,(-)}{CH_2}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-(CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}})_n-C_6H_5\right]$$

3. Termination

a) Termination with transfer of hydrogen atoms to the cat alyst

$$\left[X_nMe-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-(CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}})_n-C_6H_5 \longleftrightarrow \overset{(+)\,(-)}{X_nMe\ CH_2}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-(CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}})_n-C_6H_5\right] \rightarrow$$

$$\rightarrow\left[X_nMeH \longleftrightarrow \overset{(+)\,(-)}{X_n\ Me\ H}\right] + CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-(CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}})_n-C_6H_5$$

(b) Termination with chain transfer of the monomer

$$\left[X_nMe-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-(CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}})_n-C_6H_5 \longleftrightarrow \overset{(+)\,(-)}{X_nMe\ CH_2}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-(CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}})_n-C_6H_5\right] + CH_2=CH-CH_3 \rightarrow$$

$$\left[X_nMe-CH_2-CH_2-CH_3 \longleftrightarrow \overset{(+)\,(-)}{X_nMe\ CH_2}-CH_2-CH_3\right] + CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-(CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}})_n-C_6H_5$$

indicated both the homopolar linear form and the most probable polarized limiting form. This polymerization mechanism also includes that for the polymerization of ethylene with triethyl aluminium,[7] which we have verified by kinetic studies.

It is therefore concluded that an ionic polymerization mechanism, and more precisely an anionic one, must be attributed to the processes which we have developed for the production of isotactic polymers with catalysts obtained by the reaction of transition metal halides with aluminium–alkyl compounds.

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16

THE STRUCTURE OF CRYSTALLINE 1,2-POLYBUTADIENE AND OF OTHER "SYNDIOTACTIC" POLYMERS

by G. NATTA and P. CORRADINI

(16 Feb. 1956)
[*J. Polymer Sci.* **20**, 251 (1956)]

ABSTRACT

With the aid of anionic polymerization catalysts, a high molecular weight 1,2-polybutadiene has been obtained. It is a crystalline material with a melting point above 150°C. Electron and X-ray diffraction studies with oriented films allowed us to determine its unit cell, the space-group, and the coordinates of the individual carbon atoms in the cell. The chains of the polymer deviate slightly from the conventional planar zigzag structure, while the vinyl group substituents are arranged in the 1–3 sequence with alternating *d* and *l* configurations. It is proposed to call this type of spatial arrangement in head-to-tail vinyl polymers a "syndiotactic" arrangement. Even polyvinyl chloride obtained with free radical catalysts contains small-ordered regions, with a structure similar to syndiotactic 1,2-polybutadiene.

17

CRYSTALLINE STRUCTURE OF POLYPROPYLENE OXIDE

by G. NATTA, P. CORRADINI and G. DALL'ASTA

(14 April 1956)
[*Rend. Accad. Naz. Lincei* (8) **20**, 408 (1956)]

ABSTRACT

The elementary unit cell and the chain symmetry of polypropylene oxide, which was prepared from a racemic monomer with the aid of stereospecific catalysts, are deduced from the fibre spectra of the polymer itself. A qualitative model of the chain-packing in the lattice is indicated here. The chain exhibits a helix symmetry: therefore, each chain contains asymmetric carbon atoms of the same type (isotactic enchainment). The possibility that each crystal might contain chains, which would be isomorphous among themselves, is discussed here.

18

CRYSTALLINE BUTADIENE POLYMER WITH AN ISOTACTIC 1,2-ENCHAINMENT

by G. NATTA, L. PORRI, P. CORRADINI and D. MORERO

(14 April 1956)
[*Rend. Accad. Naz. Lincei* (8) **20**, 560 (1956)]

ABSTRACT

Only one crystalline polymer of butadiene with 1,2 enchainment has been found so far, namely, syndiotactic polybutadiene, whose properties were described in previous papers. A new crystalline polymer of butadiene having 1,2 enchainment has been obtained now with catalysts such as aluminium trialkyls and transition metal compounds. Its I.R. spectrum (in the solid state) and its X-ray spectrum differ from those of the previously known syndiotactic polybutadiene. The new polymer shows fibre spectra analogous to those of isotactic polybutene and like isotactic polybutene it crystallizes in the rhombohedric system with constants : $a = 17 \cdot 3 \pm 0 \cdot 1$ Å and $c = 6 \cdot 5 \pm 0 \cdot 1$ Å. On the basis of the analogy between the constants of the lattice and the intensity of the single reflections, it has been assumed that the molecules in the new 1,2-polybutadiene have the same isotactic configuration as poly-α-butene.

The following table shows some physical properties of isotactic and syndiotactic polybutadienes and of isotactic poly-α-butene :

	Syndiotactic polybutadiene	*Isotactic polybutadiene*	*Isotactic poly-α-butene*
Identity period along the fibre axis (Å)	5·14	6·5	6·5
Density of the crystals	0·96	0·96	0·95
X-ray melting temperature (°C)	154	120	126

The I.R. spectrum of isotactic 1,2-polybutadiene in the solid state shows the following bands, thus differentiating this polymer from the syndiotactic one : 8·12 μ ; 8·36 μ ; 9·02 μ ; 10·60 μ ; 11·42 μ ; 12·40 μ ; 14·40 μ (very strong).

The preparation of isotactic 1,2-polybutadiene has proved for the first time the possibility of obtaining, starting from the same vinyl type monomer, two crystalline polymers which are different only in the type of regularity in the configuration of the tertiary carbon atoms of the main chains.

19

STEREOSPECIFIC CATALYSIS AND ISOTACTIC POLYMERS*

by G. NATTA

(25 April 1956)
[*Angew. Chemie* **68**, 393 (1956)]
[*Chimica e Industria* **38**, 751 (1956)]

STEREOISOMERY PHENOMENA IN VINYL HIGH POLYMERS

A new chapter of considerable theoretical and practical interest has been recently opened in the field of polymerizations: namely, the field of stereospecific polymerizations.[1—15] It is closely connected with the use of stereospecific catalysts, which during the polymerization effect a sterically ordered arrangement of the monomeric units of the polymer, or of their tertiary carbon atoms.

The various stereoisomeric polymers derived from the same monomer may differ considerably in their physical properties (e.g. melting temperature, crystallinity, mechanical properties, etc.), because stereoisomery phenomena often have more striking effects in macromolecular substances than in low-molecular-weight substances (Tables 1, 2 and 3).

Table 1 shows a comparison between the properties of different stereoisomers prepared by us, starting from the same olefinic monomers.

* This paper gives an interpretation of the experimental results obtained from the stereospecific polymerizations performed at the Institute of Industrial Chemistry of the Polytechnic of Milan. Chief collaborators in this work were: P. Pino for the organic-chemical part; G. Mazzanti, L. Porri, G. Dall'Asta and P. Longi for polymerizations and fractionations; P. Corradini and I. W. Bassi for crystallographic investigations; F. Danusso and G. Moraglio for physicochemical measurements; E. Mantica, M. Peraldo and D. Morero for infrared investigations; M. Farina, I. Pasquon and E. Giachetti for kinetic measurements and G. Crespi for mechanical properties.

The crystalline polymers are high melting and have good mechanical properties; on the other hand the high-molecular-weight amorphous polymers show very low second order transition temperatures. These differences have been attributed by us to stereoisomery phenomena.

Two classes of stereospecific polymerizations must be distinguished depending on whether or not the monomers show stereoisomery phenomena before the polymerization.

TABLE 1. COMPARISON BETWEEN LINEAR, ISOTACTIC AND NON-ISOTACTIC POLYMERS OBTAINED BY ANIONIC POLYMERIZATION

Polymer	*Density (g/cm³)*	*Transition temp. (°C)*	*Identity period along the axis c (Å)*	*No. of monomer units in the identity period*
Isotactic polypropylene	0·92	160–170 I ord.	6·50	3
Atactic polypropylene	0·85	–35 II ord.	—	—
I isotactic polybutene-1	0·91	126–128 I ord.	6·50	3
II isotactic polybutene-1	—	—	6·85	4
Atactic polybutene-1	0·87	–42 II ord.	—	—
Polypentene-1	0·87	75–80 I ord.	6·60	—
Poly-3-methylbutene-1	0·90	250 I ord.	6·84	4
Poly-4-methylpentene-1	0·83	205 I ord.	13·85	7
Poly-4-methylhexene-1	0·86	188 I ord.	14·0	7
Poly-5-methylhexene-1	0·85	130 I ord.	6·50	3
Isotactic polystyrene	1·08	230 I ord.	6·65	3
Atactic polystyrene	1·05	85 II ord.	—	—

TABLE 2. TEMPERATURE OF THE SECOND ORDER TRANSITION OF SOME LINEAR AMORPHOUS POLYOLEFINS, DETERMINED BY DILATOMETRIC MEANS (AVERAGE VALUES)

Polyethylene	—21°
Atactic polypropylene	—35°
Atactic polybutene	—42°
Atactic polypentene	—50°

In the first case (i.e. presence of stereoisomeric monomers) a stereospecific selective action can exist which directs the molecules of equal steric configurations to react in such a manner that the newly formed molecules will contain the pre-existing stereoisomers in a definite order.

TABLE 3. MECHANICAL PROPERTIES OF THE STEREOREGULAR, NON-ORIENTED POLYMERS

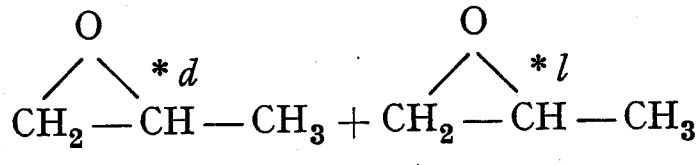
	M.W.	*Yield point (kg/cm²)*	*Tensile strength (kg/cm²)*	*Elongation at (break%)*	*Vicat (kg 1) (°C)*
Polypropylene	350·000	290-310	420–440	750–800	150
Polypropylene	100·000	320–340	400–420	650–700	150
Polybutene-1	60·000	—	200–220	350–400	99
Polypentene	45·000	—	120–150	450–500	—

This could be, for instance, the behaviour of a catalyst containing agents, some of which would act selectively on one of the stereoisomers, and others which would act on the other stereoisomer ; these agents would therefore lead to the formation of molecules, each being obtained by the polymerization of several monomers having the same steric configuration. This type of stereospecific polymerization has been proposed in order to explain the crystallinity of poly-4-methyl-hexene-1 prepared by us.[12] In fact, this could explain the structure and the high melting temperature of polypropylenoxides obtained by Price,[16] under particular conditions, from a racemic monomer.

These polypropylenoxides are crystalline, optically inactive and show a high melting temperature, which is equal to that of optically active polymers obtained from an optically active monomer. On the other hand, a low-melting amorphous polymer was obtained from the racemic monomer, by adopting the usual polymerization processes (with the use of alkaline hydroxides or alcoholates) (see scheme 1).

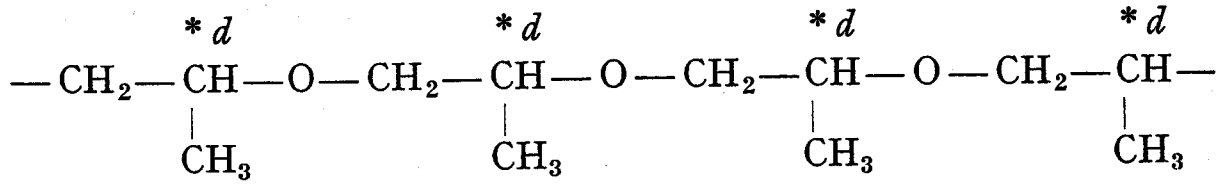
SCHEME 1

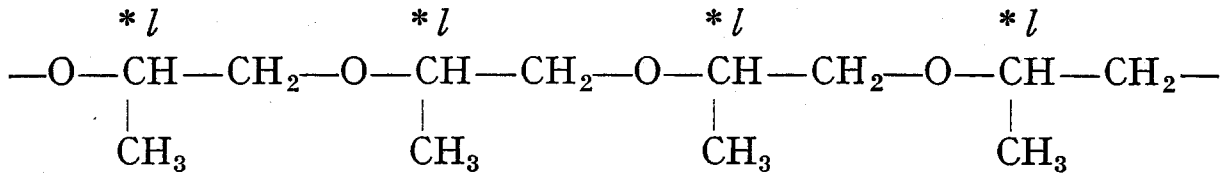
Monomer :



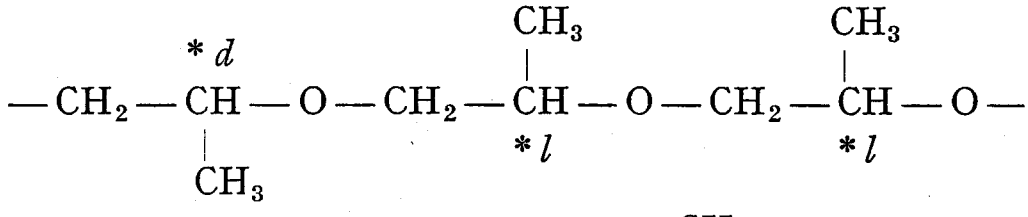
Types of enchainment :

I. Crystalline polymer of high melting temperature





II. Liquid or elastic amorphous polymer



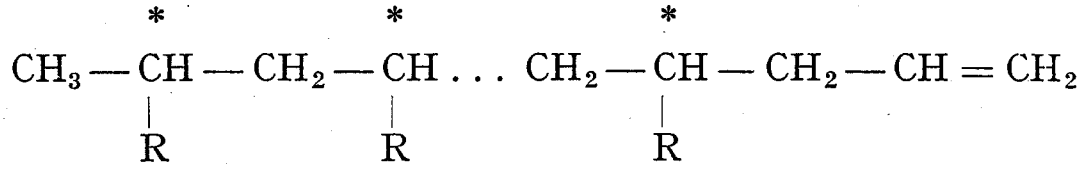
The most interesting class of stereospecific polymerizations is that in which molecules of vinyl compounds participate; in this case monomers do not exhibit stereoisomery phenomena. The stereospecific catalysts permit direction of polymerization toward the association, in each macromolecule, of the monomeric units according to a determined order, due to regular successions of determined steric configurations (scheme 2).

SCHEME 2

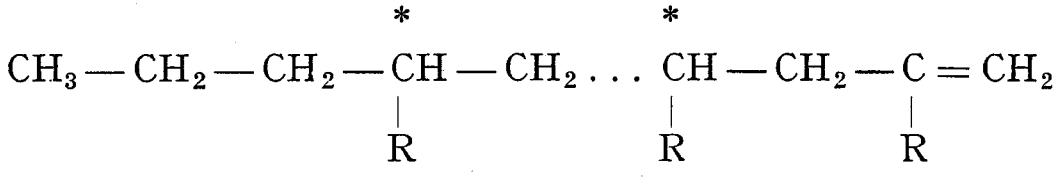
Polymers of vinyl monomers $CH_2 = CHR$:

End groups:

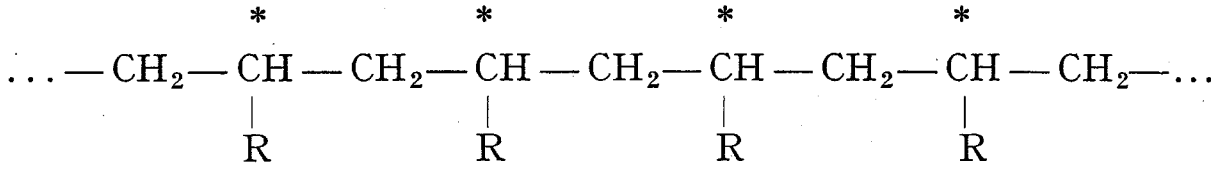
ideal cationic polymerization



ideal anionic polymerization



Central groups:



At least n-2 tertiary carbon atoms are present in a linear molecule obtained by regular polyaddition of vinyl monomers. Some of these carbon atoms, those lying close to the ends of the chain, are typically asymmetric ; the constitutional differences of the substituents are such that they can give rise to true optical isomery phenomena.

However, if very high polymers are considered, the influence exerted by the end groups on the chemical, physical and optical properties is negligible.

It is therefore to be expected that if the R group of a monomer of the type CH_2=CHR does not show the phenomena of optical isomery, each molecule of the polymer with chains of infinite length will also not exhibit the phenomena of optical isomery. The optical activity, due to the presence of an asymmetric carbon atom, clearly depends on the asymmetry prevailingly caused by the constitutional differences in the parts of the molecule which lie near the asymmetric atom.

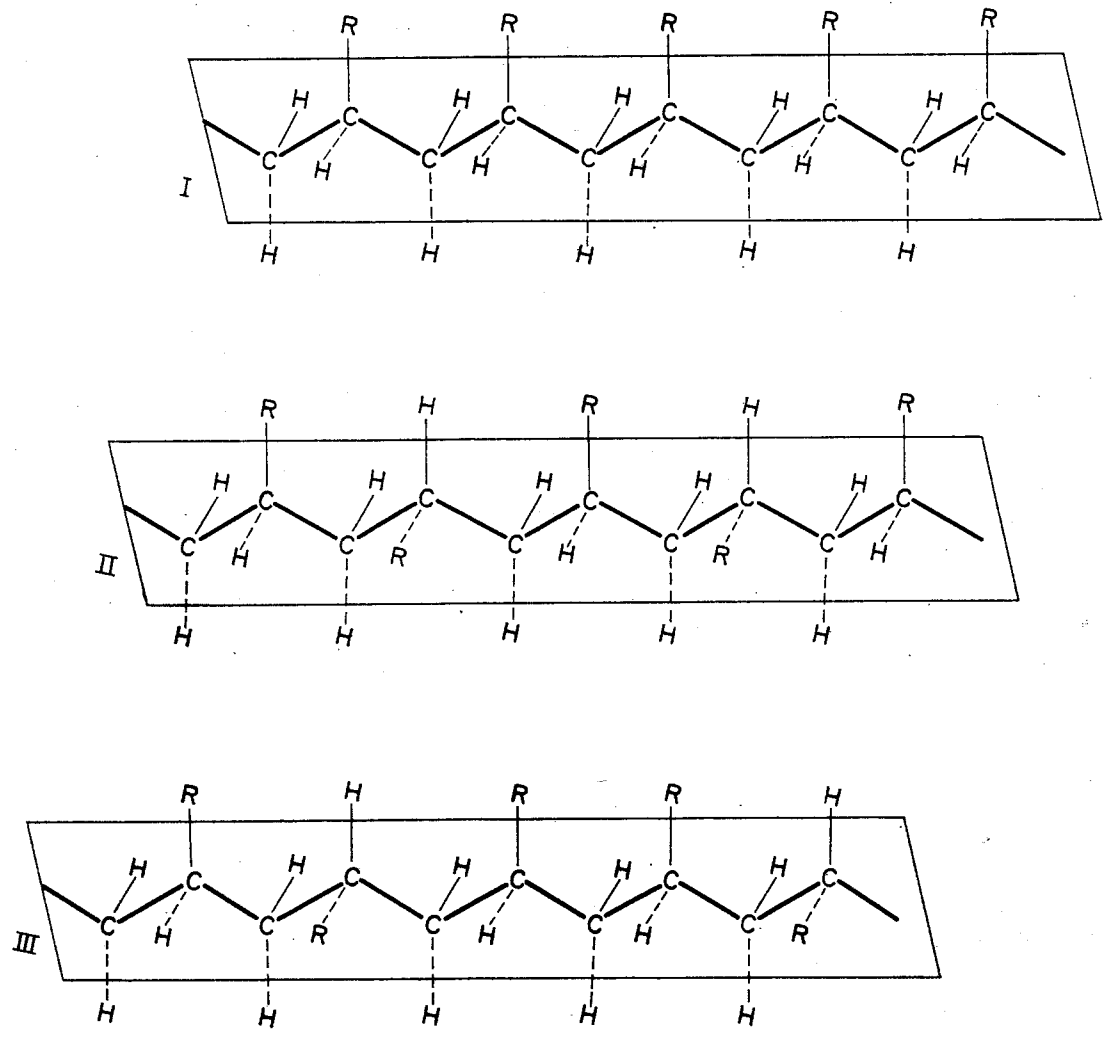


FIG. 1. Drawing of the chains of poly-α-olefins, arbitrarily stretched on a plane. I : Isotactic ; II : Syndiotactic ; III : Atactic.

These neighbouring parts are chemically identical in those polymers made from $CH_2=CHR$ monomers.

In this case, however, a particular type of stereoisomery occurs: this is exclusively due to the relative configurations of the near tertiary carbon atoms.

This type of stereoisomery can be easily understood if one considers, for the purpose of demonstration, the zigzag main chain of a paraffin stretched on a plane (Fig. 1). Different types of configuration of the tertiary carbon atoms are then possible, depending on the relative positions of the R groups. If the R groups are either all above or all below the plane of the main chain, the structure is "*isotactic*"[1, 4, 6, 8, 9] (Fig. 1).

If the R groups lie alternately above and below such a planar main chain, the structure is *syndiotactic*.[8, 9, 11] The structures in which the R groups are irregularly arranged below and above the conventional plane of the main chain are *atactic*.

Actually, in isotactic polymers, a complete equality of the configurations of all the tertiary carbon atoms is found only if the molecules are of infinite length.

With regard to molecules with finite chain length and different ends, it is to be expected that the possible very slight optical activities of each macromolecule would be compensated by the presence, in a polymer solution, of enantiomorphous macromolecules.

In the case of polymers with a disordered structure, one tertiary carbon atom may differ from another, depending on the relative configurations shown by the neighbouring tertiary carbon atoms. In atactic polymers, with a statistical distribution of opposite steric configurations, there will be evidence of intramolecular compensation taking place beside the intermolecular compensation.

In the case of the polyaddition of a vinyl monomer A (which when linked in a polymer chain may show stereoisomery phenomena) and in the presence of an initiator BH, acting through an ionic mechanism, the following types of stereospecific addition reactions will be obtained.

$BH + mA = B(A^{*l,d})_{m-1}AH$	atactic structure
$BH + mA = B(A^{*iso})_{m-1}AH$	isotactic structure
$BH + (2m+1)A = B(A^{*l}A^{*d})_mAH$	syndiotactic structure

In the case of a simple anionic polymerization of a vinyl compound, as it may derive from the preceding polyaddition when it is followed

by a dissociation with regeneration of the catalyst or by a chain transfer process with the monomer, the following types of macromolecules may be obtained :[8, 9, 15]

$$(n+2)\,CHR=CH_2 \longrightarrow CH_2=CR\,(H_2C\cdot RHC^{*d,l})_nCH_2-CH_2R$$
atactic polymer

$$(n+2)\,CHR=CH_2 \longrightarrow CH_2=CR\,(H_2C\cdot RHC^{*iso})_nCH_2-CH_2R$$
isotactic polymer

$$(2n+2)\,CHR=CH_2 \longrightarrow$$
$$\longrightarrow CH_2=CR\,(H_2C\cdot RHC^{*d}\cdot H_2C\cdot RHC^{*l})_n\,CH_2-CH_2R$$
syndiotactic polymer

To summarize : in the field of vinyl polymers, it is possible to obtain the following linear head-to-tail polymers having the regular simple structure of $CH_2=CHR$ monomers (R being an aliphatic or aromatic group, which might, or might not show stereoisomery phenomena) :

1. *Isotactic polymers:* constituted by chain segments characterized by a regular repetition of monomeric units, containing asymmetric tertiary carbon atoms, with the same steric configuration.
2. *Syndiotactic polymers:* constituted by regular sequences of monomeric units, in which each second carbon atom of the chain has an opposite steric configuration.

Moreover, linear head-to-tail vinyl polymers with a more or less irregular structure may exist :

3. *Atactic polymers:* with an irregular distribution of the steric configurations of the monomeric units.
4. *Block homopolymers:* several typical cases of block homopolymers can be visualized. They will have different physical properties depending on the predominance of one of the two block types and on the size of the single segments. For instance, the following block copolymers can be thus obtained :

(a) the isotactic–atactic type, consisting of segments of regular isotactic chains alternating with segments of irregular structure ;

(b) the syndiotactic–atactic type, consisting of segments of regular syndiotactic chains alternating with segments of irregular structure.

The differences in the properties of the various polymers are considerable, provided that the size of the R groups differ markedly

from that of the hydrogen atom and are therefore much larger than the fluoro atom and hydroxyl group. In this case, atactic polymers are amorphous, do not crystallize even at low temperature, and show a very low softening temperature (second order transition).

Polymers obtained by a free radical mechanism are generally atactic and, in the cases where a tendency for ordered structure is appa-

TABLE 4. CRYSTALLOGRAPHIC CONSTANTS OF ISOTACTIC POLYMERS WHOSE CHAINS POSSESS A TERNARY SYMMETRY

	Polystyrene	*Polybutene-1**	*Polypropylene*
Symmetry	Hexagonal: space-group $R3c$ or $R\bar{3}c$	Hexagonal: space-group $R3c$ or $R\bar{3}c$	Monoclinic or triclinic
a (Å)	$21{\cdot}9 \pm 0{\cdot}1$	$17{\cdot}69 \pm 0{\cdot}05$	$a' = 6{\cdot}56 \pm 0{\cdot}05$
b (Å)	$21{\cdot}9 \pm 0{\cdot}1$	$17{\cdot}69 \pm 0{\cdot}05$	$b' = 5{\cdot}46 \pm 0{\cdot}05$
c (Å)	$6{\cdot}65 \pm 0{\cdot}05$	$6{\cdot}50 \pm 0{\cdot}05$	$c = 6{\cdot}50 \pm 0{\cdot}05$
γ	120°	120°	$\gamma' = 106°30'$
d_{calc}	1·12	0·95	0·938
d_{exp}	1·085	0·91	0·92

Notice: a', b', γ', for polypropylene represent the projections on a plane normal to c of the minimum constants a, b, which interpret the equatorial reflections and the γ angle between a' and b'.

*The lattice constants of the hexagonal modification of polybutene-1 may be markedly varied according to the thermal and mechanical treatments that the sample has been subjected to. The a and b constants may vary from 17·30 to 17·70 Å, whereas the c constant is varied simultaneously in the opposite sense.

rent, the probability for syndiotactic enchainment is higher than for the isotactic one.[8, 9] The completely isotactic or syndiotactic polymers generally show a high melting temperature, a high degree of crystallinity and good mechanical properties.

In previous papers we described the structures of the chains of some isotactic polymers of α-olefins (Table 4) [polypropylene,[2, 1] poly-α-butene[7], polystyrene[3,6]]. It was found that such chains, in the crystalline state, show a ternary symmetry, with an identity period of 6·5 Å. These facts can be explained on the assumption that the chains assume a helix structure with a pitch corresponding to 3 monomeric units. Adopting the nomenclature proposed by Bunn,[17] this structure would correspond to the type $(AB)_3$ (Fig. 2).

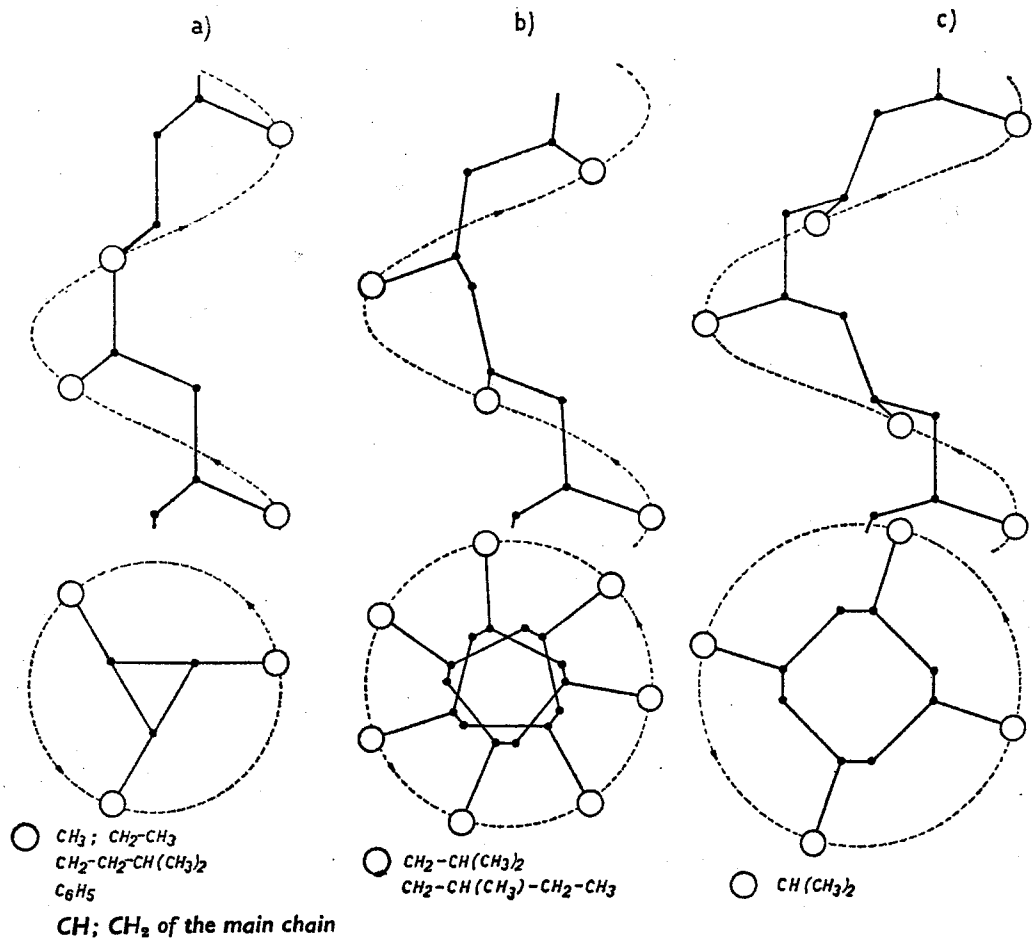


FIG. 2. Crystalline conformation of some isotactic chains having a different symmetry.

It was subsequently found [12–14] that if the monomer possesses a branched chain the isotactic polymers are still crystalline, they have a higher melting temperature than the polymers of the corresponding linear monomers, and they have in the crystalline state chains with a helix structure, but different pitches of the helices and the number of the monomeric units may vary. These structures may be considered to be of the $(A'B')_{3,5}$ and $(A'B')_4$ types, which were not foreseen by Bunn. They call for a slight deviation from the principle of maximum distance between bonds (staggered bonds) (Table 5).

Crystalline polymers have also been obtained by polymerizing olefins which, already in the monomeric state, contain asymmetric carbon atoms, such as 4-methylhexene-1. These polymers are isotactic, that is, they have a regular structure, as far as the carbon atoms of the main chain are concerned.

On the other hand with regard to the tertiary carbon atoms of the side chains, it is possible to foresee stereoisomery phenomena for those polymers with isotactic carbon atoms in the main chain, depend-

TABLE 5. COMPARISON BETWEEN THE MELTING TEMPERATURES OF THE CRYSTALLINE POLYMERS OF SOME LINEAR AND BRANCHED α-OLEFINS

Linear monomer	*Melting temp. of the polymer*[a]	*Branched monomer*	*Melting temp. of the polymer*[a]
$CH_3—CH=CH_2$	165°C	$CH_3—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—CH=CH_2$	>250°C
$CH_3—CH_2—CH=CH_2$	128°C	$CH_3—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—CH_2—CH=CH_2$	205°C
$CH_3—(CH_2)_2—CH=CH_2$	80°C	$CH_3—CH_2—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—CH_2—CH=CH_2$	188°C
$CH_3—(CH_2)_3—CH=CH_2$	not determined*	$CH_3—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—CH_2—CH_2—CH=CH_2$	130°C

[a] Determined by X-ray methods.

* The samples of poly-n-hexene-1, prepared and purified according to the same procedure as that adopted for other isotactic poly-α-olefins, are amorphous at room temperature.

ing on whether the atoms of the side chains have the *d*- or *l*-configuration, or whether there is an alternation between *d*- and *l*-configuration, or whether both configurations are present in a statistical distribution. The last mentioned type is the most probable in the isotactic polymers which we prepared from 4-methylhexene-1, because they show a fairly high solubility and an ill-defined X-ray diagram, in spite of their crystallinity and fairly high melting temperature.

As soon as we learned the results obtained by Price in the polymerization of propylenoxide, we examined its structure, in order to establish whether the crystalline polymer of propylenoxide had structural analogies with the isotactic polymers (Fig. 3).

Samples of polypropylenoxide prepared by us according to the procedures of Price and the Dow Co.[16, 18] gave fibre X-ray diagrams, from which it was possible to calculate an elementary unit cell containing 4 monomeric units[19] with lattice constants : $a = 10{\cdot}60$ Å ; $b = 4{\cdot}66$ Å ; c (fibre axis) $= 7{\cdot}16$ Å.

The crystalline structure of the main chain is planar and the methyl groups lie alternatively on one and the other side of the plane of the chain (Fig. 4).

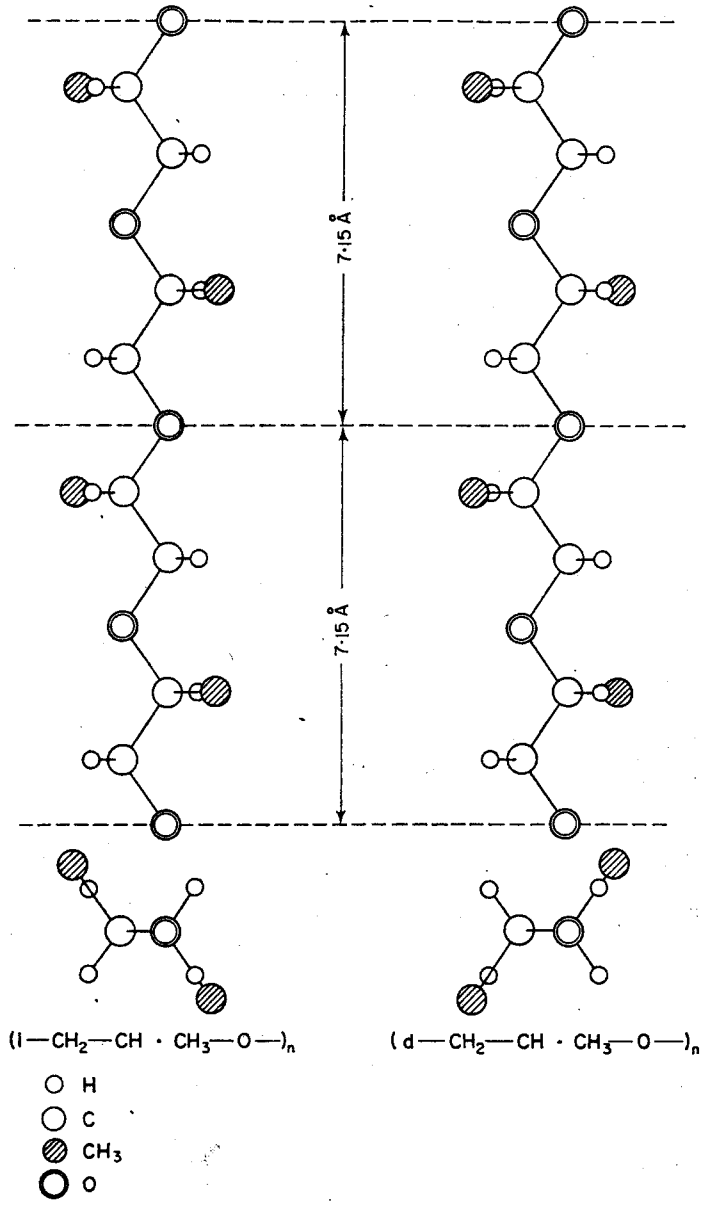
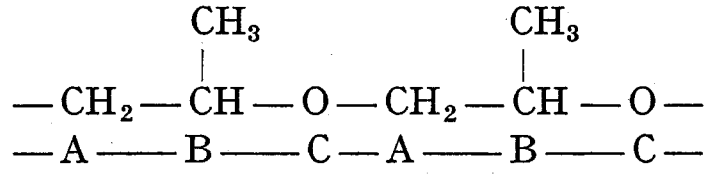


FIG. 3. Crystalline chain conformation of *l*- and *d*-polypropylenoxide.

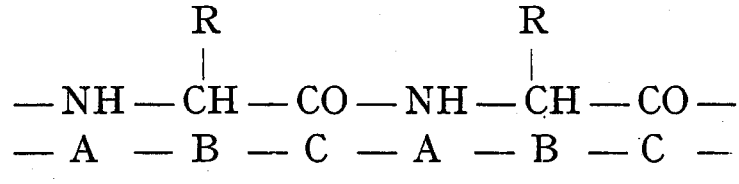
SCHEME 3

Type of chain:

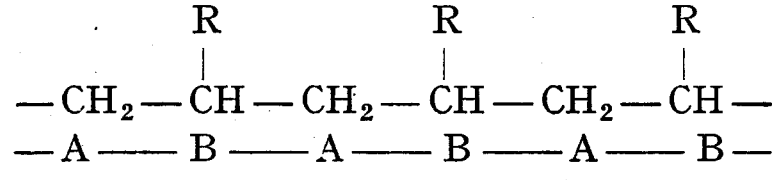
polypropylenoxide



poly-α-amino acids



poly-α-olefins



However, the tertiary carbon atoms are crystallographically equivalent, and the chains of crystalline polypropylenoxide show, in some respects, analogies to isotactic polymers. The chain can be considered as a twofold-symmetry helix, with a pitch corresponding to two monomeric units.

Crystalline polypropylenoxide shows still closer analogies to protein molecules, and like the proteins, it differs from the isotactic polymers of α-olefins, since its tertiary carbon atoms lie between groups of considerably different constitution (scheme 3).

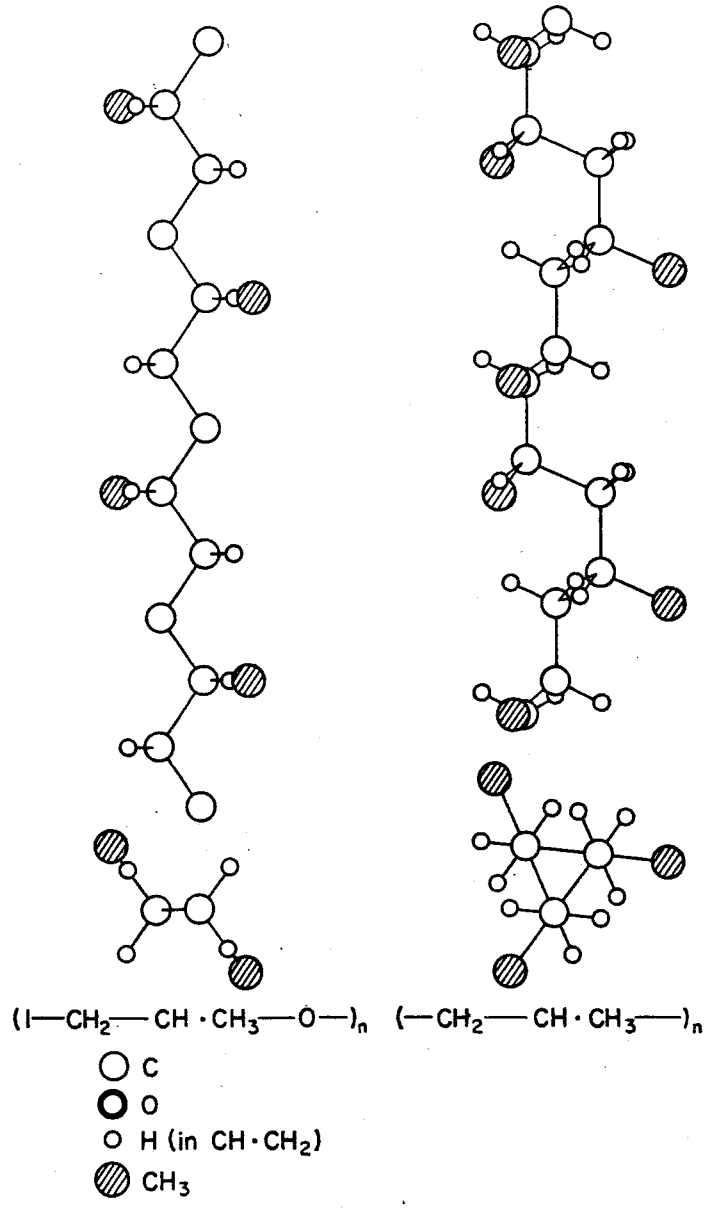


Fig. 4. Comparison between the chain structures of polypropylenoxide and of isotactic polypropylene present in the crystals.

STEREOISOMERY PHEMOMENA IN CONJUGATED POLYDIOLEFINS

The number of stereoisomers present in the conjugated polydiolefins is very high. Two main types of isomery exist: one usually called "geometric" (olefinic bonds with *cis*- and *trans*-structures) as in the case of the 1,4-enchainment; the other usually called "optical" (due to the presence of asymmetric carbon atoms) as in the case of 1,2- or 1,4-enchainments. Other cases of isomery, due to different combinations of the preceding types, can also occur, as in the case of 1,4-enchainment of some conjugated asymmetric diolefins (for instance piperylene).

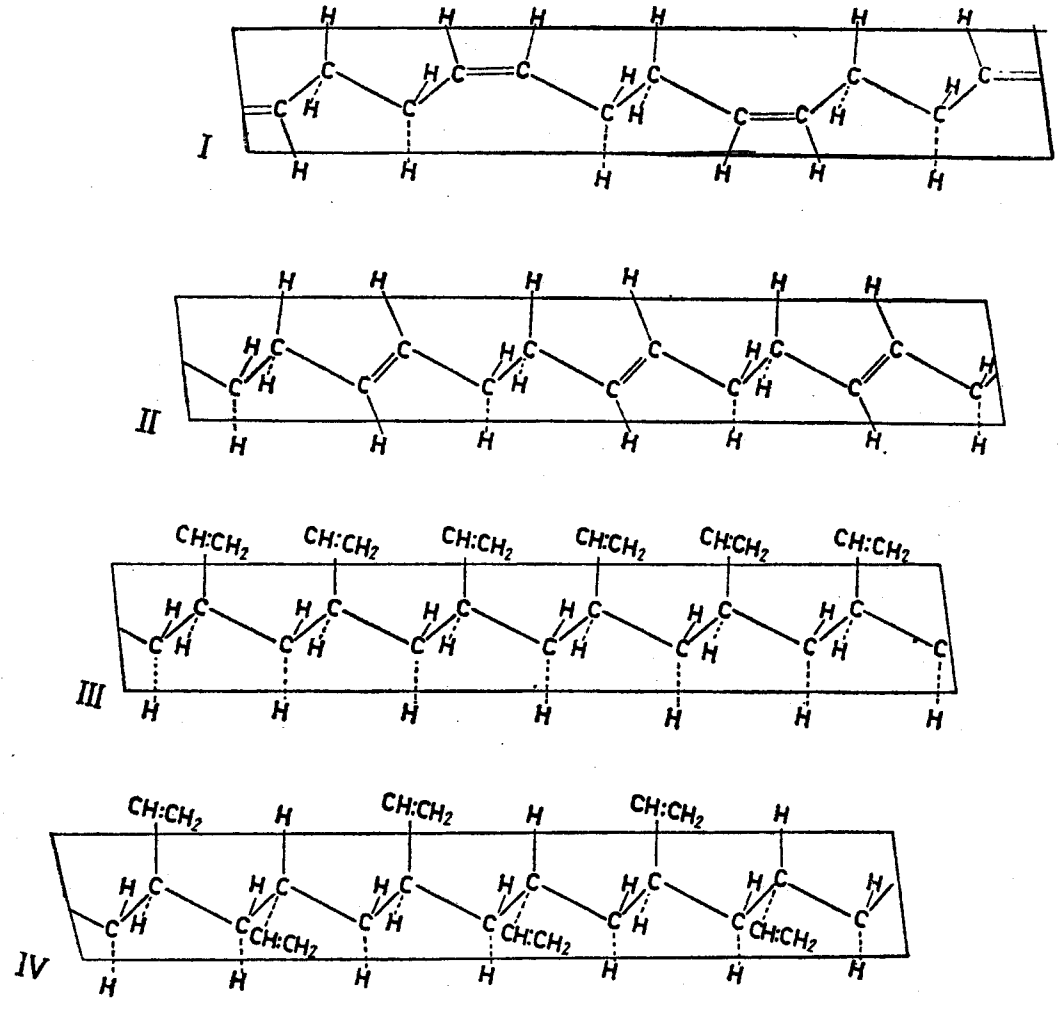


Fig. 5. Structure of some polymers of butadiene arbitrarily laid on a plane: *cis*-1,4-polybutadiene, *trans*-1,4-polybutadiene, isotactic 1,2-polybutadiene, syndiotatic 1,2-polybutadiene

In the case of the simplest conjugated diolefin, that is butadiene, four different stereoisomers with regular structure can be predicted (Fig. 5), i.e.:

isotactic-1,2-polybutadiene;
syndiotactic-1,2-polybutadiene;
trans-1,4-polybutadiene;
cis-1,4-polybutadiene.

Research work at the Polytechnic Institute of Milan permitted the isolation and the study of *trans*-1,4-, isotactic-1,2-, [20] and syndiotactic-1,2- [8, 9, 11] polybutadienes, in the crystalline state.

Also various types of amorphous polymers have been obtained: among these, mixed polymers containing the different configurations in various ratios, some of them having a high proportion of the *cis*-1,4-modification (Table 6).

TABLE 6. STEREOISOMERS OF CRYSTALLINE POLYBUTADIENE AT ROOM TEMPERATURE

	Melting temp. (°C)	*Identity period*	*Monomeric units (Å)*	*Density of crystals*
Enchainment				
Isotactic-1,2	120	6·5	3	0·96
Syndiotactic-1,2	154	5·14	2	0·96
Trans-1,4	135	4·9	1	1·01

In fact, the number of possibilities of combining different types of enchainments and of steric configurations is very high. That is why it is possible to obtain a very wide variety of products with different properties, depending on the different ratios between the single structures assumed by the monomeric units (Fig. 6).

Irregular *trans*-1,4-, *cis*-1,4- and 1,2-enchainments of monomeric units were present in the old German synthetic rubbers (Buna) obtained by the well-known polymerization processes of butadiene. A high concentration (up to 75 per cent) of *trans*-monomeric units, which was not high enough to yield highly crystalline stereoisomers, was observed in the polybutadiene obtained by Morton.[21]

In the case of isoprene (2-methylbutadiene-1,2), some of the six possible isomer and stereoisomer polymers having a linear regular structure have been prepared at the Polytechnic Institute of Milan. For instance, with regard to highly crystalline polymers, we synthesized in high yields, *trans*-1,4-polyisoprene, having the same crystalline structure as natural guttapercha. We have also obtained products of very high average molecular weight.[22] At the end of 1955, several American companies announced the synthesis of polymers having a high *cis*-1,4 content, with a structure similar to that of natural rubber.

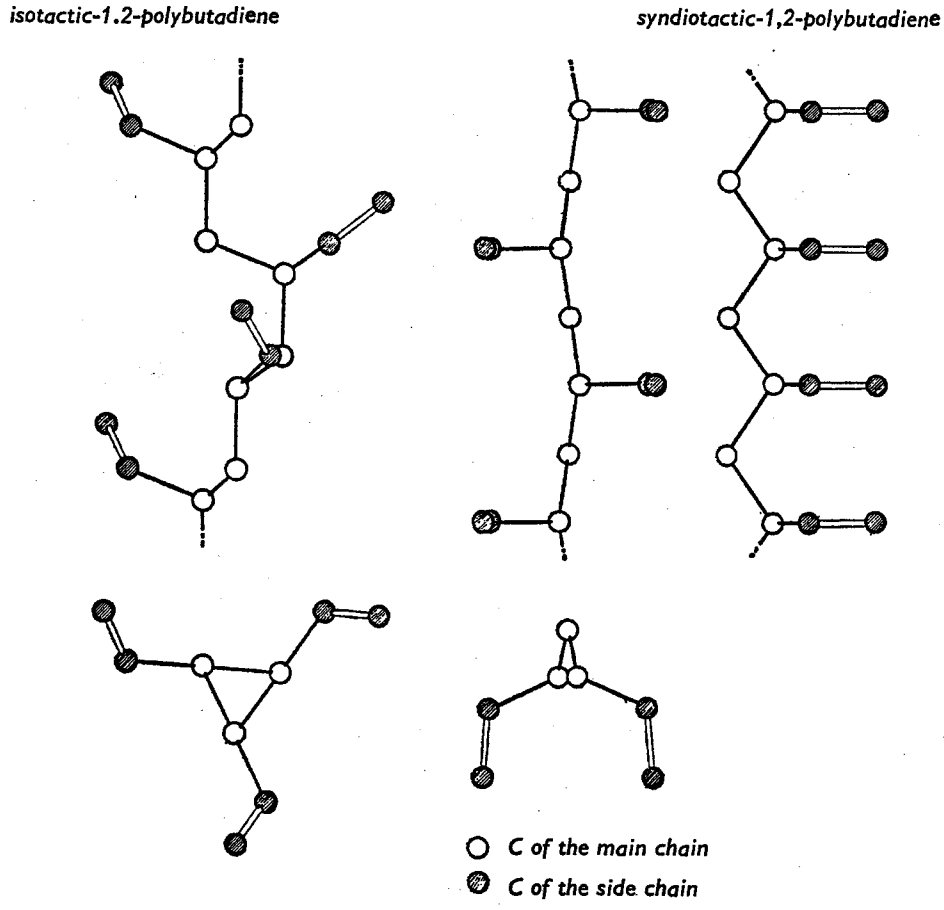


FIG. 6. Crystalline structures of the chains of the two stereoisomeric polybutadienes with 1,2-enchainment.

In the case of the asymmetric conjugated diolefins, the number of stereoisomers with a regular structure is very high. For instance piperylene (1,3-pentadiene) can have 12 typical stereoisomers, namely : four stereoisomers with a 1,4-enchainment, two of them being of the *cis*- and two of the *trans*-type, each being isotactic and syndiotactic, respectively ; four stereoisomers with 1,2-enchainment, two of them being isotactic and two syndiotactic, with double bonds in the side groups of the *cis*- and *trans*-types, respectively ; four stereoisomers with a 3,4-enchainment, depending on the relative configurations of the four tertiary carbon atoms of two neighbouring monomeric units.

PROPERTIES OF STEREOSPECIFIC POLYMERIZATIONS

In order to obtain sterically homogeneous polymers with a perfect regularity of structure, it is necessary to adopt particular processes of catalysis which meet the following fundamental requirements. The polymerization must occur :

I. Always head-to-tail (processes acting head-to-head and tail-to-tail are unknown, with the exception of the low polymers).
II. Without the formation of chain branching as a consequence of chain transfer processes.
III. Without the formation of branchings due to copolymerization of the monomer with its low polymers.
IV. In such a way that the monomeric units assume steric configurations corresponding to a definite arrangement.

As it was stated in our previous papers,[4, 8, 9] the stereospecific catalyses then considered, which yield isotactic poly-α-olefins, are always connected with the presence of solid catalysts, which are chemically bound to the growing polymer chain.

Most likely, these stereospecific catalyses are connected with the chemisorption of the monomer molecules to the surface of the solid catalyst, thus the adsorbed molecule has always the same particular orientation with respect to the growing chain.

It is evident that not all solid catalysts are suitable for stereospecific polymerizations ; what is needed is that the surface, containing the active centres, has a particular structure. Moreover, the catalytic process has to meet the first and third of the above listed conditions.

Let us consider now which of the many possible polymerization methods are better suited for effecting strictly stereospecific polymerizations.

MECHANISM OF THE PROCESSES USED FOR STEREOSPECIFIC CATALYSIS

The polymerization processes acting through a free radical mechanism are in general not stereoselective, in spite of the fact that when operating under certain polymerization conditions (e.g. low temperature), the chain transfer processes may be reduced and, in the case of some vinyl monomers, the syndiotactic head-to-tail enchainment is more probable. Generally, however, it is impossible to produce polymers with a high regularity of structure by a free radical mechanism.

Cationic polymerization processes have the disadvantage that they show frequent chain transfer phenomena, which can be reduced only by operating at a very low temperature, and by polymerizing monomers of the vinylidene type. In the rare cases where the monomer contains polar groups able to be associated with the catalyst, it is

possible to obtain vinyl polymers containing fractions with a regular structure. In fact, Schildknecht[24] described crystalline polymers of alkylvinyl ethers, which when examined by us showed an isotactic structure.[25]

Our investigations in the field of stereospecific polymerization were mostly conducted on α-olefins and diolefins, with the aid of particular catalysts, to which we attributed an anionic mechanism ; this mechanism satisfies the first and third conditions better than the cationic one.

The catalysts which we used first were chosen from those proposed by K. Ziegler for the low-pressure polymerization of ethylene.[26, 27] These catalysts permit the polymerization of vinyl hydrocarbons $CH_2=CHR$ to yield high polymers,[28, 29] but not the polymerization of vinylidene hydrocarbons ($CH_2=CR_1R_2$).

These catalysts are characterized by the presence of transition metal compounds which belong to groups IV—VIII of the periodic table, in a valency state of the metal lower than its maximum. The structure of these atoms is characterized by the incompleteness of the *d* shell ; their compounds with a lower valency (greater stability towards bases) may be associated with metal hydrides, or with metal–alkyls to form complexes, which, in some cases, exist as surface compounds. In such complexes strongly polarized metal–hydrogen or metal–alkyl bonds are present with electron displacements favouring the formation of a carbanion, or a hydride ion (Table 7).

TABLE 7

Transition metal of the catalyst	*Ionization energy (eV)*	*Ionization potential volt*			*Electronic structure of the atom*	
		I	*II*	*III*		
Ti	*3·9*	*6·8*	13·6	27·6	3 d^2	4 s^2
V	*3·8*	*6·7*	14·1	26·5	3 d^3	4 s^2
Cr	*3·7*	*6·7*	16·7	32	3 d^6	4 s
Mn	3·8	7·4	15·6	34	3 d^6	4 s^2
Fe	4·7	7·8	16·5	30	3 d^6	4 s^2
Ni	5·0	7·6	18·2	36	3 d^8	4 s^2
Zr	*3·7*	*6·9*	14·0	24·1	4 d^2	5 s^2
Mo	4·11	7·06		(27)	5 d^5	5 s
W	4·5	7·94		(24)	5 d^4	6 s^2

Not all the transition metals will yield good catalysts. We found that the best catalysts are those obtained from metals which, in their

elementary state, are the best electron donors. As a measure for this property, we can consider their ionization energy and ionization potential.[30]

Those transition metals (italicized in Table 7) yield the best catalysts in practice; when their compounds are associated with the metal alkyls, the ionization energy of the first electron of these metals is small (lower than 4 eV), as is the first ionization potential (lower than 7 V). Only metals like Na, Li, Ba, Al, which have an ionization energy lower than 4 eV, can yield stable hydrides. In these compounds the polarization of the Me—H bond increases (up to a limit of a H^- ion in hydrides of metals with a lower valency) with a decrease in the ionization energy.

In the Pauling series of electronegativity, these elements have an electronegativity lower than 1·7.

In metal–alkyl compounds of elements with low electronegativity the Me—C bond is polarized like a carbanion.

In the case of the above-mentioned transition metals, only the lowest-valency compounds have a considerable basic activity. This is the reason for the difference in the behaviour of compounds of the lowest and highest valency. The latter, for instance, $VOCl_3$ and $TiCl_4$, behave as Lewis acids, and with co-catalysts (such as HCl, H_2O, alkyl halides) form complexes, which, due to the presence of protons or carbonium ions, yield cationic catalysts. Those compounds with a lower valency, such as VCl_2 and $TiCl_2$, combine with substances such as metal hydrides or metal–alkyls, and yield catalysts acting according to an anionic mechanism, because of the presence of hydride ions or carbanions.

A good catalyst for our anionic catalysis can be obtained by the reaction of transition metal salts with metal alkyl compounds. This is only possible when an exchange reaction is accompanied by the formation of unstable alkyl compounds, which decompose (often with formation of free radicals or their combination or disproportionation products) into transition metal compounds of a lower valency. For instance, Ziegler has already observed[27] that this reduction occurs in those catalysts which he proposed for the polymerization of ethylene, that is those obtained by reacting $TiCl_4$ with $Al(C_2H_5)_3$.

A comparison of the catalytic processes, which are usually considered to be of the cationic type, with those studied by us, supports the hypothesis that the latter act through an anionic mechanism. This hypothesis is further supported not only by the presence of metal–

hydride and metal–carbanion bonds in the most typical catalysts, but also by the results obtained by the spectrographic examination of the polymers, and by the kinetic study of the polymerization reaction of ethylene[31] and propylene[32] with metal alkyls.

We believe that in the case of vinyl monomers, the polymerization reaction takes place by the insertion of monomeric units between the catalyst and the growing polymer chain in such a way that the CH_2 group is connected with the catalyst. The growth of the polymer chain stops mainly because of dissociation (regeneration of the catalyst with formation of a metal–hydride bond) or because of a hydrogen anion transfer from the growing polymer chain to a monomer molecule (chain transfer with the monomer). In any case, the stoppage takes place with the formation of polymeric macromolecules, which are unsaturated because of a terminal vinylidene group.

These statements are proved by the following experimental results.

(1) When using catalysts obtained by treating aluminum alkyls with transition metal compounds, those organic groups (alkyl or aryl) which originally belonged to the aluminum alkyl compound, were then found in the polymer. For instance, when using a catalyst, obtained by treating a titanium compound with aluminum triphenyl, a polymer is obtained which contains phenyl groups bound to tertiary carbon atoms (absorption bands at $13 \cdot 26\ \mu$ and $14 \cdot 33\ \mu$, were present in the various fractions of the polymer).

(2) With the use of certain stabilized catalysts, the polymerization rate is constant with time, provided the concentration of the monomer is kept constant. The polymerization proceeds therefore with a constant number of active centres, which demonstrates that no catalyst is consumed during the polymerization process.

(3) When the catalyst is prepared by reacting titanium salts with aluminum-triphenyl, the number of phenyl end groups in the polymer decreases as the polymerization proceeds.

For instance, after a 4–5-hr reaction at 90°C, the ratio of the number of polymer molecules to the number of phenyl end groups ranges from 3 to 8, depending on the fractions considered. This proves that, even if the catalyst initially contains metal–phenyl bonds, the polymerization goes on when the phenyl groups have been removed and replaced by other metal–alkyl bonds.

(4) Our kinetic measurements show that the mean life of each polymeric chain is fairly long, and, depending on the polymerization conditions, it ranges from a few minutes to a few hours.

(5) The polymer chains contain double bonds, which are mostly of the vinylidene type. The number of vinylidene bonds is approximately equal to the number of polymer molecules as determined by viscosimetric molecular weight measurements. Since such double bonds are formed by the splitting of the metal–alkyl bond, it must be assumed that a carbanion belonging to a primary carbon atom is bound to the cation of the catalyst.

(6) A comparison between the osmometric and viscosimetric measurements of the solutions and the behaviour of the very high-molecular-weight polymers in the molten state, indicate that the macromolecules are linear and free from long branchings.

(7) The well-ordered structure of the polymers obtained by this

TABLE 8. COMPARISON BETWEEN THE TYPICAL ANIONIC AND CATIONIC POLYMERIZATION PROCESSES

	Cationic	*Anionic*
Catalysts	Salts or acids of carbenium ions	Carbanion salts or metal hydrides
Chain initiators	H^+, $—R'R''C^+$	H^-, $—CH_2—$, Ar—
Co-ions	Anions: e.g. $(BF_3OH)^-$, $(AlBr_4)^-$	Cations: e.g. $(TiAlX_n)^+$, AlX_2^+, etc.
Main catalyst	Salts of strong acids and weak bases. Electrophilic substances. Maximum valency compounds of metals from the 2nd to the 4th group ($AlCl_3$, $TiCl_4$, etc.), and higher groups	Nucleophilic substances. Lowest valency compounds of metals of the 4th to the 8th group ($TiCl_2$, VCl_2, etc.)
Cocatalyst	Substances yielding ions H^+ or carbenium cations. Halogen-hydrogen acids. Alkyl halides (HCl, H_2O, CH_3Cl, etc.)	Substances yielding hydrogen anions: H^- or carbanions. Metal hydrides, metal—alkyls: LiH, $LiCH_3$, $Al(C_2H_5)_3$
Order of increasing reactivity of the aliphatic olefins		
$CH_2 = CH_2$	small	large
$CH_2 = CHR$	medium	lower
$CH_2 = CR'R''$	large	null or very small
Inhibitors	Electron acceptors bases, amines, alcohols	Electron donors, acids, H_2O, halogenated aliphatic compounds
Solvents	Hydrocarbons	Hydrocarbons, chlorinated aromatic compounds

Table 8 *cont.*	*Cationic*	*Anionic*
Kinetics	Mostly 1st order with respect to the catalyst and monomers and zero order with respect to the cocatalyst (within a certain range of concentration of the latter). Exceptions and anomalies are frequent	1st order with respect to some stabilized catalysts and to the monomer and zero order with respect to the cocatalyst (within a certain range of concentration of the latter). Anomalies with heterogeneous non-stabilized catalysts
Apparent activation heat	Always small (lower than 15,000 cal). Sometimes negative	Always small
Stoppage of chain growth of the macromolecule	Transfer of a proton to the catalyst (dissociation) or on the monomer (chain transfer) and other secondary processes	Transfer of an anion H^- to the catalyst (dissociation) or to the monomer (chain transfer)
Removal of an ionic charge from one carbon atom to another one of the same chain	Frequent from a secondary to a tertiary atom	Not observed and improbable by a primary, secondary or tertiary atom.
Possibility of copolymerization of the monomer with its polymers	Frequent	Possible in some cases with ethylene; not yet observed for the α-olefins.
Structure of the polymers formed	Often irregular. Presence of long branchings and sometimes cyclization in the chain	Regular. Absence of long branchings in the polymers of α-olefins

type of anionic catalysis and the probable absence of long branchings may be attributed to the higher stability of the primary carbanion. This higher stability prevents the transfer of the charge to a secondary or tertiary carbon atom (Table 8).

The heat of activation of the overall polymerization reaction is not very high and in general does not exceed 15,000 cal. For instance, we found that the heat of activation for the polymerization of propylene to an isotactic polymer was 11,000 cal if referred to propylene gas (15,000 if referred to propylene in heptane solution).

Considerable analogies exist between anionic and cationic catalyses ; but the two processes differ with respect to their chain transfer mechanism and possibilities. The high regularity of structure, which can be observed in those products of anionic polymerizations, can be attributed to the presence of the carbeniate end ion ($-CH_2$), whose charge is not readily transferred to other atoms of the polymer chain.

In the case of cationic catalysis, on the contrary, the transfer of a hydride ion from a tertiary atom to a secondary carbonium ion accompanied by neutralization and formation of a tertiary carbonium ion is possible and it occurs frequently. This process is responsible for the formation of branchings in the polymer.

Since transfer reactions are less frequent in the anionic processes, they are better suited than the cationic ones for the production of polymers with a regular structure. In the case of cationic polymerizations, regular structures are obtained only when operating at very low temperatures. Moreover, the anionic polymerizations considered by us, carried out at the same polymerization temperature, yield high molecular weight polymers, which even if they were atactic, would have a linear head-to-tail structure.

The transfer of a "hydrogen anion" (hydride ion) represents the most frequent case for the termination of the growth of a macromolecule. It can occur in two ways :

$$(1)\quad P_1-CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-\bar{C}H_2 + B \rightarrow P_1-CH_2-\underset{\displaystyle R}{\underset{|}{C}}=CH_2 + BH^-$$

In the case that B is the cation of the catalyst, the regeneration of the catalyst takes place.

The transfer of the hydrogen anion to a monomer molecule is more frequent :

$$(2)\quad P_1-CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-\bar{C}H_2 + \underset{\displaystyle R}{\underset{|}{CH}}=CH_2 \rightarrow$$

$$\rightarrow P_1-CH_2-\underset{\displaystyle R}{\underset{|}{C}}=CH_2 + RCH_2-\bar{C}H_2$$

Another relatively infrequent case in our anionic polymerizations, and which will be described in another paper, consists in the transfer of the charge to a hydrogen ion derived from a different molecule,

and accompanied by the regeneration of the catalyst. This case differs from the first and second cases, because the polymer formed is saturated with the R′ group :

$$-CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-\bar{C}H_2 + R'H \rightarrow -CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-CH_2R' + H^-$$

In cationic polymerization, the transfer of the charge from a carbon ion to another carbon atom occurs frequently, even with atoms within the same polymer chain and this causes some irregularities of structure. On the other hand, this cannot occur in the case of anionic polymerizations carried out with the aid of catalysts used by us for the stereospecific polymerization of α-olefins (scheme 4).

The reaction :

$$R'R''\overset{+}{C}H + R'R''R'''CH \rightarrow R'R''CH_2 + R'R''R'''\overset{+}{C}$$

occurs very frequently in cationic polymerization,[33] if one does not operate at very low temperatures ; it leads to the neutralization of the secondary carbonium ion with formation of a tertiary carbonium ion.

Whereas in the case of the carbon cation, the stability of the ion follows the order $\overset{+}{C}H_3 < \overset{+}{C}H_2R < \overset{+}{C}HR_2 < \overset{+}{C}R_3$, in the case of the carbon anion, an opposite order of stability must be expected :

$$\bar{C}H_3 > \bar{C}H_2R > \bar{C}HR_2 > \bar{C}R_3 .$$

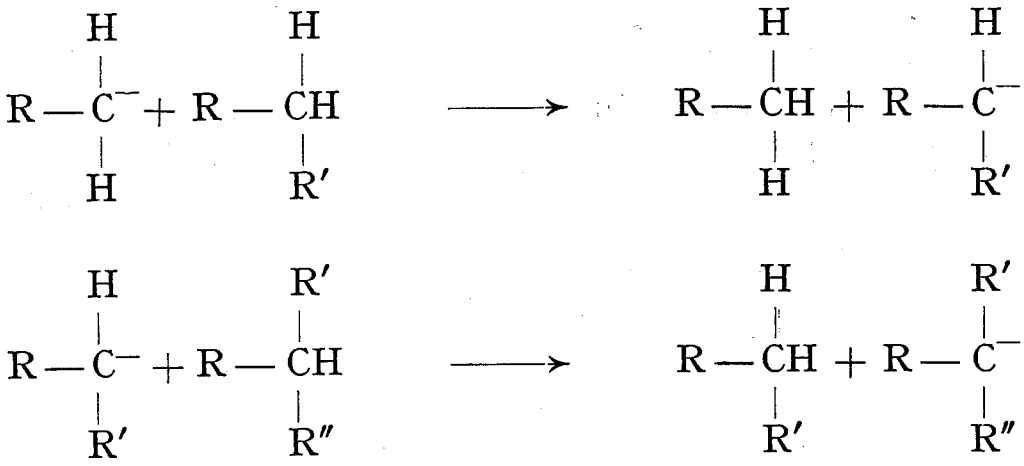
SCHEME 4

Transfer reactions of H^- as observed during the cationic polymerization

$$R-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C^+}}}} + R'-\underset{\displaystyle R''}{\underset{|}{\overset{\displaystyle H}{\overset{|}{CH}}}} \longrightarrow R-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle H}{\overset{|}{CH}}}} + R'-\underset{\displaystyle R''}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C^+}}}}$$

$$R-\underset{\displaystyle R'}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C^+}}}} + R-\underset{\displaystyle R''}{\underset{|}{\overset{\displaystyle R'}{\overset{|}{CH}}}} \longrightarrow R-\underset{\displaystyle R'}{\underset{|}{\overset{\displaystyle H}{\overset{|}{CH}}}} + R-\underset{\displaystyle R''}{\underset{|}{\overset{\displaystyle R'}{\overset{|}{C^+}}}}$$

Reactions which are supposed to be improbable in the anionic polymerization :



In a growing polymer chain, which ends with a $-\bar{C}H_2$ ion, the transfer of the charge to a carbon atom within the chain is most unlikely. Therefore, chain branchings do not take place.

For this reason the poly-α-olefins, obtained with the aid of anionic catalysts used by us, even if they are not stereospecific, are linear and strictly head-to-tail.

I.R. analysis did not reveal $-CH_2-CH_2-$ or $-CHCH_3-CHCH_3-$ sequences in the chain of polypropylene obtained with the aid of such catalysts.

With cationic catalysts, it is possible to obtain regular chains, only if the carbonium ion is already a tertiary carbon atom, and if the polymeric chain does not contain any nucleophilic carbon atom (such as polyisobutylene).

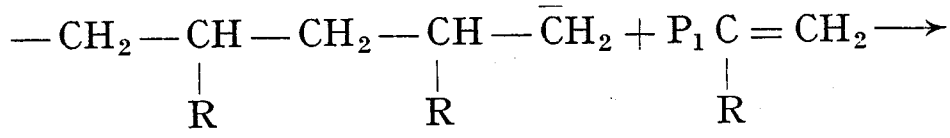
In anionic catalysis, there is a greater regularity in the polymerization of α-olefins than in that of ethylene. In the case of the polymerization of ethylene, in fact, copolymerizations of ethylene with low-molecular-weight polyethylene molecules may take place :

$$P-CH_2-\bar{C}H_2 + CH_3-CH_2(CH_2-CH_2)_n-CH=CH_2 + mCH_2=CH_2 \longrightarrow$$

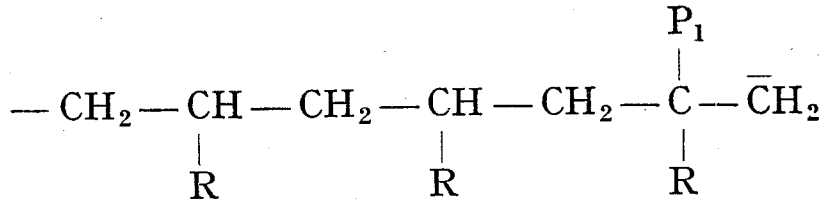
$$\longrightarrow P-CH_2-CH_2-CH(CH-CH_2)_n-CH_2-CH_3$$
$$\qquad\qquad\qquad

This, we believe, is the reason why a small amount of branching can occur in the polymerization of ethylene in the presence of those catalysts which, in the polymerization of α-olefins, yield linear polymers.

This does not occur in the polymerization of α-olefins. In fact using, as we did, the most typical anionic catalysts, the addition reaction:



with formation of a compound, such as



cannot take place probably because of steric reasons.

In fact even in low-molecular-weight polymers, quaternary carbon atoms could not be found. This peculiar behaviour of the anionic polymerization is also observed in poly-α-olefins having a sterically disordered structure.

Amorphous polypropylenes, polybutenes, polyamylenes, polyhexenes of medium and high molecular weight differ from the corresponding polymers of the same molecular weight, obtained by cationic processes. They show a visco-elastic behaviour similar to that of non-vulcanized rubbers.

STEREOSPECIFIC CATALYSTS FOR ISOTACTIC POLYMERS

In the preceding section, we have observed that a certain regularity of structure (head-to-tail enchainment with absence of branchings) is possible in vinyl polymers, at a temperature above the ordinary one, only when adopting certain polymerization processes which most probably act through an anionic mechanism. Other polymerization processes can yield a certain regularity of structure only at very low temperatures.

Let us investigate now which of the catalysts previously considered can act stereospecifically.

The first stereospecific polymers obtained by us were poly-α-olefin with an isotactic structure, and *trans*-1,4-polydiolefins.

The conditions for the preparation and purification of highly stereospecific catalysts and of isotactic, crystalline polymers of α-olefins, have already been described in published Italian patents.[28]

Meanwhile, Prof. Ziegler has filed a patent for the production of high polymers of α-olefins,[29] in which however the steric structure of the polymers is not discussed.

As we have pointed out already in our first publications on this subject, the stereospecific catalysts used up to now for the preparation of isotactic poly-α-olefins, are heterogeneous because of the presence of a solid phase. The term "solid phase" must be understood in a broad sense, since it includes certain catalysts of colloidal, preferably microcrystalline, dimensions.

Typical anionic catalysts are those obtained by treating crystalline solid halides of transition metals (of the group indicated in the previous chapter) having a valency lower than maximum, with metal–alkyls. The amount of metal–alkyl necessary to obtain a very high catalytic activity is fairly small, of the order of tenths of moles of AlR_3 per mole of transition metal halide. It should be kept in mind that an excess of such metal–alkyl compounds is advantageous, because it exercises a protective action by destroying traces of oxygen or water, which could deactivate such catalysts. This leads us to believe, using the nomenclature applied to cationic catalysis, that in the anionic catalysis, the transition metal compound may be considered as a catalyst, and aluminum trialkyl or aluminum dialkyl hydride as a co-catalyst. The use of metal–alkyl compounds is not essential for obtaining stereospecific catalysts acting through an anionic mechanism ; however, it represents a very simple and effective method for obtaining them. It seems to be sufficient for the formation on the surface of Me—H bonds which are polarized to favour the formation of a hydride ion, which can then react with the olefins yielding a carbenium compound. The surface of a transition metal can very well act as a catalyst, if it is surface-oxidized by a process yielding metal–alkyl bonds. Our statement, namely that certain solid catalysts have an orientating action in the stereospecific catalysis for the production of isotactic polymers, has been subsequently confirmed. The examination of products, obtained by other polymerization processes, and which contained small amounts of high-melting polymers, showed that they appeared to possess an isotactic structure.

In fact, we have demonstrated that the polymer obtained by Schildknecht in the low temperature (—80°C) polymerization of vinyl ethers with BF_3 etherate is an isotactic crystalline polymer.[9, 10, 25]

Since BF_3 acts as a catalyst only in the presence of a cocatalyst (e.g. traces of H_2O) and since boron trifluoride easily forms compounds

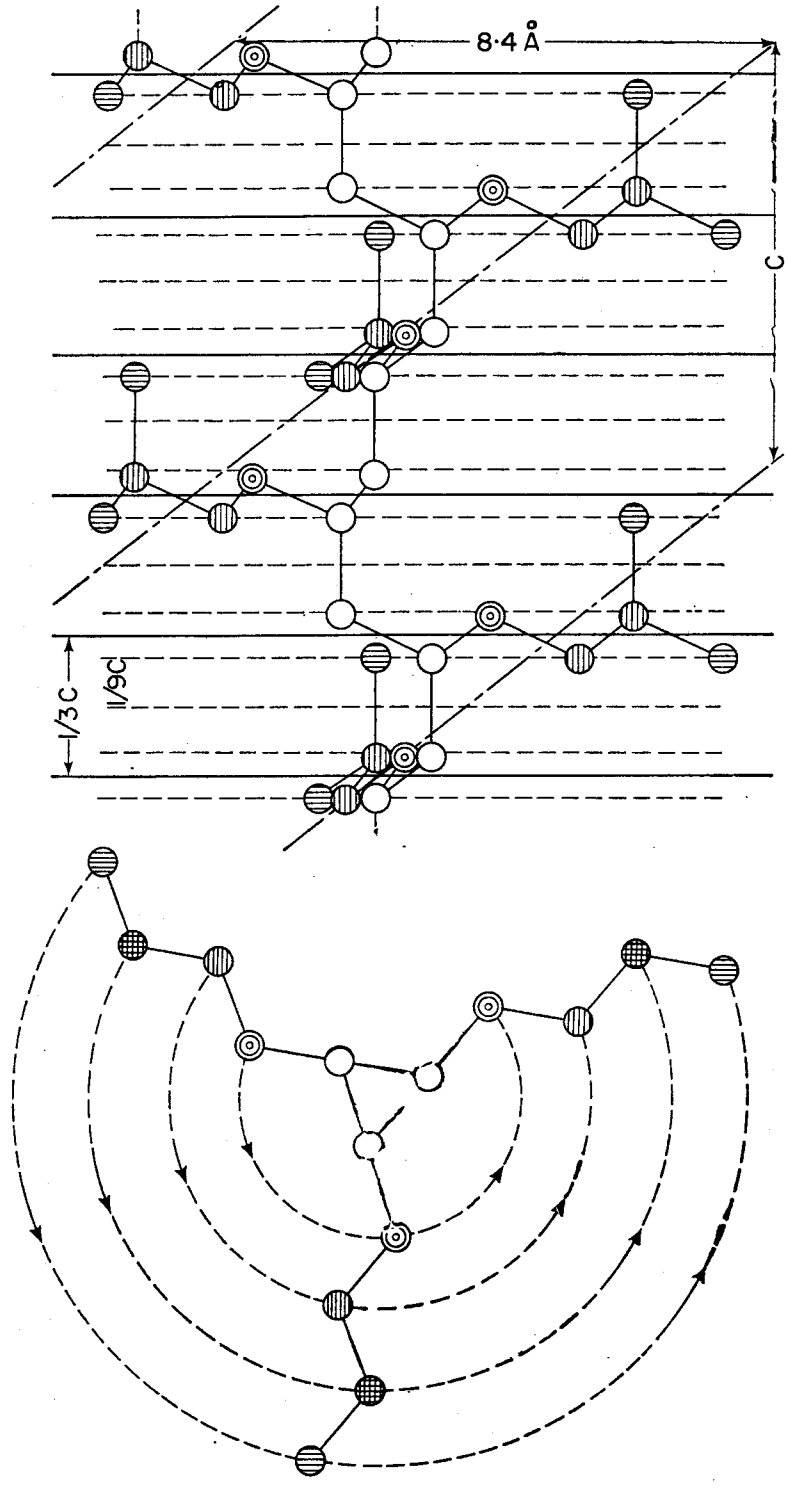
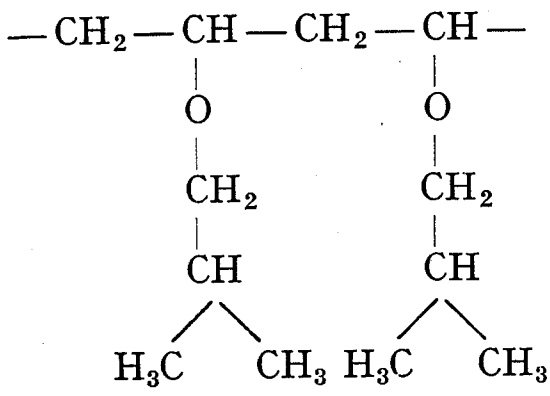


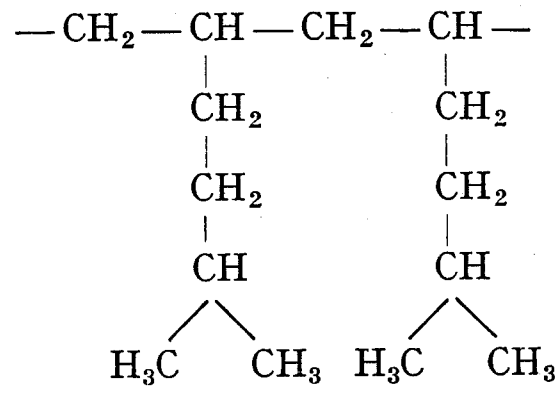
FIG. 7. Side and end views of the isotactic chain of polyvinylisobutyl ester (the intersection lines of planes of a periodicity equal to that of the 003, 009 and 201÷111 planes are indicated).

(e.g. with water), which are solid at low temperature, it is not excluded that even in this case, the production of isotactic polymers is connected with the presence of a solid catalyst. The structures of isotactic polyisobutylether and of poly-5-methylhexene-1 are compared in scheme 5 and Fig. 7.

SCHEME 5



Poly-isobutyl-vinyl ether
$c = 6{\cdot}50 \pm 0{\cdot}05$ Å
$v = 529$ Å^3
$d = 0{\cdot}94$



Poly-5-methylhexene-1
$c = 6{\cdot}50 \pm 0{\cdot}05$ Å
$v = 585$ Å^3
$d = 0{\cdot}84$

(v = volume of the molecule in elementary unit cell).

Schildknecht himself had observed that the formation of the crystalline polymer occurs when the catalysis is heterogeneous. We too have demonstrated that very small amounts of solid polymers present in those obtained with the aid of Phillips's catalysts[34] exhibit a certain crystallinity[15] due to isotactic chain segments even if these polymers have a rather low molecular weight and a lower melting temperature than that of the crystalline high-molecular-weight polymers. Now we think it is possible to attribute the formation of these isotactic segments to the presence of a solid phase, which contains a compound of hexavalent chromium reduced to a lower valency number by the olefins present.

By treating the Phillips's catalysts with metal-alkyls, the amount of isotactic polymers increases, but it is still a small proportion with respect to the total amount of the polymer.[15]

In the heterogeneous catalysis with solid catalyst, the adsorption of the reagents on the surface must play an important role, since it can impose a determined orientation of the adsorbed molecules relative to the growing chain which is bound to the active centres of the catalyst.[8, 9]

If the catalyst is dissolved or if it is very finely dispersed, non-isotactic molecules are formed. We are led to attribute this fact to the lack of solid surface, which enforces a definite orientation of the monomer molecule with respect to the growing chain.

If the probability that the monomer molecule assumes a definite orientation is very high, but not equal to 1, then the possibility of obtaining molecules which exhibit more or less long portions of isotactic chains (polymers with isotactic blocks) must be foreseen.

OTHER STEREOSPECIFIC CATALYSIS

The synthesis of isotactic polymers of α-olefins or of *trans*-1,4 conjugated diolefins yielding highly crystalline and high-melting products is a particular case of stereospecific synthesis. Other stereospecific syntheses, such as those of syndiotactic vinyl polymers and of 1,2- and *cis*-1,4 polymers of conjugated diolefins are also of considerable theoretical and practical interest.

Each stereospecific synthesis requires a particular orientation of the monomer molecule in a particular activated form with respect to the end group of the growing polymer chain.

We have already pointed out that, in the case of isotactic polymers, this orientation is given by the adsorption of the monomer on a surface which has a characteristic definite structure. It can be assumed, however, that the extent of this surface is very small, and that it may be comparable to molecular dimensions, which would be much smaller than those shown by crystals observed by X-ray methods.

A stereospecific polymerization can be foreseen if a complex contains an active centre (cation–carbanion bond in the case of the anionic polymerization) and if it can adsorb the monomer molecule and can direct it towards a particular orientation with respect to the growing chain. This concept has been proved to be widely applicable to the synthesis of some stereoisomeric polymers of conjugated diolefins.

Some of these syntheses have been effected by us with the use of catalysts consisting of complexes which contain transition metals and act according to an anionic mechanism. The nature of these complexes will be described in another paper.

CONCLUSIONS

Stereospecific polymerizations are not only of great theoretical interest, but also deserve attention because of their important practical applications, which have been recognized already in the field of plastics, textiles and synthetic rubbers.

From low-priced olefins (propylene, butylene) it is possible to obtain crystalline polymers, having a high melting temperature, which represent a new class of thermoplastics having a low density, good mechanical properties and wide applicability (at very low cost) (Table 9).

TABLE 9

Polymer	*Raw material*	*Price (cents/lb)*
Polypropylene	propylene (mixed with propane)	2–3
Polybutylene	butylene-1 (enriched)	3–5
Polystyrene	styrene	16·0
Polybutadiene	butadiene	15·0
Nylon	adipic acid	35·0
Terylene	terephthalic acid (68%)	35·0
	ethyl glycol (32%)	13·5

The isotactic and syndiotactic polymers give hard fibres suited for textile applications. Fibres can be obtained from polypropylene, which have a tenacity higher than 7 g/denier, corresponding to a tensile strength above 70 kg/mm^2. This tensile strength is equal to that of steel, and is obtained with materials which have only one eighth of the specific gravity of steel.

Certain isotactic polymers with melting temperatures ranging from 160° to 300°C are particularly interesting in the field of fibres and transparent films; whereas in the field of plastics, the greatest interest is given to isotactic polypropylene, whose properties are, in many respects, better than those of polyethylene.

Less than three years have elapsed since the first synthesis of isotactic polypropylene. During this time dozens of new stereoisomeric polymers have been synthesized. Many of them are intended for widespread practical applications.

In the field of diolefins, it is now possible to produce by stereospecific polymerization of isoprene, either crystalline polymers with *trans*-1,4-structure like that of guttapercha, or synthetic rubber having excellent hysteresis properties, consisting of macromolecules in which the majority of the monomer units are sterically identical to those of natural rubber.

The interest in stereospecific catalysis is not limited to polymers of olefins and diolefins.

A deeper knowledge of the chemical and geometric nature of catalytic processes and of the orientating substrates, which make possible stereospecific syntheses, may well shed new light on the study of the fascinating but up to now obscure field of the stereospecific biochemical syntheses and of the catalytic action of enzymes.

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20

THE CRYSTALLINE STRUCTURE OF THE NEW POLYMERS OF CONJUGATED DIOLEFINS WITH A *TRANS*-1,4 ENCHAINMENT

by G. NATTA, P. CORRADINI and L. PORRI

(12 May 1956)
[*Rend. Accad. Naz. Lincei* (8) **20**, 728 (1956)]

ABSTRACT

Trans-1,4 polymers of some conjugated diolefins, e.g. butadiene, isoprene, and pentadiene, have been prepared by different stereospecific, heterogeneous catalytic processes. The crystalline structure of these *trans*-1,4 polymers is examined in this paper.

The molecules of these polymers, like those of the crystalline polymers of α-olefins, previously examined by us, satisfy the general principle of maximum displacement of the simple bonds.

The melting temperature, which for polybutadiene is higher than for other examined *trans*-1,4 diolefin polymers, depends on the efficiency of packing of the molecules in the crystalline lattice.

21

CRYSTALLINE STRUCTURE OF *CIS*-1,4-POLYBUTADIENE AND OF *CIS*-1,4-POLYISOPRENE

by G. NATTA and P. CORRADINI

(13 Sept. 1956)
[*Angew. Chemie* **68**, 615 (1956)]

ABSTRACT

Cis-1,4 crystalline polymers of butadiene are described for the first time. The elementary unit cell is monoclinic with constants: $a = 4{\cdot}60$ Å, $b = 9{\cdot}50$ Å, $c = 8{\cdot}60$ Å (fibre axis) and $\beta = 109°$. The space-group is: $C2/c$. Here it is given a chain model and the packing of the chains, that show good agreement between the experimental and the observed intensities. The close analogy existing between the structure found for *cis*-1,4-polybutadiene and that of natural rubber, as described by Nyburg, is indicated here.

22

THE CRYSTALLINE STRUCTURE OF ISOTACTIC POLY-α-BUTENE

by G. NATTA, P. CORRADINI and I. W. BASSI

(2 Oct. 1956)
[*Makromol. Chemie* **21**, 240 (1956)]

ABSTRACT

The structural properties of modification I of poly-α-butene are studied by electron-ray and X-ray diffraction spectra.

The macromolecule of isotactic poly-α-butene, crystallized in this modification, shows a threefold helix symmetry, with a repetition period of 6·5 Å. The unit cell is rhombohedric, and its constants referred to the hexagonal axes are: $a = 17{\cdot}7$ Å, $c = 6{\cdot}50$ Å. Two space-groups $R3c$ or $R\bar{3}c$ are possible.

The number of monomeric units contained in the unit cell is 18; each macromolecule is surrounded by three enantiomorphous macromolecules. An interesting phenomenon of statistical vicariance, concerning the $R\bar{3}c$ space-group is described here. It is possible that around each of the six threefold screw-axes, contained in the unit cell, isomorphous anticlined macromolecules may also vicariate.

23

SOME SOLUTION PROPERTIES OF ISOTACTIC AND ATACTIC POLYSTYRENES

by F. Danusso and G. Moraglio

(4 Oct. 1956)
[*J. Polymer Sci.* **24**, 161 (1957)]

ABSTRACT

Results of viscometric and osmotic measurements as well as solubility experiments with isotactic and atactic polystyrene fractions are reported.

The fractionation of isotactic polystyrene, in spite of its crystallizability, can be carried out by the usual techniques of fractional precipitation at ordinary temperatures. This is possible because of its state of metastability in solution and its low kinetic tendency toward crystallization.

The relation between $[\eta]$ and M in benzene and in toluene was found to be the same for the two types of polymer. On the other hand, the second virial coefficients B (in toluene) are appreciably different. Calculated values of the "limiting interaction affinity" φ_E in toluene and the results of solubility experiments in MEK and in toluene–methanol mixtures show that atactic polystyrene is always more soluble than isotactic polystyrene, regardless of whether the latter is in the crystalline or in the amorphous (metastable) state. MEK is shown to be a selective solvent in the separation of the two types of polystyrene. The value of B or φ_E is suggested as a possible measure of the isotacticity.

24

ISOTACTIC AND STEREOISOMERIC POLYMERS*

by G. NATTA

(18 Nov. 1956)
[*Chimie et Industrie* **77**, 1009 (1957)]
[*Materie Plastiche* **23**, 541 (1957)]

ISOMERISM PHENOMENA IN ALIPHATIC HIGH POLYMERS

The discovery of stereospecific polymerization processes producing pure stereoisomers has permitted the production of new classes of synthetic polymers which are of interest in the field of plastics, synthetic rubbers and textiles.[1]

This discovery has lessened the difference which existed between natural and synthetic high polymers. In fact, the structure of natural polymers corresponds, in the most typical cases, to a precisely constructed model, whereas, the structures of artificial polymers having the same composition correspond, in most cases, to an irregular and disordered association of their constitutive elements. The most frequent irregularities are determined by the different steric configurations which the monomeric units can assume during the polymerization, and by their order of succession along the chains.

Before the discovery of stereospecific polymerization processes, a limited number of crystalline synthetic hydrocarbon polymers were known. In particular those obtained by polyaddition of symmetric monomers such as ethylene and the vinylidene monomers (isobutylene). All the synthetic high polymers of α-olefins (as well as other vinyl monomers) and of diolefins were amorphous, because of the steric irregularities in their structure. In order to produce crystalline polymers from vinyl monomers or from diolefins, the monomeric units

* Lecture given at the 29th International Conference of Industrial Chemistry Paris, 18–24 Nov. 1956.

have to assume a regular arrangement with definite and non-statistical configurations ; this had not been possible before the discovery of stereoselective or stereospecific polymerization processes.

Various well-known types of stereoisomerism exist in organic chemistry. The best examples correspond to two typical cases : the stereoisomerism called "geometric", due to the *cis*- and *trans*-configuration (e.g. in compounds containing double bonds) and that called "optical" due to the presence of carbon atoms to which are attached four different substituents. Both these cases are important in macromolecular chemistry. In fact a crystalline polymer can be obtained only when all the monomeric units have all the same configuration, or else when opposite configurations follow one another in an ordered way. On the other hand, amorphous polymers are obtained when different configurations, e.g. the *cis*- and *trans*-double bonds or the "levo" or "dextro" forms, follow one another in a disordered way.

The new crystalline poly-α-olefins studied by us,[2] and those of olefin oxides studied by Price[3] are examples of synthetic stereoisomeric polymers, in which the crystallinity is due to the order of the configurations of the tertiary carbon atoms in the chain of each molecule.

In the case of propylene oxide polymer (Fig. 1), as in the case of the condensation products of α-amino acids, the tertiary carbon atoms

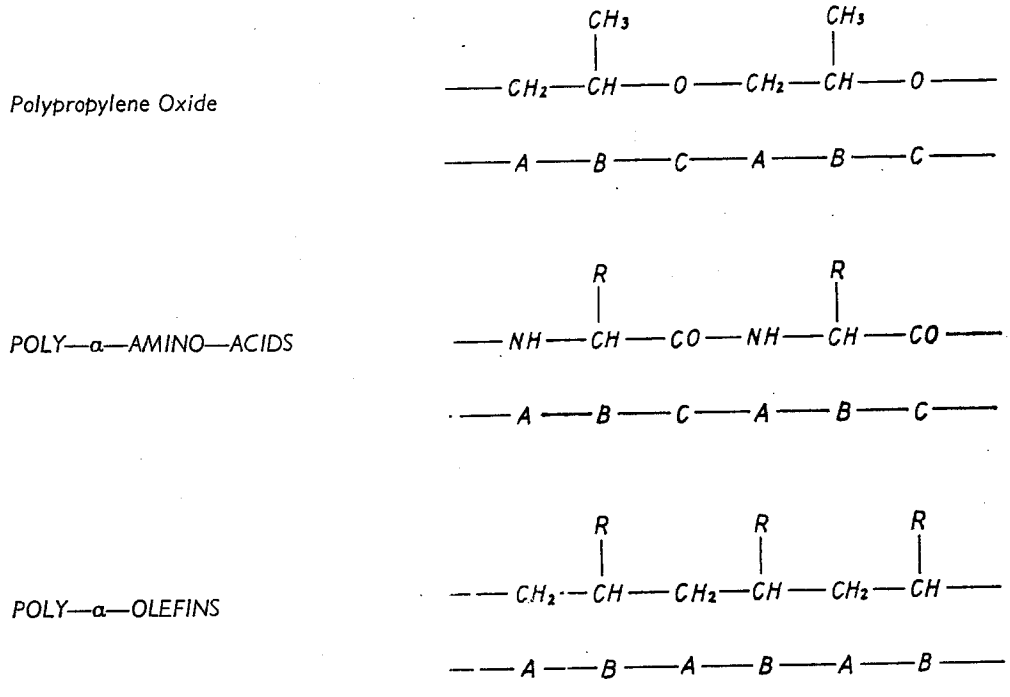


FIG. 1. Polymer chains containing asymmetric carbon atoms.

are always asymmetric, even in the monomeric state. In the case of poly-α-olefins, they become so only after their polymerization, providing the two chain portions at the two sides of the tertiary atom have different structure and length.

Figure 1 of paper 19 shows the molecules of the stereoisomeric poly-α-olefins stretched on a plane: (a) the isotactic polymers, in which the tertiary carbon atoms have the same relative steric configuration for long chain portions; (b) the syndiotactic polymers, in which each tertiary carbon atom shows a steric configuration opposite to that of the neighbouring atoms in the chain; (c) the atactic polymers in which the tertiary carbon atoms of different configuration are disorderly arranged in the chain.[2b, 2c, 4]

In the field of macromolecular geometric stereoisomerism, the natural stereoisomers of polyisoprene, i. e. natural rubber, which exhibits an almost entirely *cis*-structure (97 per cent) and guttapercha which, on the contrary, exhibits a *trans*-structure are well known. Research efforts on the polymerization of diolefins made by thousands of chemists during the last 40 years to obtain products with the same steric structure as that of natural products were not successful.

Those polymerization processes were for the most part of a free radical nature, hence not well-suited for the production of regular enchainments of the asymmetric units.

Only during the last three years, has the use of stereospecific catalysis permitted the production of stereo-homogeneous polydiolefins, and also of polyisoprenes having the same structure as that of natural rubber and of guttapercha.

Figure 5 of paper 19 shows the four crystalline isomers of polybutadiene which were synthesized by us. We have also determined the lattice structure of these 4 stereoisomers.[5—8] In theory isoprene could yield six stereoisomers; one *cis*- and one *trans*- with 1,4-enchainment, two with a 3,4-enchainment, and two with a 1,2-enchainment, isotactic and syndiotactic respectively. Only the first two were known to exist in nature. These two stereoisomers,[9, 10] as well as the others, have now been prepared in the laboratory.

Nothing will be said here about the nature of stereospecific catalysis, even though this topic is extremely interesting; it will be discussed, however, at the next International Symposium of Chemistry to be held in Paris in July 1957. We are going to refer here to the physical properties of these polymers, since they represent important aspects for their possible practical applications. The specific physical

properties of the isotactic polymers justify a great interest in the field of plastics and of textiles. The atactic stereoisomers of the same high-molecular-weight polymers show entirely different properties from the isotactic ones and are only of interest in the field of synthetic rubbers.[13]

Properties, such as the crystalline chain configuration, the relative position of the chain in the crystal, the arrangements of the side groups, the crystallization rate and the dimensions of the crystals determine the practical interest of these polymers in the field of plastics. They possess hardness, high mechanical strength, narrow and high melting temperature, ease of processability, and the capacity to yield high-tenacity fibres. Therefore, before describing the technological properties of the isotactic polymers, it is more useful to describe their crystalline structure.

CRYSTALLINE STRUCTURE OF POLY-α-OLEFINS

The synthesis of isotactic and syndiotactic polymers of olefins and of diolefins has markedly increased the number of hydrocarbon crys-

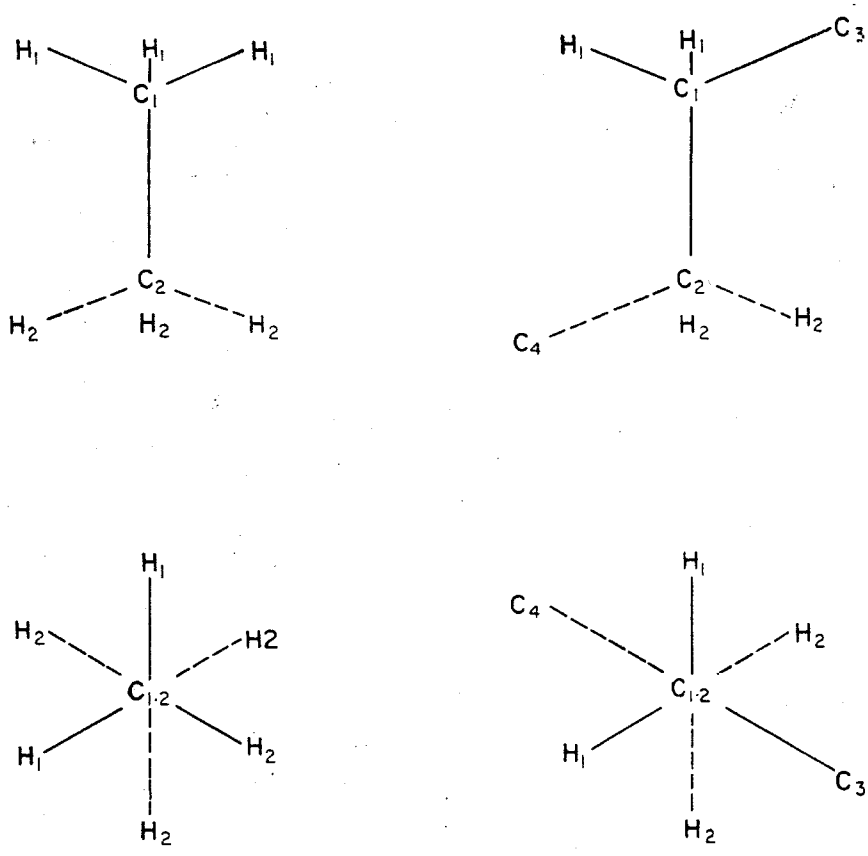


FIG. 2. Orientation of the bonds in ethane and in a paraffinic chain.

TABLE 1. X-RAY DATA OF CRYSTALLINE ISOTACTIC POLYMERS

Polymer	*Melting temperature (°C)*	*Space-group and symmetry*	*No. of monomers in the elementary unit cell*	*Dimensions of the elementary unit cell (Å)*			*α*	*β*	*γ*	*X-ray density (rhombohedric)*
				a	*b*	*chain axis c*				
Polystyrene	235	$R\bar{3}c$ (rhombohedric)	18	21·9	21·9	6·65	90°	90°	120°	1·12
Poly-α-butene	130	$R\bar{3}c$ (rhombohedric)	18	17·7	17·7	6·55	90°	90°	120°	0·96
Isotactic 1,2-polybutadiene	130	$R\bar{3}c$ (rhombohedric)	18	17·3	17·3	6·50	90°	90°	120°	0·96
Polypropylene	175	C_2/c (monoclinic)	12	6·65	20·96	6·50	90°	99·20°	90°	0·936

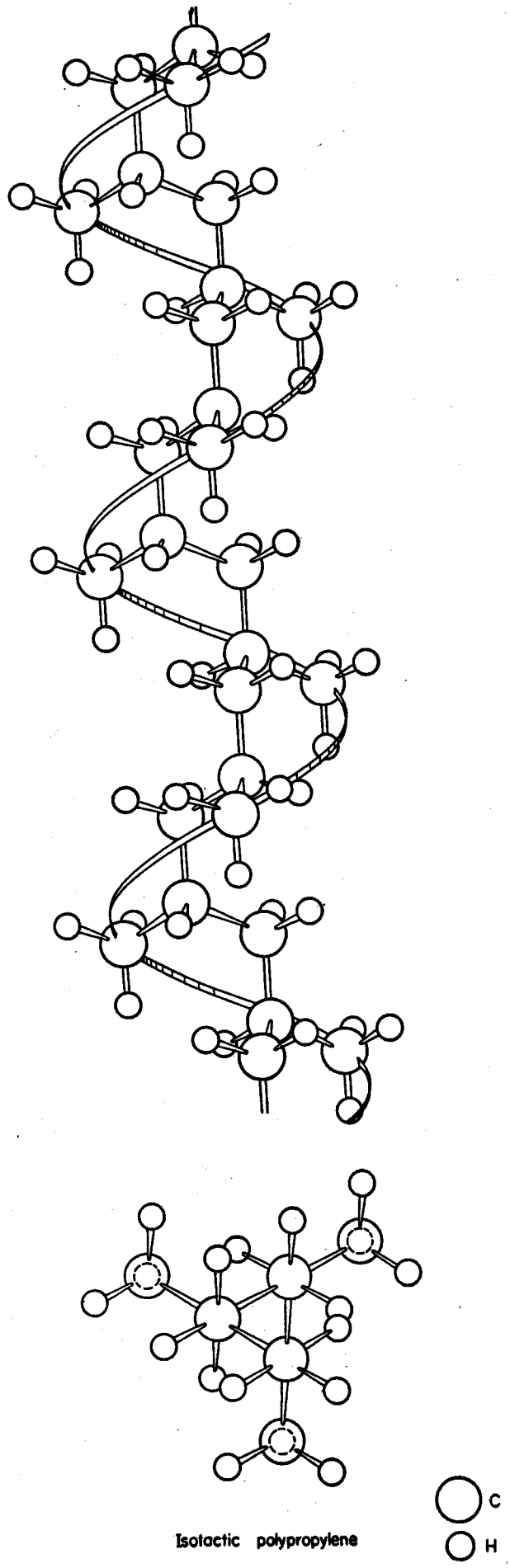


FIG. 3. Chain configuration of crystalline isotactic polypropylene.

talline polymers. By studying their structure, one can demonstrate the validity of some general principles used for determining the chain configurations of crystalline linear high polymers. If one applies these principles, it is possible to foresee the lattice structure and the physical properties of some of the new linear polymers and, in several cases, it allows one to predict their structures.[14] Some of these principles are indicated below:

TABLE 2. PROPERTIES OF POLYPROPYLENES HAVING A DIFFERENT STEREOISOMERIC STRUCTURE, SEPARATED BY SOLVENT EXTRACTION

Fractions obtained by different solvent extractions	*Extraction temperature (°C)*	*Structure of the fraction*		*Crystallinity*	*M.T. (°C)*
Ether	35	atactic	0·46	0	—
Pentane	36	stereoblock	0·51	27	114
Hexane	69	stereoblock	0·61	37	130
Heptane	98	stereoblock	0·68	54	159
Ethylhexane	120	stereoblock	1·22	64	170
Residue	126	isotactic	2·08	68	174

(1) In the linear crystalline high polymers, the axes of the main chains in the crystal are parallel to a single crystallographic axis (the chain axis is a straight line which joins the baricentres of the subsequent chain portions corresponding to the crystallographic identity period).

(2) The different monomeric units, contained in an even number in the identity period, have equivalent positions, which they assume by simple translations, along the chain axis c/m, where c is the identity period accompanied by a rotation of $n360/m$ (where m and n are integer numbers) or else by a mirror reflection.

(3) The chains assume such a position so that the highest approach between the atoms of the different chains, as allowed by the van der Waals' forces, is obtained.

The most stable chain configuration in the crystal is determined by the following principles:

(a) Constant bond length, considered as the distance between the centres of the atoms bound by a determined covalent bond.
(b) Constant angles between the valence directions starting from the same atom.

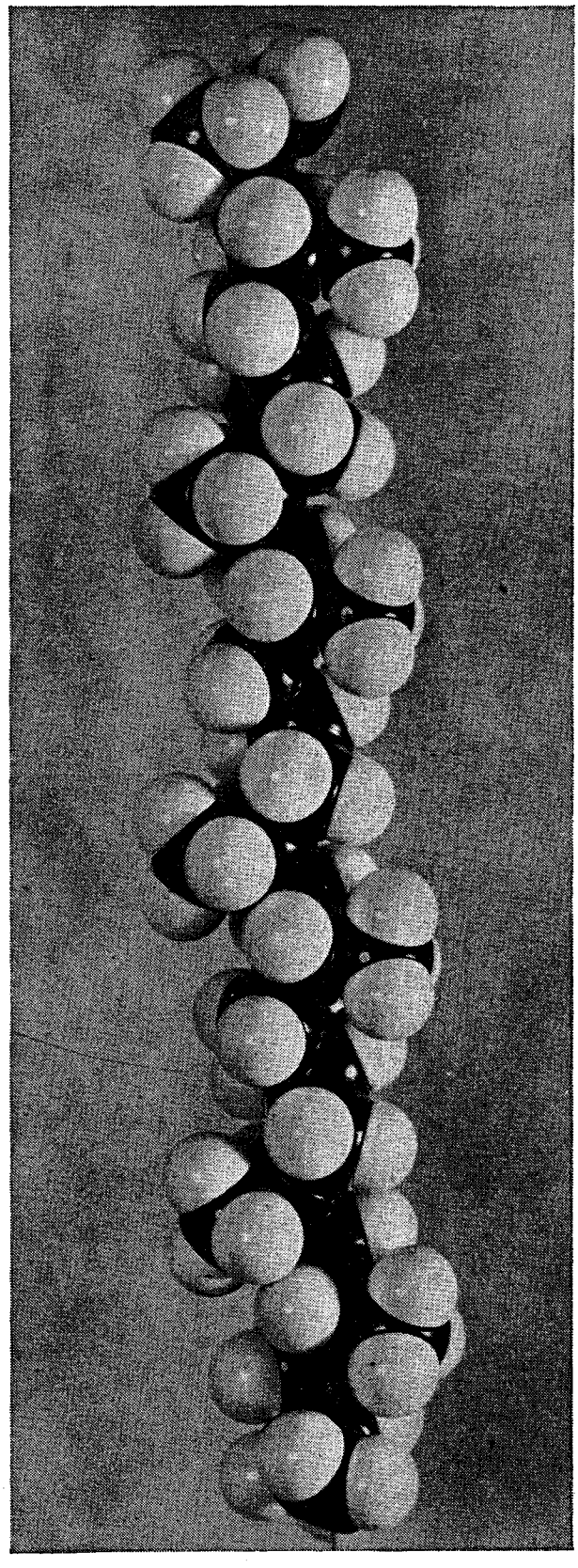


FIG. 4. Chain model of isotactic polypropylene.

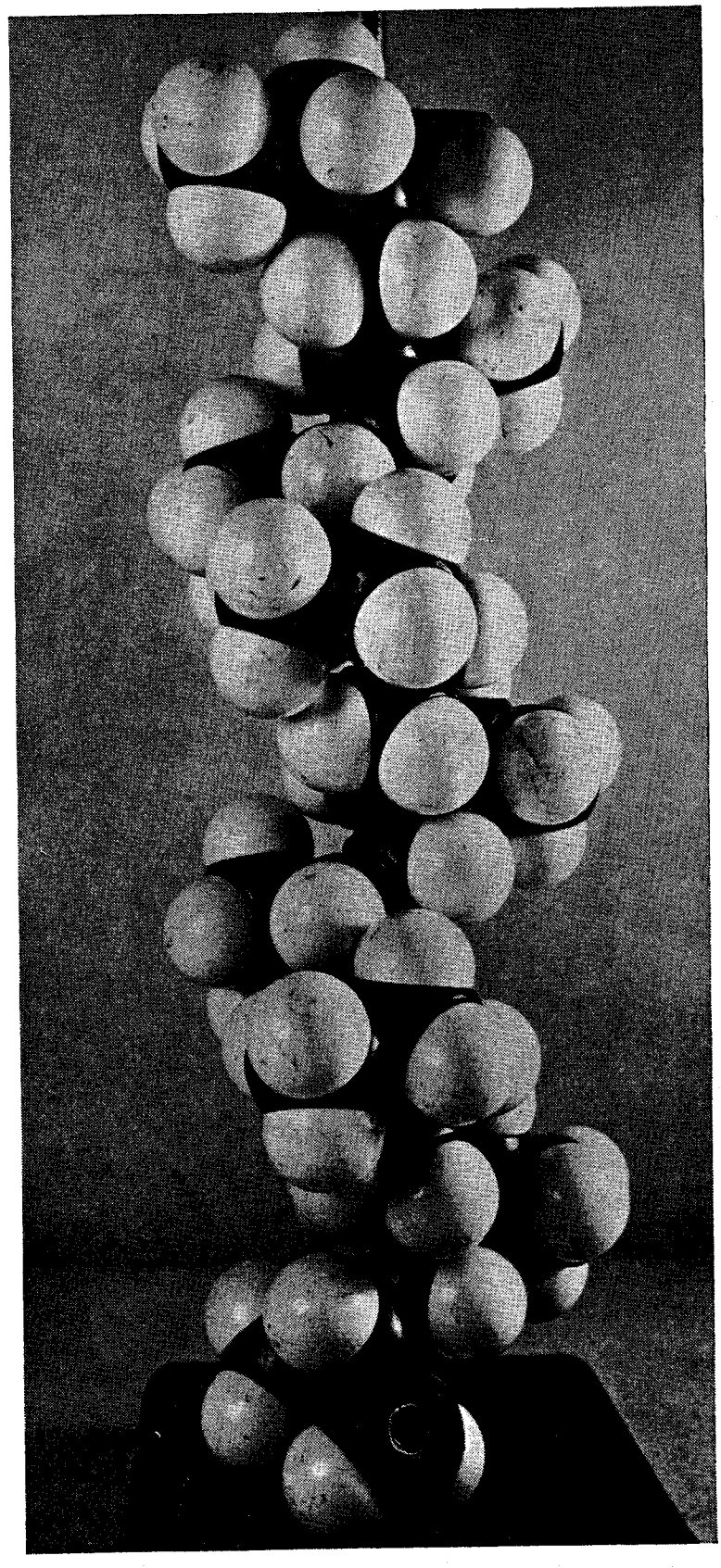


FIG. 5. Chain model of the stable modification (I) of isotactic polybutene.

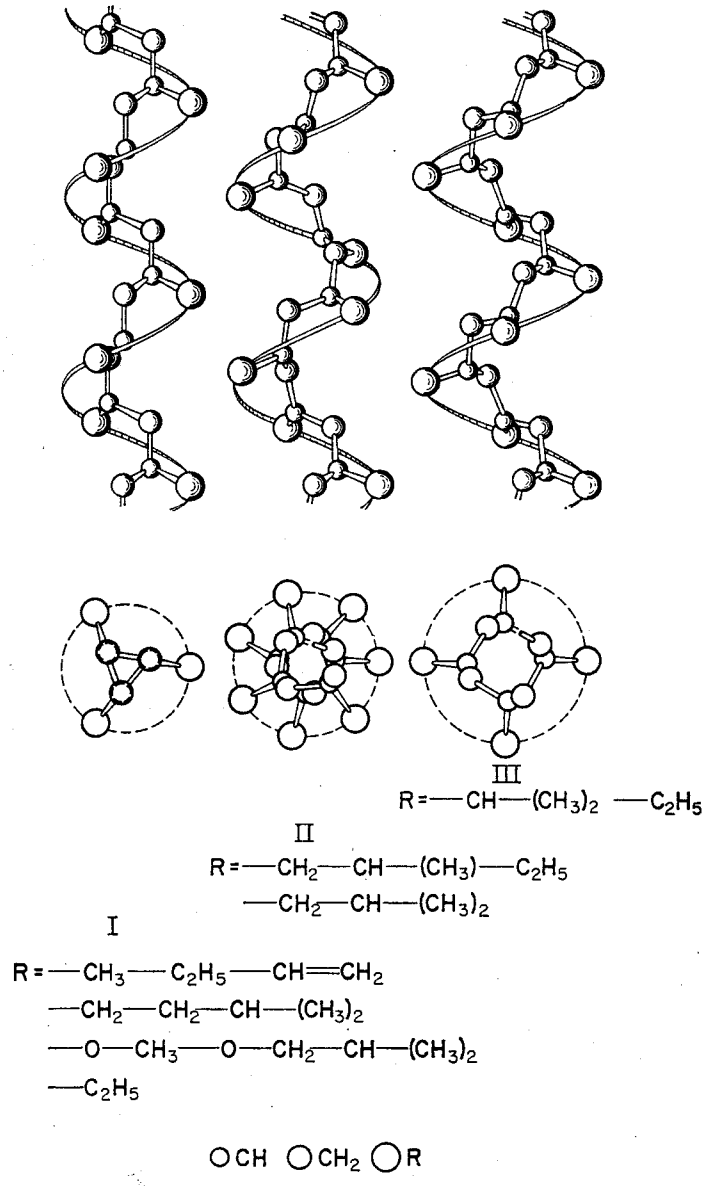


FIG. 6. Chain configurations of isotactic polymers of branched poly-α-olefins.

(c) A chain configuration in agreement with the principle of the maximum separation from subsequent bonds (staggered bonds).

This last principle is preferably applied to the carbon–carbon bonds in comparison with the carbon–hydrogen and carbon–oxygen bonds. It determines, for instance, the planar zigzag chain configurations of normal paraffins. The principle of the maximum separation of the bonds may also be applied to those which are adjacent to double bonds. In this case one must consider that the double bond is contained in a plane which is normal to the one containing the other carbon atoms which are bound to the double bond in consideration. Owing

to this principle, a four-carbon-atom chain with a central double bond is contained in a plane ; this does not occur in a longer chain having two or more double bonds.

TABLE 3. PHYSICAL PROPERTIES OF SOME CRUDE ISOTACTIC POLYMERS

	Measure unity	*Polypropylene*			*Polybutene*	
Intrinsic viscosity	10^2 cm^3/g	2·66	5·25	1·84	1·12	2·64
Residue of the heptane extraction	%	89	91	100	—	—
Residue of the ethyl ether extraction	%	—	—	—	72	91
Viscous flow	kg/cm^2	360	376	400	—	—
Tensile strength	kg/cm^2	385	410	400	150	365
Elongation at break	%	320	670	100	165	320
Stiffness	kg/cm^2	8500	8200	10000	1300	1670
Brinell hardness	—	1900	1550	2000	—	—
Hardness Shore "A"	—	—	—	—	95	97
Softening point Vicat :						
1 kg	°C	> 150	> 150	> 150	100	129
5 kg	°C	99	99	111	—	—

(4) If sometimes, steric hindrances do not allow to maintain strictly the values of the distances between the atoms and the bonds, which should be foreseen by the application of the preceding principles, the chain undergoes elastic deformations which are distributed in agreement with the principle of the minimum of potential energy.

Polyethylene is the only polymer of the poly-α-olefin series free from tertiary carbon atoms. Its planar structure is well known. The use of new polymerization processes at low or at medium pressure (Ziegler[15] and Phillips[16]) has permitted the production of polymers which are less branched and more crystalline than those obtained by high-pressure procedures. With the use of special catalysts, essentially derived from Ziegler's catalysts, we have obtained, by operating at low pressure, high-molecular-weight ethylene polymers (of the order of one hundred thousand to 1 million). It was impossible to observe with I. R. analysis the presence of branchings. These ethylene polymers show a very high melting temperature (138–9°C), a high degree of crystallinity and very good mechanical properties.[17]

Isotactic polypropylene, polybutene, polystyrene, etc., which show sequences of asymmetric carbon atoms having the same configura-

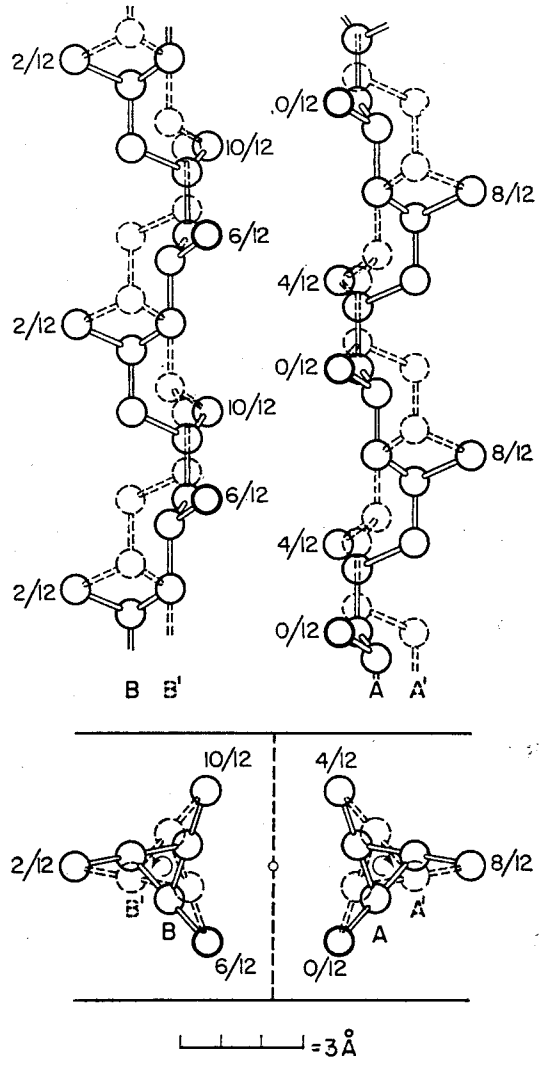


FIG. 7. Types of enantiomorphous chains of isotactic polypropylene. The corresponding isomorphous anticlined chains are represented as dots.

tion, all have the same characteristic structure. The principle that the monomeric units of a macromolecule must possess in a crystal equivalent positions, with respect to the chain axis, defines the configuration of the chain itself, which necessarily assumes a helix shape, as is the case for crystallizable proteins. For instance, polypropylene exhibits a helix chain with a ternary symmetry, which agrees with the principle of the highest separation of the bonds.[18, 19]

Polystyrene and the most stable modification of polybutene show an analogous structure,[20] with a slight variation of the bond angles of the main chain (116° and 114° respectively). Sometimes steric hindrances prevent the formation of this structure, because it would create conditions which are in contrast with the principle of the maximum approach allowed by the van der Waals' forces. In these cases, other types of helix are formed.

TABLE 4. PHYSICAL PROPERTIES OF POLYPROPYLENE AND OF OTHER THERMOPLASTIC MATERIALS

	Polypropylene: degree of crystallinity>60%	*Polyethylenes*			
		Rotene	*Rotene L*	*Marlex 50*	*Fertene 7*
Density	0·90–0·92	0·95	0·96–0·97	0·96	0·92
Melting temperature (°C)	165–170	132–137	134–138	135	107-112
Yield stress (kg/cm²)	360–400	220	280–310	270	105
Elongation at break (%)	100–600	700	650–850	400	400
Stiffness (kg/cm²)	8200–10000	4000–6000	7000–8000	9900	1700
Brinell hardness (kg/cm²)	1500–2000	750	—	—	470
Softening point Vicat					
5 kg (°C)	99–111	81–88	94–98	—	—
1 kg (°C)	>150	124–128	133–138	—	92

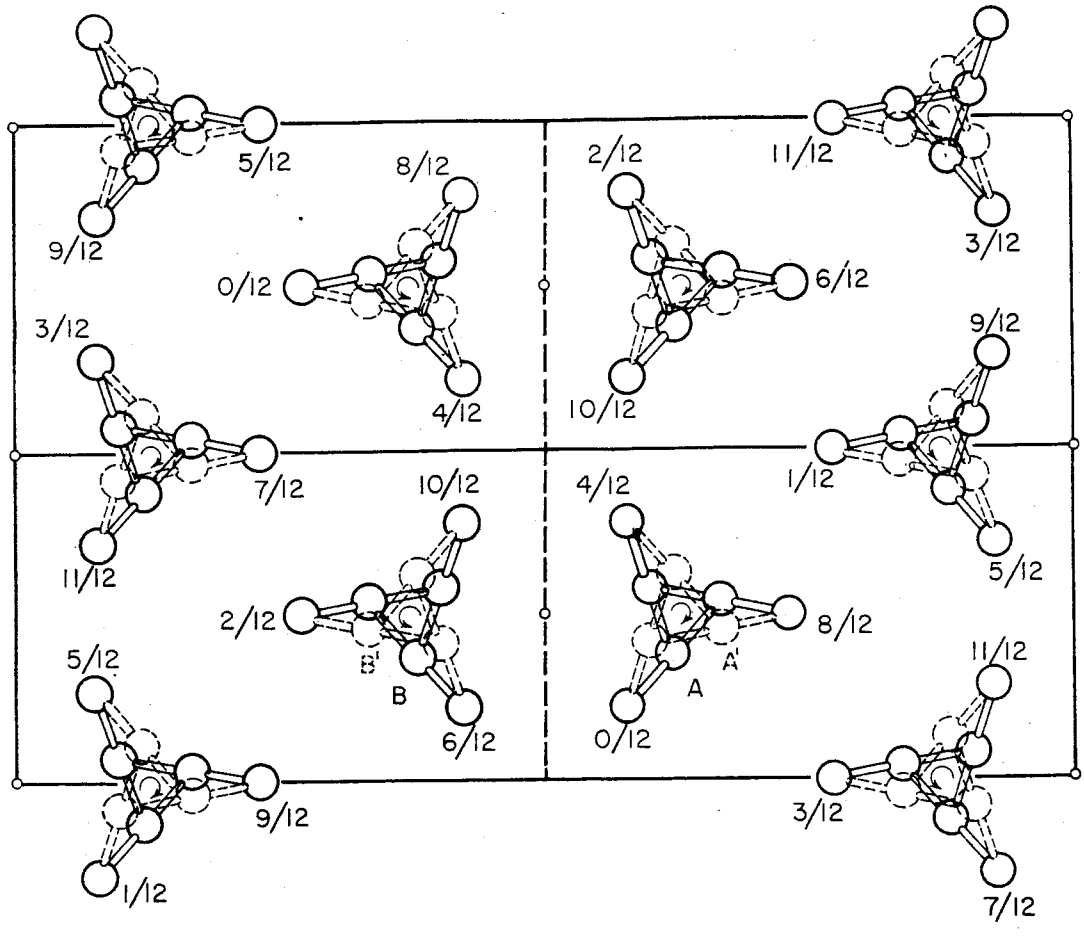


FIG. 8. End view of an elementary lattice of isotactic polypropylene. The anticlined isomorphous chains are represented as dots.

For instance, the helix of poly-3-methyl butene-1 shows a quaternary symmetry, and the helix of poly-α-olefins branched in the 4 position shows a sevenfold symmetry.[21]

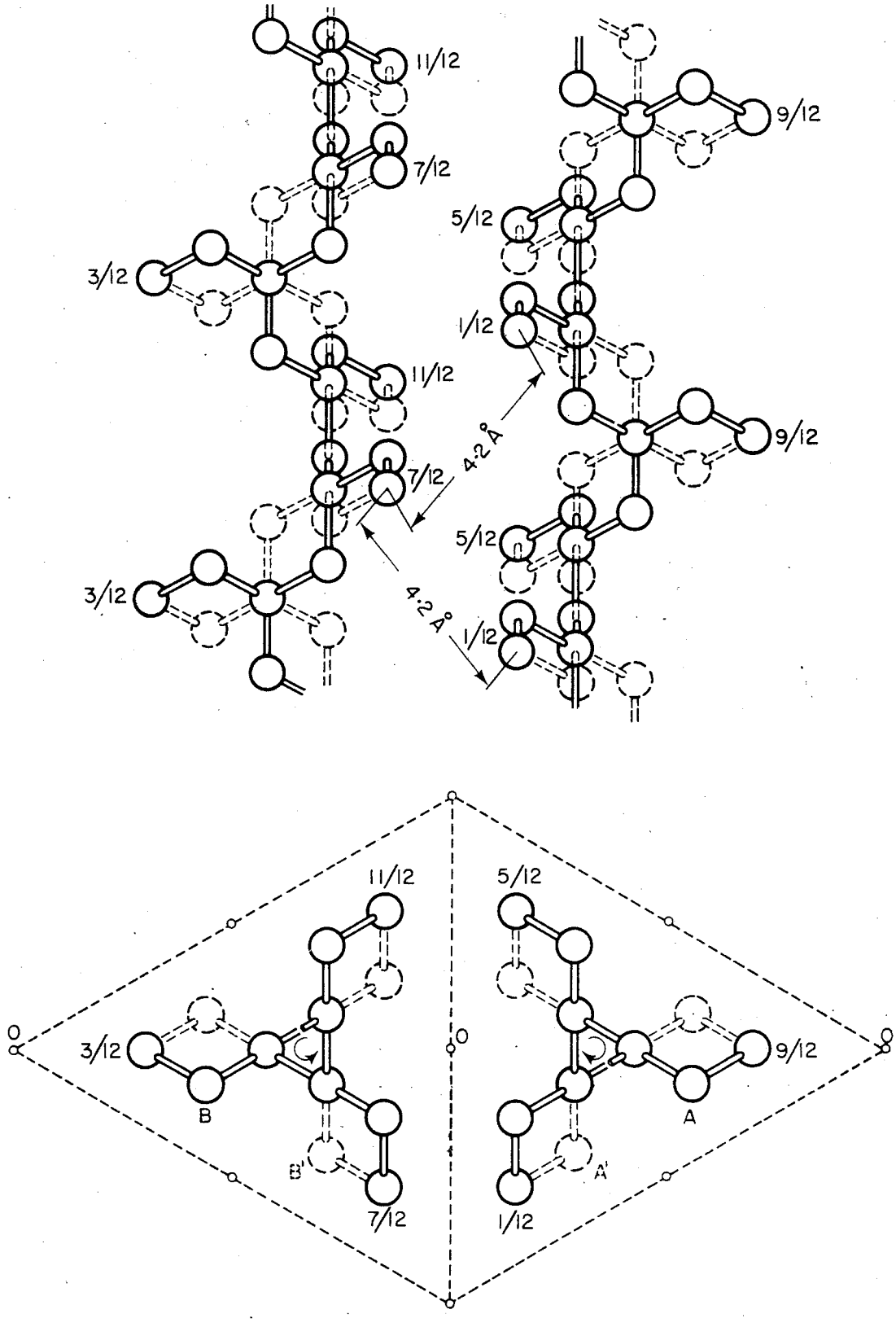


FIG. 9. Enantiomorphous chains present in the crystals of isotactic polybutene. The anticlined isomorphous chains are indicated by dots.

Obviously the chain axis symmetry does not correspond, in many cases, to the crystallographic symmetry of the same axis.

In the isotactic polymers, the bonds linking the side groups of the tertiary carbon atoms of the main chain are always inclined in the same sense (isoclined), for reasons of symmetry. Since it is possible to have *d* or *l* helices, considering the sense of the inclination of the side groups with respect to a determined end group, one can represent two types of helices in crystals : *d* with opposite inclinations, one with respect to the other (anticlined helices), which are superimposable by 180° rotation around a straight line normal to the chain axis, and two types of *l* helices.[18]

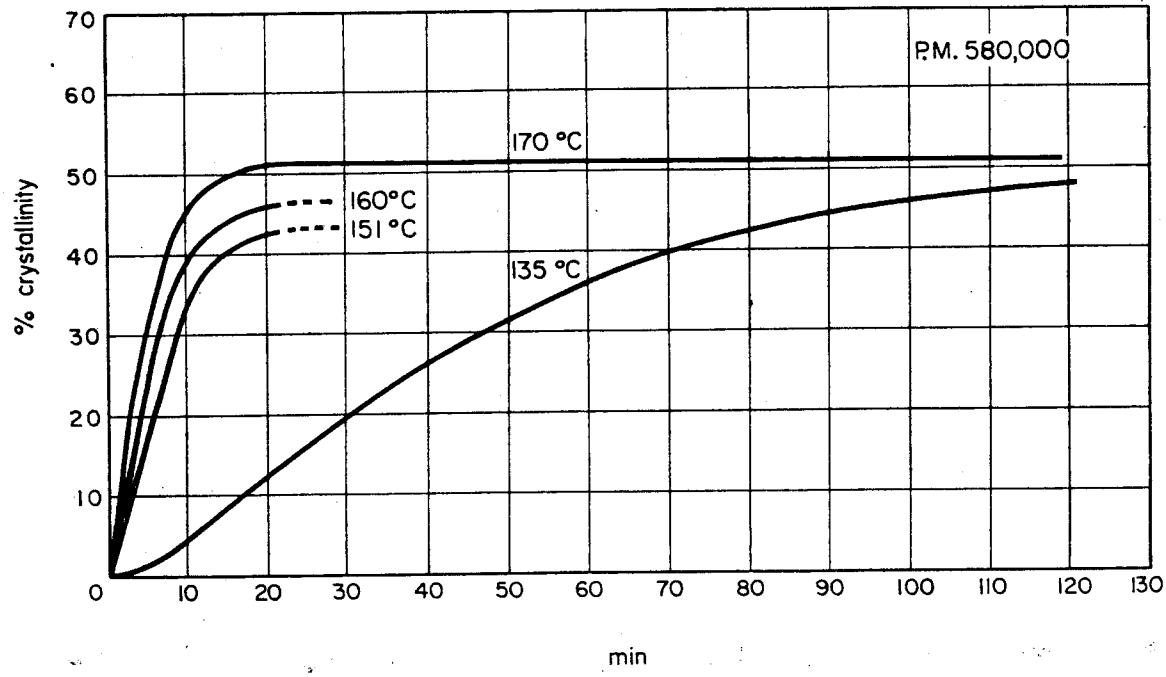


FIG. 10. Kinetics of crystallization of polystyrene having a medium degree of crystallinity.

Two anticlined chains occupy about the same space in the crystal; that is why we consider them to be crystallographically isomorphous and statistically distributed in the same plane. The symmetry of the synthetic isotactic crystals (racemic) is in agreement with the distribution of the helices, because the "right-handed" ones surround the "left-handed" helices, and vice versa (Figs. 7-8).

Figure 9 shows the chains of isotactic 1,2-polybutene and 1,2-polybutadiene.

CRYSTALLINITY OF ISOTACTIC POLYMERS

In our preceding papers we used the X-ray and electron-ray methods to determine both the crystallinity and the orientation of isotactic polymers. More recently, we have developed a quantitative X-ray method to determine the order of crystallinity.[18] We have

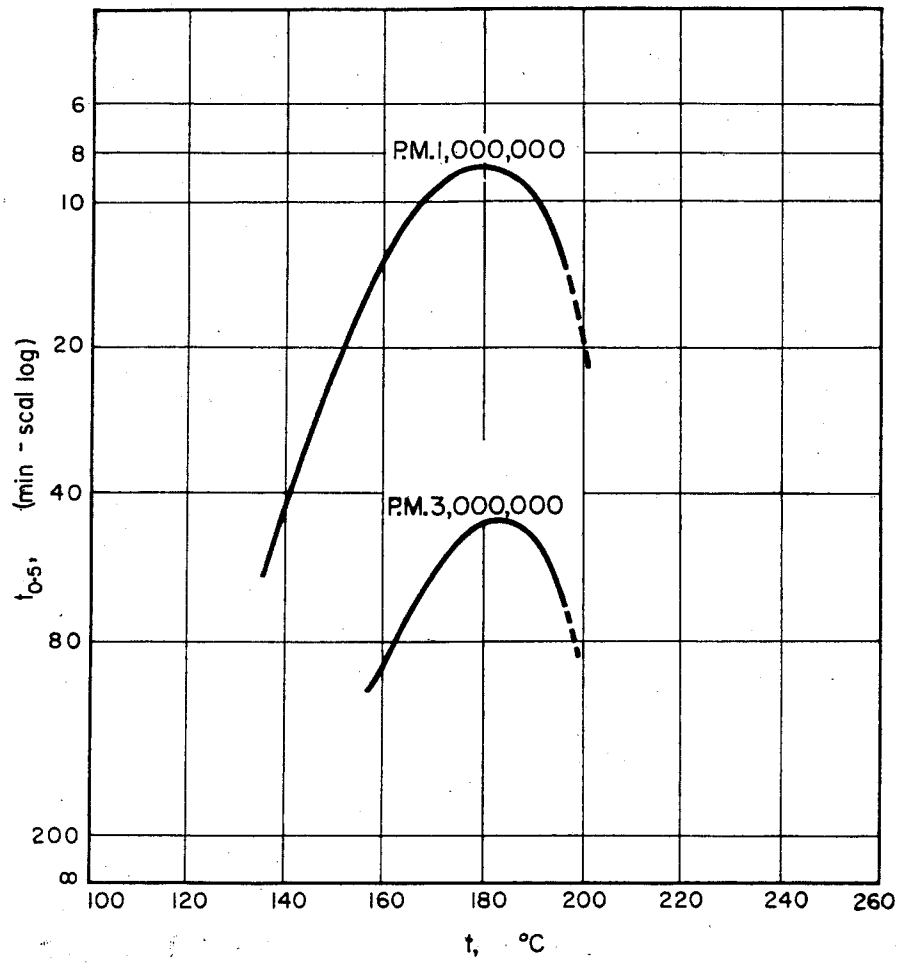


FIG. 11. Time of semi-crystallization of crystallizable parts of two polystyrenes having different molecular weights.

also used the X-ray method, in addition to densimetric methods (Figs. 10 and 11) to measure the kinetics of crystallization. It has been observed, for instance, that very high-molecular-weight polystyrenes have their highest crystallization rate at a temperature of about 50°C below their melting temperature. The rate of crystallization depends on the viscosity of the system, which increases as the molecular weight of the polymer increases. For high molecular weights, it is very slow. Even if the crystals have a size lower than the wavelength of light (generally several hundreds of Å), the crystallites can be observed by optical methods, since they gather in spherulites which at times

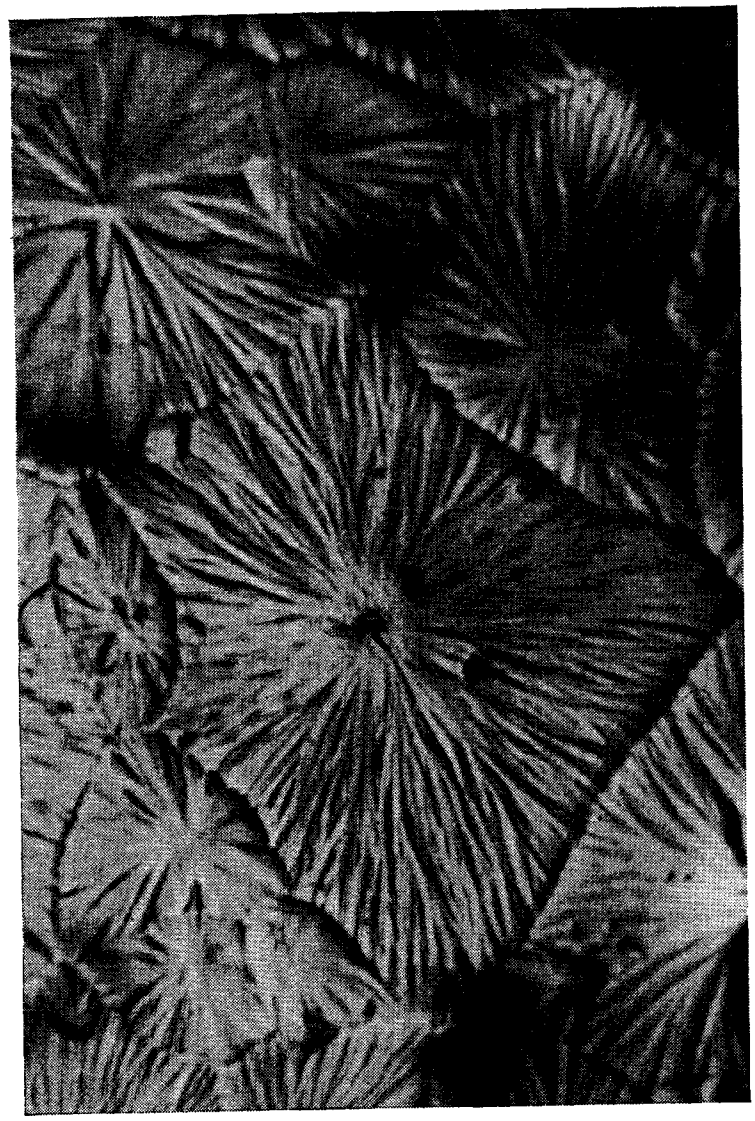


FIG. 12. Examination by normal light of isotactic polypropylene spherulites obtained by slow cooling of the molten polymer.

are quite large, of the order of a tenth of a millimetre or even of a millimetre (polybutene-1). Excellent photographs of spherulites have been obtained at the Castellanza Laboratories of Montecatini.[22]

Figures 12 and 14 show the spherulite shapes of polypropylene and of polystyrene, obtained by cooling the molten polymer. Figures 13 and 15 show the same spherulites as observed by polarized light.

In the case of very low-molecular-weight polymers, it is possible to observe crystalline aggregates, with a microscope, confirming the symmetrical properties previously determined by X-ray examination.

Figure 16 shows crystalline aggregates of isotactic polystyrene, having a molecular weight of the order of about 10,000. Hexagonal

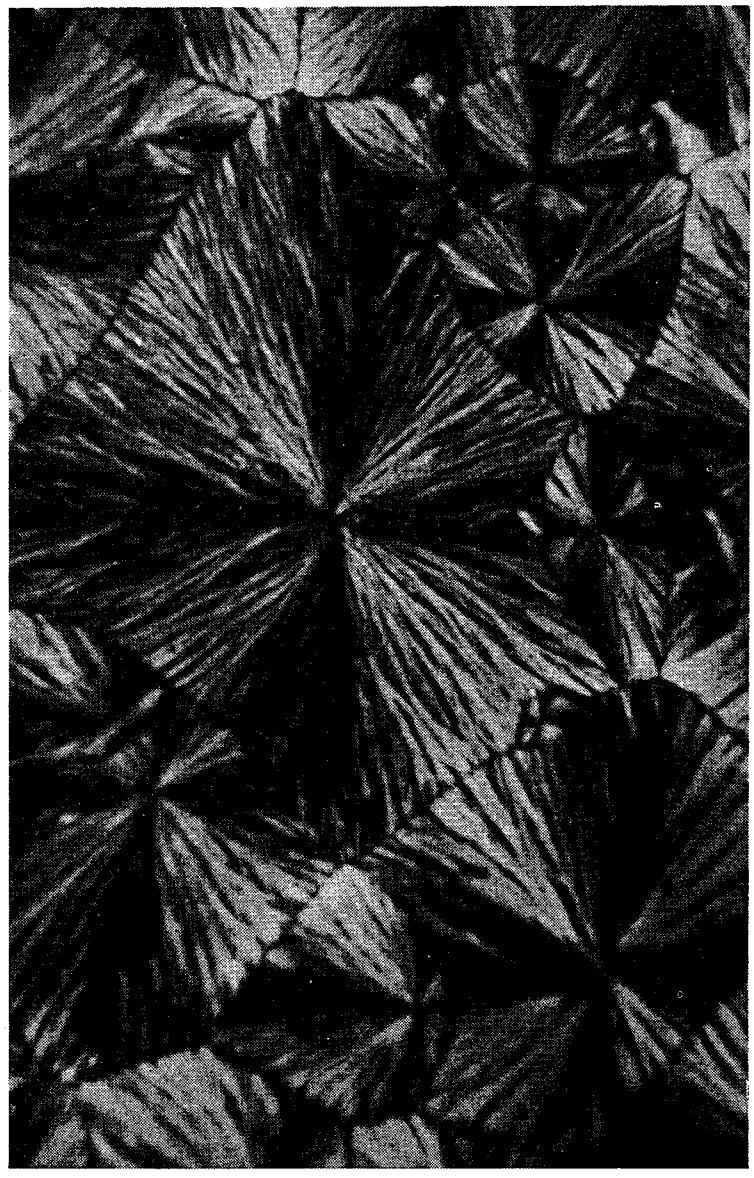


FIG. 13. Examination by polarized light of isotactic polypropylene spherulites obtained by slow cooling of the molten polymer.

laminae can be observed, which when well-oriented, are not birefringent by polarized light, as opposed to the spherulites which give the typical interference figures of anisotropic crystals.

The formation of spherulites obtained by crystallization of a solution in suitable solvents is much less evident. Polybutene spherulites are particularly well developed. The presence ol small amounts of low-molecular-weight amorphous products, which reduce the viscosity of the crude polymer, and possibly occupy intercrystalline space, enhances the formation of big spherulites, which are well separated and visible with a microscope. In some cases, the spherulites may approach a size of hundreds and even of thousands of microns (Fig. 17).

Figure 18 shows a part of a crystallite examined by an electronic microscope at the Novara Laboratories of Montecatini.

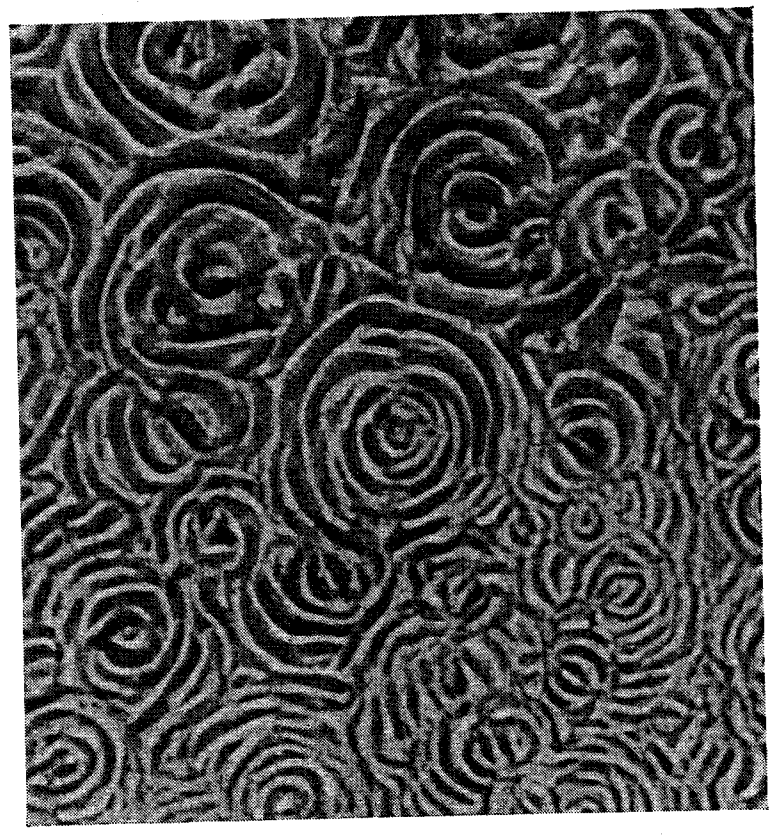


FIG. 14. Examination by normal light of isotactic polystyrene spherulites obtained by slow cooling of the molten polymer and annealed at 180°C.

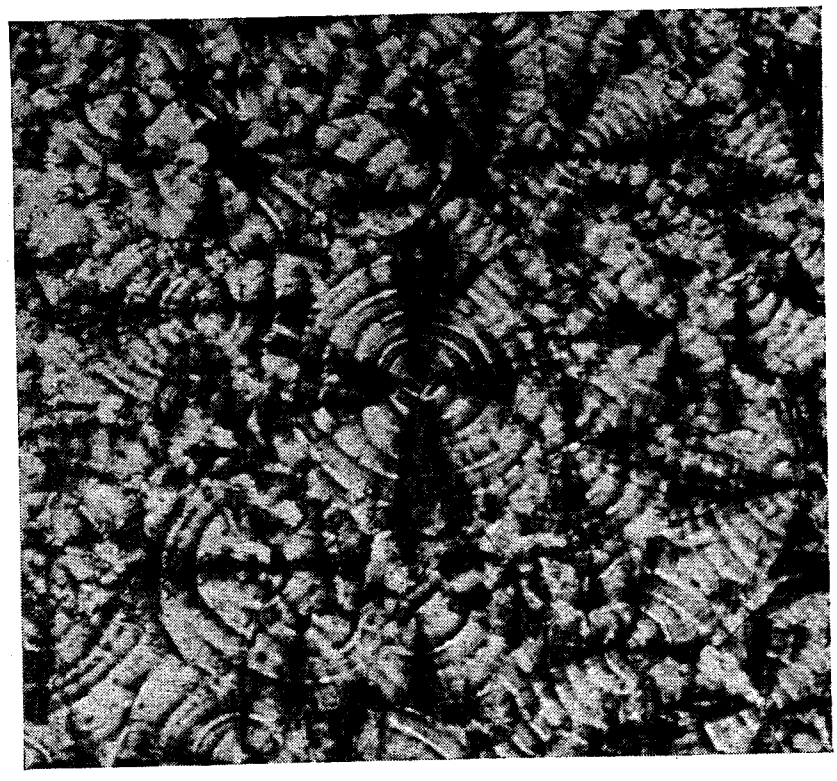


FIG. 15. Examination by polarized light of isotactic polystyrene spherulites obtained by slow cooling of the molten polymer, annealed at 180°C.

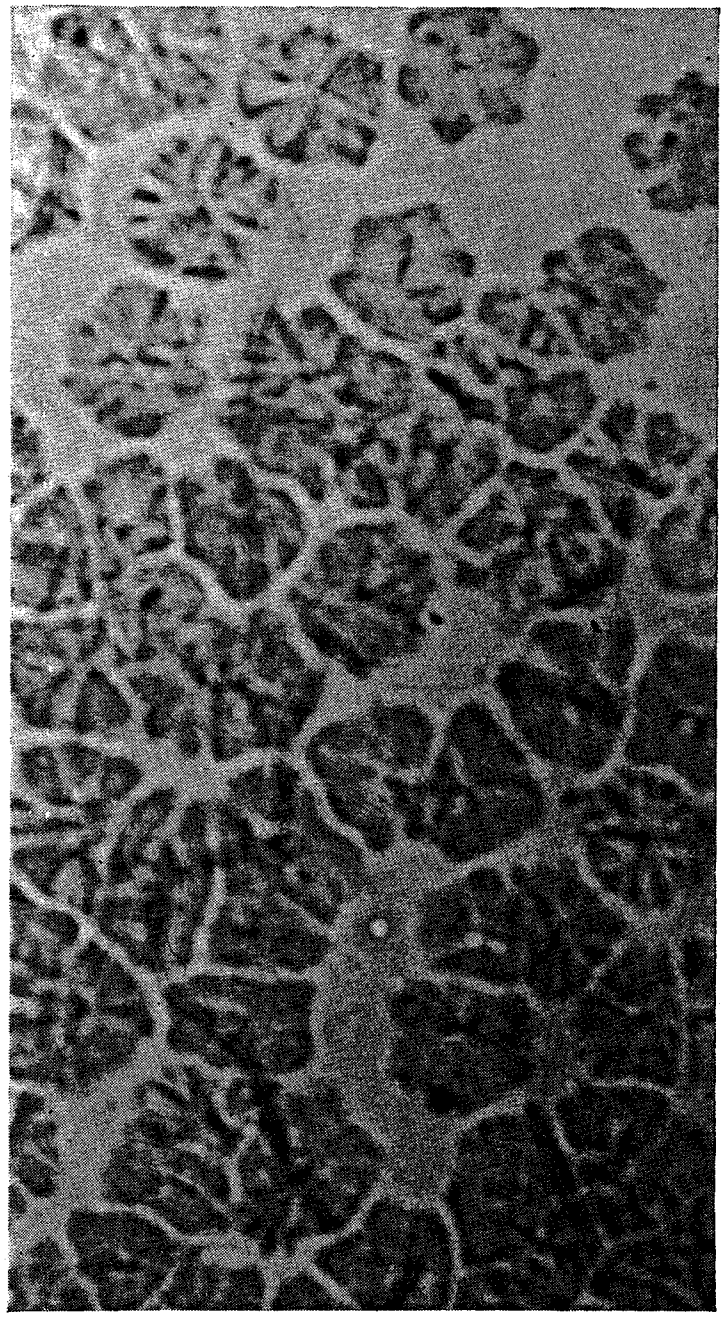


FIG. 16. Crystalline aggregates of isotactic polystyrene with a hexagonal symmetry obtained by starting from a solution of isotactic polystyrene in atactic polystyrene, melted and annealed at 180°C after rapid cooling.

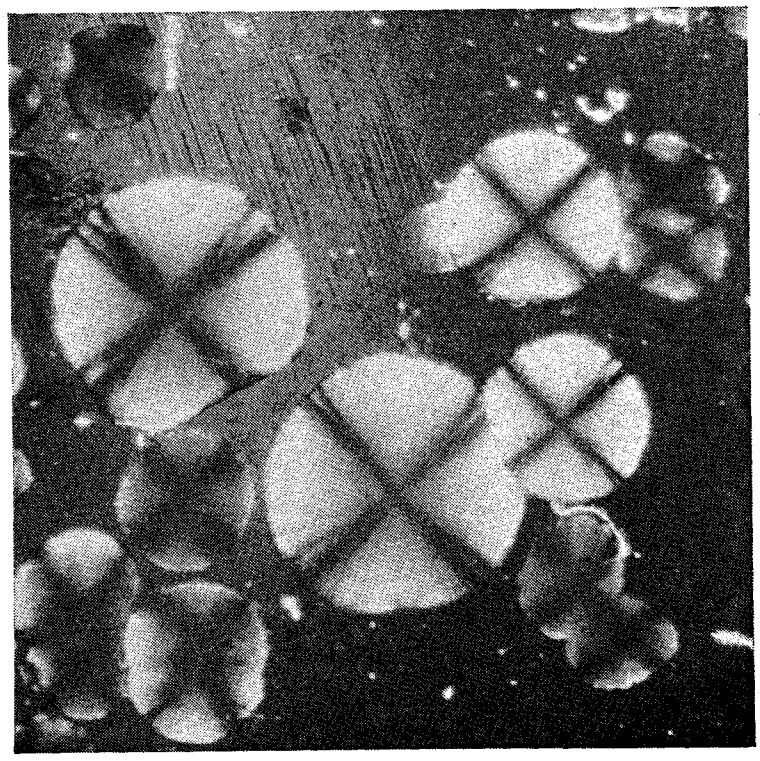


FIG. 17. Spherulites having the size of the order of a millimeter, obtained by evaporation of a solution of poly-α-butene in n-heptane.

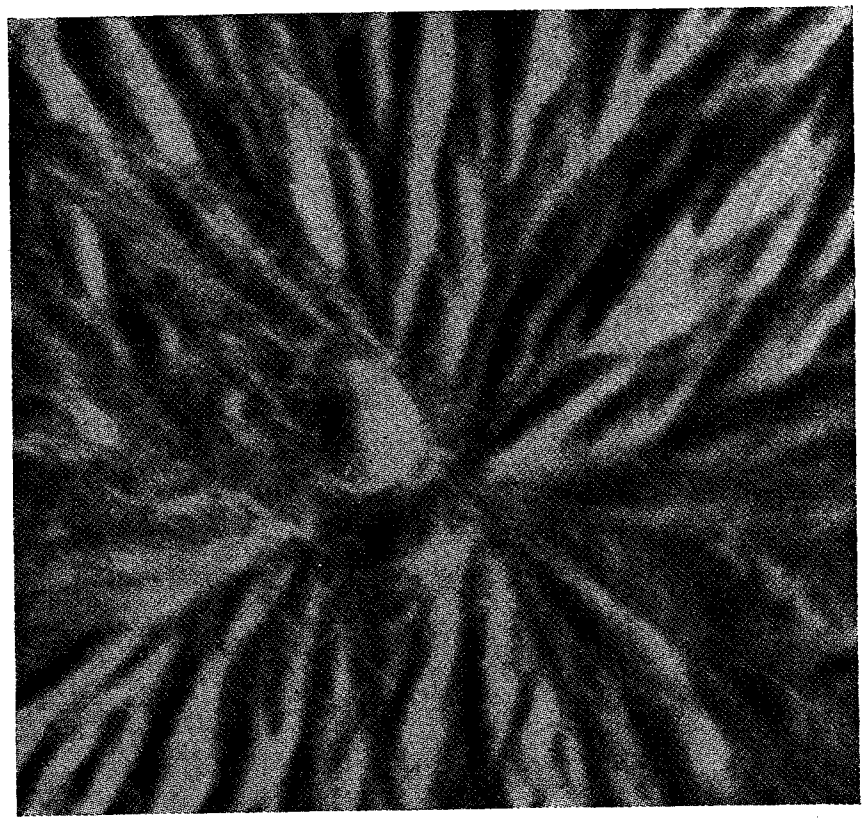


FIG. 18. Photograph taken by the electronic microscope of a portion of poly-α-butene spherulite.

ATACTIC AND BLOCK POLYMERS

The new polymerization processes, acting through an anionic mechanism and based on catalysts consisting of organometallic compounds and of very electropositive transition metal compounds, have allowed us not only to produce crystalline linear polymers of α-olefins, but also, with the aid of non-stereospecific catalysts, amorphous polymers. These polymers, which lack the regularity of the steric distribution of the monomer units, have a linear main chain, and can even be obtained with very high molecular weights.

The perfectly linear polymers of aliphatic olefins with a molecular weight of some hundreds of thousands were previously known only in the case of vinylidene monomers. As a matter of fact, all the previous polymerization processes were not very suitable for the production of linear polymers of α-olefins. Due to the frequent chain transfer processes, these procedures generally yielded low-molecular-weight polymers, or else chains containing long branchings.

A comparison of the properties of amorphous poly-α-olefins having a truly linear structure, called "atactic" by us, with the properties of the crystalline isotactic polymers, illustrates the great influence that stereoisomeric phenomena have on the physical properties of macromolecular substances.

The viscoelastic properties are those which are mostly influenced by regularities or irregularities of the chain structure. Whereas the isotactic polymers, even those having a low molecular weight, for instance corresponding to several tens of monomeric units, are high melting crystalline solids, the atactic polymers with the same molecular weight are liquids. They become more and more viscous as the molecular weight increases, and when their molecular weight reaches a value of some hundreds of thousands, they acquire the viscoelastic properties of non-cured rubbers.

These last products, which may be considered as liquids of very high viscosity, can be transformed into true elastomers, when the bridge-like formation of bonds between macromolecules, hinders the viscous flow of one molecule with respect to the other.[13] As a result of this a new class of saturated elastomers was obtained; generally these elastomers possess better properties, even with regard to the elastic hysteresis, than those of the previously known saturated rubbers, mainly obtained by olefins (butyl rubber), or by sulphur chlorinated polyethylene (Hypalon).

Besides the crystalline isotactic and amorphous atactic polymers, there escists a series of products with intermediate properties, whose chains contain regular and irregular structural segments.[23] The properties of these products can be compared with those of a block polymer, consisting of segments having elastomer-like properties and of segments having the properties of crystalline or crystallizable plastomers. When either of these two types of stereoisomers pre-

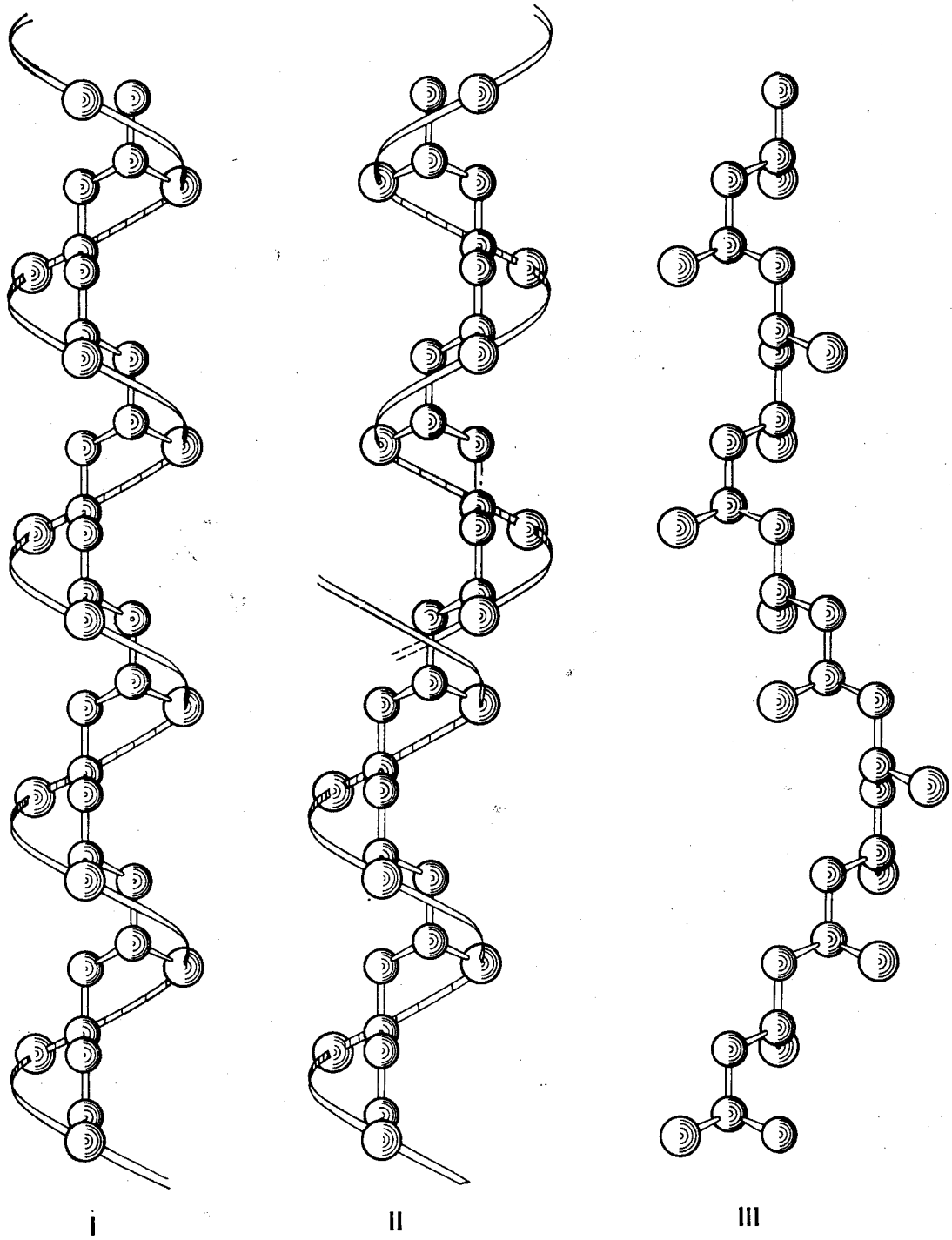


FIG. 19. Types of stereoisomeric chains:
(I) isotactic chain; (II) chain with isotactic segments, having a different steric configuration; (III) atactic chain.

vails, and the sections of the polymer chain with an irregular or respectively regular structure are small, then the properties of the polymers approach those of either of the extreme stereoisomers.

In the intermediate cases, some properties are modified and new characteristics seem to appear. In fact a small amount of amorphous sections present in the isotactic chains, or a minute irregularity caused by alternation of the long isotactic portions of different steric configuration (Fig. 19), produces only a slight lowering of the melting

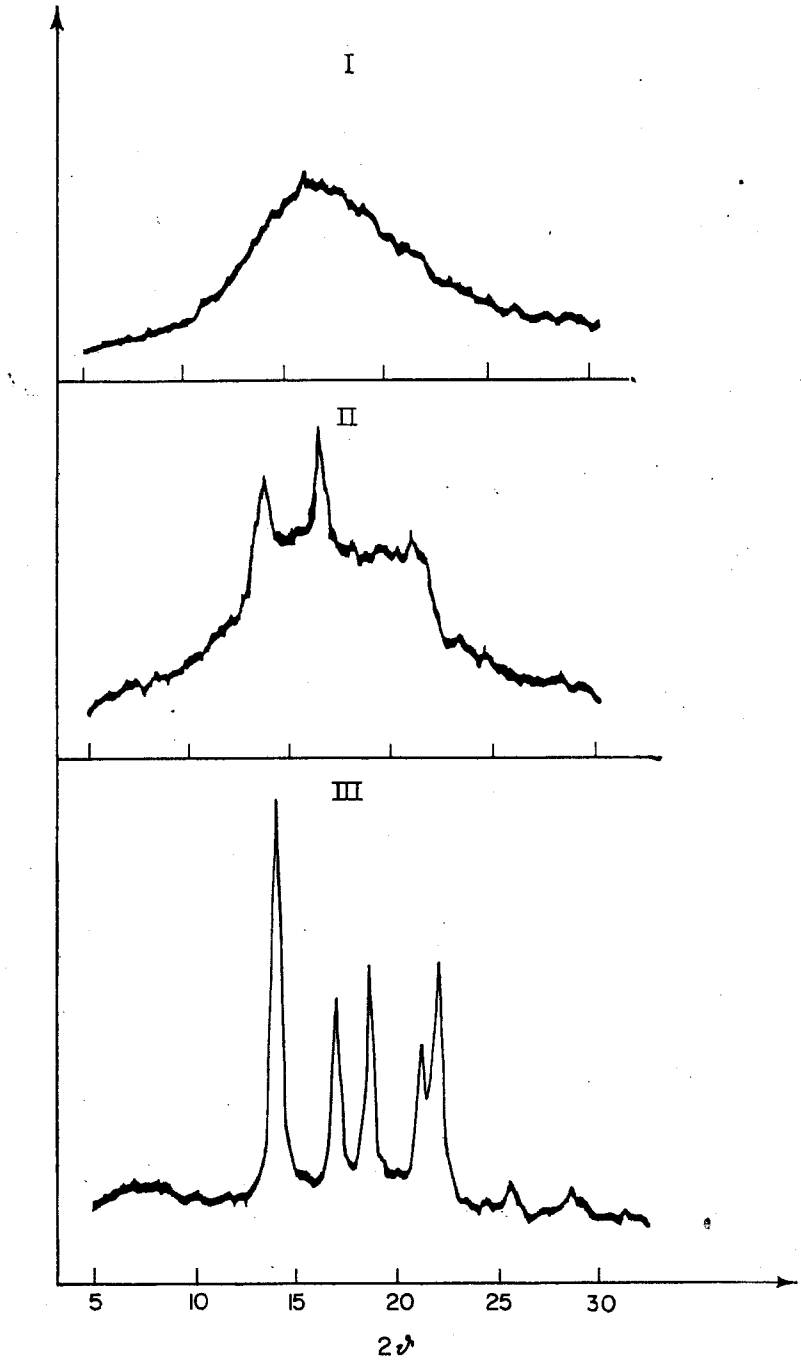


FIG. 20. Comparison of the X-ray Geiger spectra:
(I) atactic polypropylene; (II) block polypropylene; (III) isotactic polypropylene

temperature and a slight increase of the elastic elongation, whereas the tensile strength and the elongation at break are almost unaltered. The properties of these polymers are not very different from those of the completely isotactic polymers provided they possess sufficiently high molecular weights.

Similarly, the presence of small isotactic portions in a chain which is

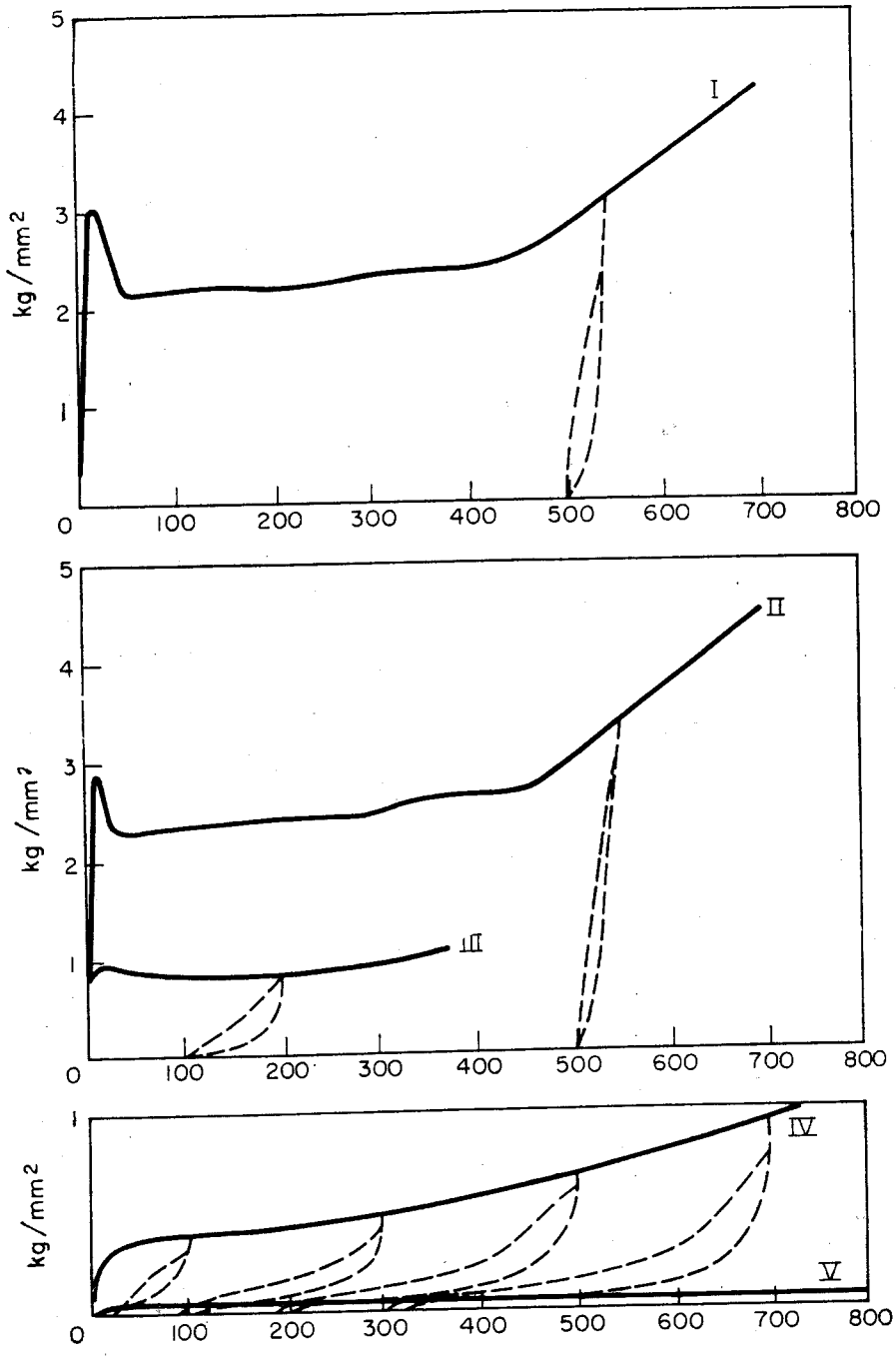


FIG. 21. Stress–strain diagram %:
(I) isotactic polymer (crystallinity ~ 75%);
(II) polymer rich in isotactic parts (crystallinity ~ 65%);
(III) stereoblock polymer (crystallinity ~ 40%);
(IV) stereoblock polymer (crystallinity ~ 15%);
(V) atactic polymer.

almost completely atactic does not markedly alter the properties of the atactic polymer. New and interesting properties appear only when the isotactic portions are long enough to enable the stereoblock polymer to partially crystallize.

Figure 20 shows a comparison between the X-ray Geiger spectra of amorphous and crystalline polymers with that of a stereoblock polymer.

The ability of molecular parts to participate in the crystalline lattice provides the orientated products with properties, which are similar to those caused by physical curing, such as the rapid stretching of natural rubber. In the pure state (non-cured) these block polymers show, soon after being subjected to the process of orientation under stretching, reversible elongations, of the order of 50–100 per cent, and at times even higher, and tensile strengths higher than most amorphous cured rubbers having no reinforcing fillers in them.

In Fig. 21, curve I represents a fairly pure polymer, curve II represents an isotactic polymer containing very few stereoblocks, curves III and IV indicate stereoblocks, and curve V a high-molecular-weight amorphous polymer.

The vulcanizing effect of crystallinity alone, which is observed in

TABLE 5. MECHANICAL PROPERTIES OF FILMS OF POLYPROPYLENE, OF POLYBUTENE AND OF OTHER THERMOPLASTIC MATERIALS

	Polypropylene: degree of crystallinity 60—65%	*Polybutene: degree of crystallinity 40—50%*	*Polyethylenes*			*Cellophane*
			Rotene	*Marlex 50*	*Fertene 7*	
Tensile strength: (kg/cm^2)						
Machine direction	350—400	400—450	251	270	196	308—1300
Transverse direction	300—350	300—350	243	238	181	
Elongation (%)						
Machine direction	700—750	200—230	807	200	284	14—15
Transverse direction	730—750	300—320	774	72	234	
Tear strength: (kg/cm)						
Machine direction	160—190	100—110	128	184	87	20—91
Transverse direction	140—160	100—110	115	178	75	

block homopolymers, differs from that caused by chemical bonds, because it disappears when the product is heated at temperatures higher than the melting temperature of crystals, while it reappears if the material is cooled and stretched again.

Usually, block polymers are characterized by higher solubility and by lower melting temperatures than those of the pure crystalline polymers, which can be foreseen in theory. In fact those theories developed by various authors, in particular by Flory,[24] on the lowering of the melting temperature of a copolymer due to the presence of chemically different monomer units in the chain, could be perfectly applied in the case of linear homopolymers, when the irregularities of the structure are due only to the different steric configurations of chemically identical monomer units.

PROPERTIES OF STEREOISOMERIC MIXTURES, DIRECTLY OBTAINED BY THE POLYMERIZATION OF α-OLEFINS

According to what has been stated above, the polymerization of α-olefins can yield several types of products, which exhibit very different properties, depending on the type and on the relative proportion of the various stereoisomers present in them. Generally the properties of a crude polymer depend on the following variables:

(1) The percent of well-crystallizable isotactic polymers, the size and the distribution of their molecular weights.
(2) The percent and the type of block polymers, their crystallinity, the size and the distribution of their molecular weights.
(3) The percent of atactic, amorphous polymers and their molecular weight.

Possible modifications of these variables can yield a wide variety of products. In practice, the products which have proved to be the most interesting as plastics are those which are very rich in isotactic polymers and those having very high-molecular-weight blocks, which are free or almost free from completely atactic molecules of low molecular weight.

The simplest methods for the characterization of commercial products are:

(1) the crystallinity, which can be determined either by X-rays or just simply by density measurements.

(2) The determination of the content of the three types of stereoisomers mentioned above, using the method of solvent extraction.

(3) The determination of the viscosimetric average molecular weight of the various fractions.

It must be borne in mind that several physical properties (such as the density and the melting temperature) vary very slightly with the change of the molecular weight above a certain limit (above 50,000). The viscosity in the molten state, however, varies markedly and influences the conditions employed for the injection and extrusion procedures.

Crude products having a good crystallinity (higher than 60 per cent) and a few atactic parts can be obtained directly by polymerization without any subsequent fractionation. These products exhibit good mechanical properties which differ very little from those of a sterically purer polymer. The presence of a small amount of very high-molecular-weight block polymers increases both the elongation and the tensile strength of the polymer.

Below are reported some data of the crude polymerization products, which are considered to have the greatest practical interest in the manufacturing of cheaper products. They concern those products that in their crude state, before fractionation, already exhibit satisfactory technical properties for their practical applications.

One of the possible applications of crystalline polymers is in the production of textiles. Before the discovery of these polymers, one thought that macromolecules which contained groups able to exert strong associations between neighbouring molecules, in order to avoid viscous flows, were necessary to obtain textiles with good mechanical properties.

The high tensile strength of nylon is attributed to the forces of association caused by hydrogen bonding. In other cases, where no such a bond can exist, such as in Terylene, an associative action between the chains is attributed to the presence of polar groups.

After the recent discovery of isotactic polymers, we found that synthetic fibres could be obtained with a very high tenacity, which corresponded to that of the best known synthetic fibres, with the use of polyolefins, where neither hydrogen bondings nor polar groups exist. However, in the case of polyolefins it was necessary that the polymers had a very high molecular weight and a perfectly linear structure. In the case of Nylon, where the associative forces of the

TABLE 6. MECHANICAL PROPERTIES OF POLYPROPYLENE FIBRE PR 56 WITH A RATHER LOW MOLECULAR WEIGHT: $[\eta] = 1$

Tenacity (20°C, 65% relative humidity)	6–7 g/denier
Wet tenacity (20°C in water)	6–7 g/denier
Elongation at break (20°C, 65% relative humidity)	30–40%
Elongation at break (20°C in water)	30–40%
Average stiffness	17 g/denier
Initial modulus	35–45 g/denier
Elactic recovery	100% at 70% of elongation
Shrinkage at 100°C	1–2%

hydrogen bonding are 5000–6000 cal, it is possible to obtain fibres with good mechanical resistance, even with a molecular weight of 10,000–20,000. On the contrary, in the case of isotactic poly-α-olefins, where the associative forces are weak van der Waals' forces between the CH_3 and CH_2 groups (of the order of one thousand calories), if one wants to obtain fibres with very high tenacity, one must use very high-molecular-weight macromolecules, i.e. of the order of 40,000–50,000 for polypropylene, corresponding to about 1000 monomeric units.

It is of interest to observe that polypropylene fibres exhibit a much higher tensile and elastic strength than those of the best types of linear polyethylene and polymethylenes. As a matter of fact, it is possible to obtain isotactic polypropylene fibres with a tensile strength

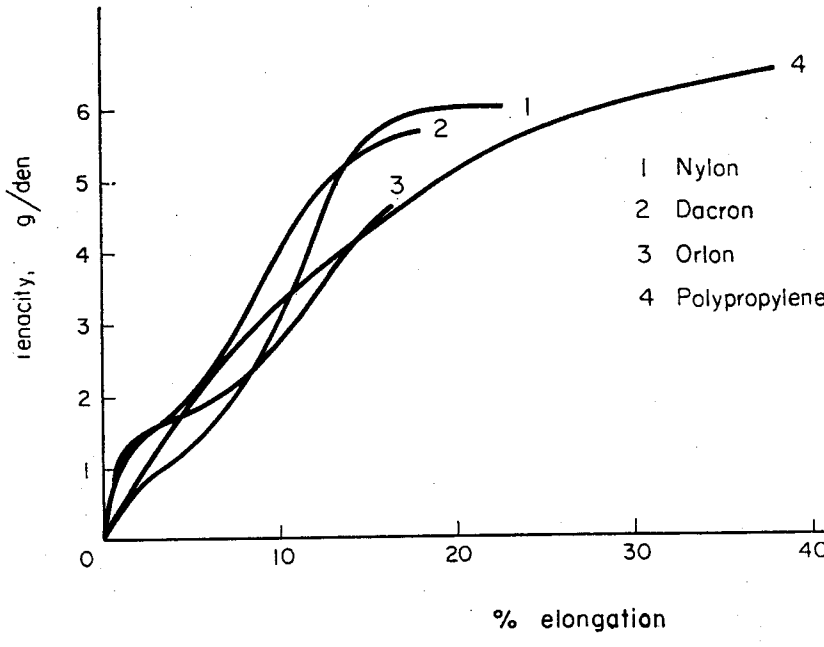


FIG. 22. Stress–strain diagram of some synthetic fibres.

of the order of 6 to 8 g/denier and with very high reversible flows. Polypropylene fibres possess the lowest density known (0·91–0·92). They can be melt-spun without solvents and plasticizers, using spinning methods similar to those of Nylon. The low melting temperature (176°C for the completely isotactic polymer, and 165–170°C for the crude polymers) makes the spinning process much easier.

Polypropylene fibres possess very good electric and thermal insulating properties, and also very good mechanical properties — in particular a high capacity to adsorb a great amount of energy of deformation. Moreover, propylene as a raw material is available in very large quantities and at a very low cost. Nowadays, no monomer could be available at a lower price than that of propylene (about 3 cents, U.S. currency, per pound).

The polymerization yields are high when the monomer is very pure. The crude polymer can be directly spun after a simple removal of traces of catalyst. Table 6 shows the main mechanical properties of polypropylene fibres, while Fig. 22 shows a comparison with other synthetic fibres.

STEREOISOMERIC POLYMERS OF DIOLEFINS

Stereospecific polymerization processes are of particularly great interest in the field of aliphatic polydiolefins.

From a practical point of view, the most interesting properties of polydiolefins are the visco-elastic ones, which are mostly influenced by the stereoisomerism phenomena present in the polymer main chain.

There exists in nature two polymers of isoprene with a unitary steric structure, namely guttapercha and Hevea rubber. Before 1953 all the synthetic polymers of diolefins possessed disordered and irregular structures, which were due either to the presence of both types of 1,4- or 1,2-enchainment, or to the *cis*- and *trans*-olefinic geometric stereoisomerism, or even to that caused by the different configurations of the tertiary carbon atoms. These structural irregularities are the cause for the lower properties exhibited by the synthetic rubbers.

By operating with high charges of finely dispersed substances, such as carbon black, it was possible to improve the hardness and the tensile strength of the old synthetic rubbers, but it would deteriorate their elastic hysteresis. In the case of tires, the old synthetic rubbers adsorbed, in an irreversible way, a great amount of the energy of

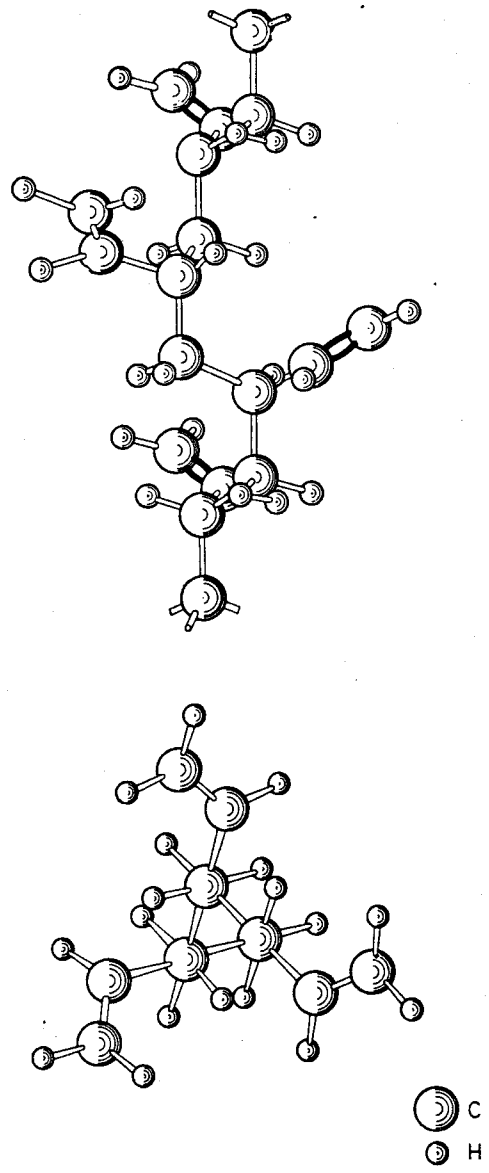


FIG. 23. Chain configuration of isotactic 1,2-polybutadiene.

deformation ; in fact in their use they get warmer than natural rubbers, and are not suitable for the manufacture of frame tires requiring considerable thickness.

The stereospecific procedures have allowed us to obtain two polymers of butadiene with 1,4-enchainment *(cis-* and *trans-)* and two others with 1,2-enchainment (isotactic and syndiotactic) in their crystalline state. Amorphous polymers with 1,4- and 1,2-enchainment were also obtained. Each crystalline polymer possesses a typical crystalline structure and characteristic physical properties.[11, 13]

The amorphous 1,4-polymers show a very low hysteresis to elastic deformations, which is lower than that of the 1,2-polymers.

Some of the properties of some crystalline stereoisomeric polymers of butadiene, which were determined by us, are indicated in Table 7 and in Figs. 23–26.

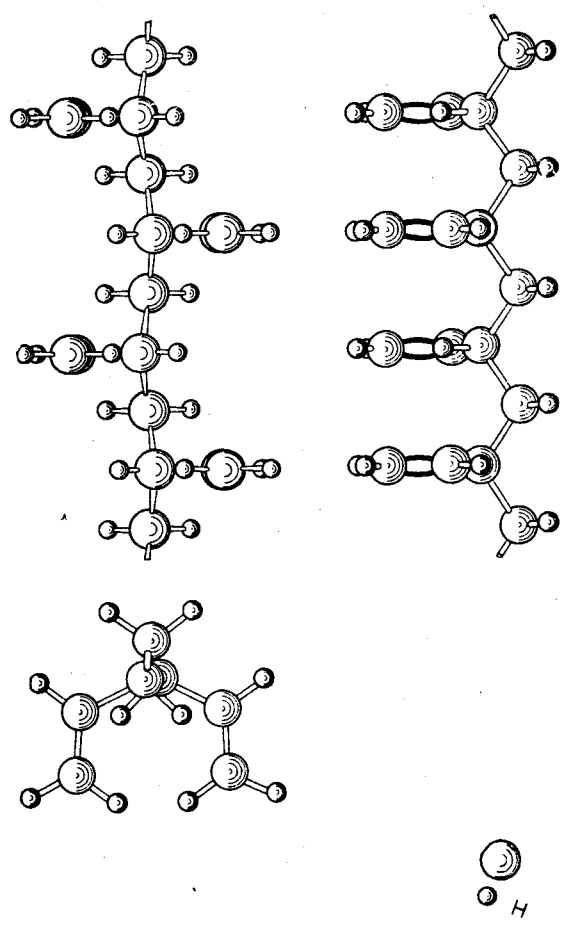


FIG. 24. Chain configuration of syndiotactic 1,2-polybutadiene.

The melting temperature of *cis*-1,4-polybutadiene is not indicated, because it is extremely difficult to obtain this product in the pure state.

We have also obtained crystalline polymers from other diolefins (isoprene, piperylene, etc.). The lattice structure of the crystalline 1,4-stereoisomeric polymers of isoprene is identical with that of natural products.

The synthesis of polymers containing a high content of *trans*-1,4 and *cis*-1,4-monomer units, with properties similar to those of gutta-percha and of natural rubber, had already been announced in the United States, in 1955.[9, 10] It is of interest that both in Europe and in the United States, at almost the same time and using different methods, stereoisomeric polymers of diolefins having a structure very similar to that of the natural ones were obtained.

We have determined the lattice constant and in particular the chain configuration in the crystals of a great number of new polymers. Isotactic 1,2-polybutadiene in the crystalline state exhibits a helix chain structure, similar to other isotactic polymers.[6] In fact, it can be considered as a vinyl polymer, since the double bonds, which are

left after the polymerization, are still present in the side chains. Its main chain shows a structure, which is practically identical with that of isotactic polybutene,[20] where, at times, its side chains have ethyl groups instead of vinyl groups.

Two types of helices exist: "right-handed" and "left–handed". They occupy well-determined positions in the crystalline lattice of the polymer, but in any position the two anticlined chains are statistically distributed.

The structure of syndiotactic 1,2-polybutadiene is quite different.[7] It represents the first case of a synthetic polymer in which monomer units, of opposite steric configuration, alternate in a regular fashion. In this case, the main chain assumes an almost planar shape. Each monomer unit can be placed in such a shielding position with respect to its neighbour of opposite configuration, only by a translation along the chain axis of $1/2c$.

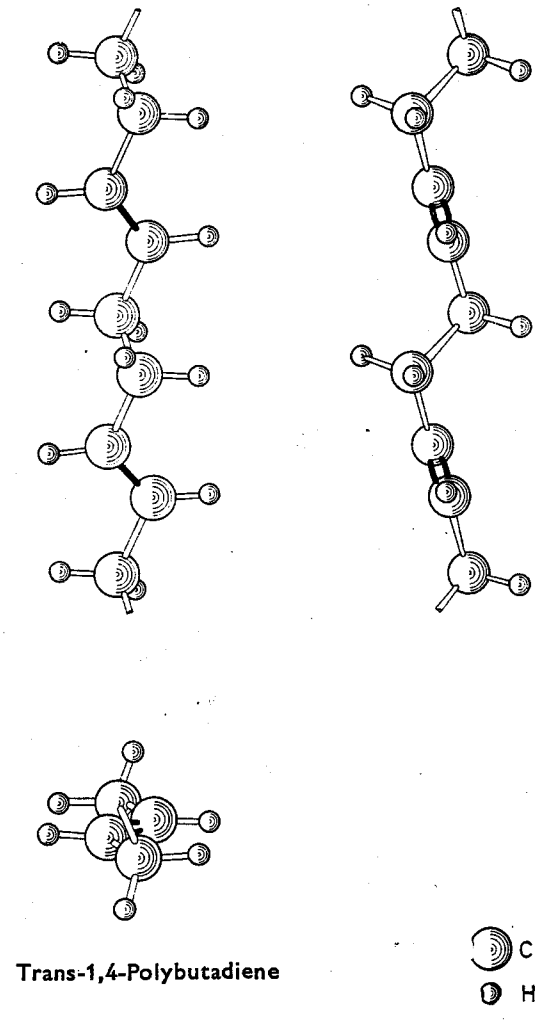


FIG. 25. Chain configuration of *trans*-1,4-polybutadiene.

TABLE 7. X-RAY DATA OF CRYSTALLINE STEREOISOMERIC POLYBUTADIENES

Polymer	*Space-group and symmetry*	*No. of monomeric units per unit cell*	*Dimensions of the unit cells (Å)*			α	β	γ	*Density*	*Melting point by X-rays*
			a	*b*	chain axis *c*					
trans-1,4	(pseudo-hexagonal)	(1)	(4·54 Å)		4·9 Å				1·02	>140°C
cis-1,4	*C*2/*c* (monoclinic)	4	4·60	9·50	8·60	90°	109°	90°	1·01	*
syndiotactic-1,2	*Pacm* (rhombic)	4	10·98	6·60	5·14	90°	90°	90°	0·96	>155°C
isotactic-1,2	*R*3*c* (hexagonal)	18	17·3	17·3	6·50	90°	90°	120°	0·96	>125°C

* The melting temperature depends on the purity and on the stress of the samples.

Figure 25 shows the chain structure of *trans*-1,4-polybutadiene. Each monomer unit contains a double bond and possesses a symmetry centre, which is contained in the plane inclined toward the chain axis. The principle of maximum separation of the bonds, when applied also to the carbon atom adjacent to a double bond, justifies the orientation of the C—C bond, which stands at a 55° angle with respect to the plane containing the monomer unit.

The structure of *cis*-1,4-polybutadiene is characterized by an identity period of two monomer units. These are so placed to allow their mutual interchangeability, with a displacement of $1/2c$, accompanied by a mirror reflection (analogous to what happens with the syndiotactic polymers). The chain segment, corresponding to the identity period, has a symmetry centre and, consequently, only one type of chain in the lattice.

A considerable amount of work has been done in the field of copolymers, to obtain homogeneous products, which show various and interesting possibilities.[26]

With regard to diolefin polymers, it is possible to obtain amorphous copolymers of sterically different monomeric units and stereoblock polymers.

Obviously, crystalline high-melting polydiolefins, in the pure state at room temperature, are not rubbers as they are commonly understood. However, they tend to become real rubbers at high temperatures or when their crystallinity is greatly reduced.

Better elastic properties are observed when the flexibility of the main chain, containing unsaturated bonds (like the one of 1,4-polydiolefins), is further increased by low melting temperatures and fusion entropies of the crystals.

The field of rubbers with high elasticity and low elastic hysteresis at room temperature, is still confined to the field of polydiolefins. In the field of synthetic rubbers, the application of stereospecific polymerizations to the synthesis of *cis*-1,4-polyisoprene, having the same structure as natural rubber, represents an important advance in the obtainment of high-quality elastic rubbers.

Even though the U.S. price of isoprene should not exceed by more than 5 or 6 cents per pound the price of butadiene, and though it seems also that an industrial production of *cis*-1,4-polyisoprene is foreseen in Russia, it is believed that *cis*-1,4-polyisoprene will not be the only solution to the problem of synthetic production of high-quality rubbers.

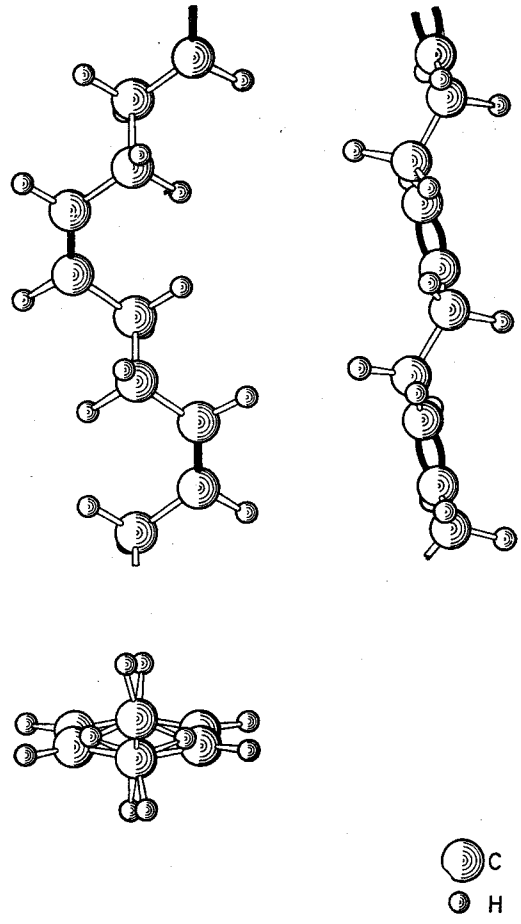


Fig. 26. Chain configuration of *cis*-1,4-polybutadiene.

The great difficulty, which prevented the production of artificial macromolecules with an ordered structure like the natural polymers, was the lack of simple methods for introducing regularly enchained stereoisomeric units in macromolecules. This difficulty has now been overcome, at least in the field of hydrocarbon polymers, by the discovery of stereospecific processes.

A number of chemists are at present working on the improvement of the stereospecific processes and their application to other classes of monomers.

The synthesis of crystalline, high-melting oxygenated, chlorinated and nitrogenous vinyl polymers (polyvinyl chloride, polyacrylonitrile, polyvinylether, and polyvinylester, etc.) will be the next in line for the use of stereospecific processes. Such a task will certainly bring interesting results in the field of polymer science.

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25

CRYSTALLINE STRUCTURE OF ISOTACTIC POLYPROPYLENE

by G. NATTA, P. CORRADINI and M. CESARI

(15 Dec. 1956)
[*Rend. Accad. Naz. Lincei* (8) **21**, 365 (1956)]

ABSTRACT

The complete crystal structure of isotactic polypropylene is described here for the first time. The unit cell is monoclinic with constants: $a = 6{\cdot}65$ Å, $b = 20{\cdot}96$ Å, $c = 6{\cdot}50$ Å, $\beta = 99°20''$, space-group $= C2/c$ It is confirmed that the threefold helix symmetry of the chains present in the lattice possesses a mode of translation of two by two on the plane of symmetry. The model of the packing is similar to that already found for isotactic polybutene-1, but it differs from it because the chain symmetry is not maintained in the lattice.

At the resolution level of the structure presented, the agreement between the calculated and observed structure factors is already satisfactory and is shown for the equatorial reflections and for the reflections of the first and second layer lines.

26

QUANTITATIVE DETERMINATION OF THE CRYSTALLINITY OF POLYPROPYLENE

by G. NATTA, P. CORRADINI and M. CESARI

(15 Dec. 1956)
[*Rend. Accad. Naz. Lincei* (8) **22,** 11 (1957)]

ABSTRACT

A method for the quantitative determination of the degree of crystallinity of polypropylene, based on X-ray methods, is proposed here. The percent crystallinity obtained from the correlation of several examined crystals, may approximately be determined by the formula

$$\text{per cent cryst.} = \frac{I_c}{I_c + 0{\cdot}9\, I_a}$$

where I_c is the diffracted intensity by the crystalline part, and I_a is the diffracted intensity by the amorphous part in the angular interval ranging from 10 to 25° (Cu$K\alpha$) ; this latter intensity is corrected for the usual angular factors. The agreement between the calculated and the found degrees of crystallinity in some series of mixtures, for values of crystallinity between 10 and 80 per cent is satisfactory.

27

THE NATURE OF SOME SOLUBLE CATALYSTS FOR LOW-PRESSURE ETHYLENE POLYMERIZATION

by G. NATTA, P. PINO, G. MAZZANTI, U. GIANNINI, E. MANTICA, and M. PERALDO

(19 Dec. 1956)

[*Chimica e Industria* **39**, 19 (1957)]

Although the Ziegler process for the polymerization of ethylene[1] has been largely investigated,[2] the nature of the catalytic agents obtained by reacting a metallorganic compound with a transition metal compound is still obscure.

Recently Nenitzescu and others[3] have described some ethylene polymerization experiments carried out by catalysts prepared from $TiCl_4$ and sodium alkyls, zinc alkyls, or aluminum alkyls. They concluded that the catalyst is a titanium organic compound, but Ziegler[4] has pointed out that the constitution of the new catalysts is much more complex than that postulated by the Rumanian authors.

Most of the Ziegler catalysts for ethylene polymerization are insoluble in the reaction medium and largely change their composition and activity by ageing. Therefore they are difficult to investigate.

Recently, soluble catalysts for the low-pressure ethylene polymerization have been found[5] which are less active than the best heterogeneous catalysts, but which are much more suitable for basic research on the chemical nature of the catalysts.

We have investigated the soluble catalytic system obtained from organo-aluminium compounds and Ti compounds in which the Ti atom is bound to two cyclopentadienyl groups, and the following results have been obtained (Table 1).

TABLE 1[a]

Expt.	Catalyst				Polymerization conditions				Reaction time (hr)	Polyethylene obtained(g)	CCl_4 extractable fraction (%)
	Titanium compound	mole	Added organometallic compound	mole	Solvent	cm^3	Temp. (°C)	Pressure (atm)			
I	$(C_5H_5)_2TiCl_2Al(C_2H_5)_2$	0·018	—	—	heptane	40	95	40	15	8·4	30
II	$Ti(C_5H_5)_2Cl$	0·025	$Al(C_2H_5)_3$	0·05	heptane	200	80–90	35–45	16	23	n. d.
III[b]	$TiCl_4$	0·025	$Al(C_6H_5)_3 \cdot (C_2H_5)_2O$	0·025	benzene	250	60–70	20–30	2	30	16
IV[b]	$Ti(C_5H_5)_2Cl_2$	0·025	$Al(C_6H_5)_3 \cdot (C_2H_5)_2O$	0·05	benzene	100	100–110	25–35	40	8	55
V[c]	$Ti(C_5H_5)_2(C_6H_5)_2$	0·009	—	—	benzene	130	150	50–60	24	—	—
VI[d]	$Ti(C_5H_5)_2(C_6H_5)_2$	0·006	$Al(C_2H_5)_3$	0·05	benzene	120	70–80	20–25	4	10	21
VII[b]	$Ti(C_5H_5)_2(C_6H_5)_2$	0·009	$Al(C_6H_5)_3 \cdot (C_2H_5)_2O$	0·02	benzene	120	70–80	20–21	5	15	7
VIII[c]	—	—	$Al(C_6H_5)_3 \cdot (C_2H_5)_2O$	0·067	benzene	75	150	180–200	20	—	—

[a] Phenyl groups have been recognized by the 14·36 μ band. The presence of a band at 13·45 μ accompanying the 14·36μ band suggests that the phenyl groups are bound to $-CH_2-$ groups, and therefore are terminal groups.

[b] Phenyl groups present in the polymer.

[c] No polymer.

[d] The polymer does not contain phenyl groups.

(1) By reacting $Al(C_2H_5)_3$ with $Ti(C_5H_5)_2Cl_2$ a crystalline complex $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$[6] has been isolated which is soluble in hydrocarbons and slowly polymerizes ethylene to high polymers at low temperature and pressure (Expt. I). The same results have been obtained by using the product of the reaction between a solution of $Al(C_2H_5)_3$ in n-heptane and $Ti(C_5H_5)_2Cl_2$ without separating the complex from the reaction mixture (Expt. II).

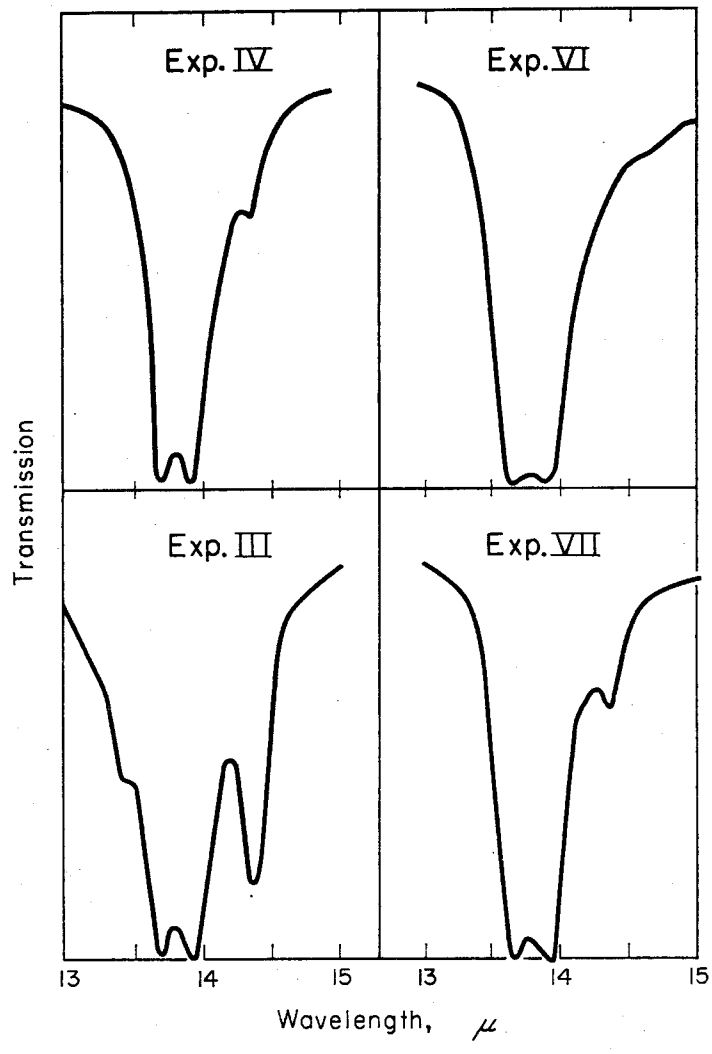


FIG. 1.

(2) After the reaction between $Ti(C_5H_5)_2Cl_2$ and AlR_3, the cyclopentadienyl groups are still bound to the titanium atom.

(3) By reacting $Ti(C_5H_5)_2Cl_2$ with $Al(C_6H_5)_3.(C_2H_5)_2O$ a catalyst has been obtained which polymerizes ethylene. In the polymer $—C_6H_5$ terminal groups have been detected by I.R. spectra (Fig. 1) (Expt. IV).

The same terminal groups have been observed by the I.R. method (Fig. 1) in the polyethylene produced from the heterogenous catalyst obtained by reacting $TiCl_4$ with $Al(C_6H_5)_3 \cdot (C_2H_5)_2O$ (Expt. III).

(4) No polyethylene has been obtained using $Al(C_6H_5)_3 \cdot (C_2H_5)_2O$ alone as catalyst (Expt VIII).

(5) No polyethylene has been obtained using $Ti(C_5H_5)_2$-$(C_6H_5)_2$ as catalyst (Expt. V).

(6) By reacting $Ti(C_5H_5)_2(C_6H_5)_2$ with $Al(C_2H_5)_3$ a catalyst has been obtained which polymerizes ethylene. No phenyl groups have been detected by I.R. analysis (Fig. 1) in the polymer (Expt. VI).

(7) By reacting $Ti(C_5H_5)_2(C_6H_5)_2$ with $Al(C_6H_5)_3 \cdot (C_2H_5)_2O$ a catalyst has been obtained which polymerizes ethylene. The polymer obtained contains terminal $-C_6H_5$ groups detected by I.R. analysis (Fig. 1) (Expt. VII).

From these results, the following conclusions can be drawn.

(1) A crystallizable bimetallic complex has been synthesized which is a catalyst for the polymerization of ethylene.

(2) Catalytically active complexes of a similar type can be reasonably hypothesized although they have not been isolated in Experiments III, IV, VI, and VII.

(3) Experiments III and IV show that the $(C_5H_5)_2TiCl_2$-AlR_3 catalysts polymerize ethylene at low pressure like $TiCl_4$-AlR_3, but they are less active catalysts and yield polymers having a lower molecular weight.

(4) In opposition to the Nenitzescu hypothesis, a Ti — C bond present in a compound containing only one metallic atom, like pure $(C_5H_5)_2Ti(C_6H_5)_2$, seems not to be able to polymerize ethylene at low pressure.

(5) From Experiments III, IV, VI, and VII it is seen that the organic groups initially bound to the aluminium, but not the groups bound to the titanium, appear as terminal groups in the polymer. This suggests the hypothesis that in the complex containing Ti and Al the polymerization starts at the Al—C bond.

On the basis of the above results, obtained using soluble catalysts containing the $Ti(C_5H_5)_2$ groups, we suggest that the Ziegler-type polymerization catalysts are complexes containing organometallic bonds and more than one metal atom.

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28

ISOPHASIC DILATOMETRIC TRANSITIONS OF SOME POLY-α-OLEFINS

by G. NATTA, F. DANUSSO and G. MORAGLIO

(11 Jan. 1957)

[*J. Polymer Sci.* **25,** 119 (1957)]

In a previous communication[1] we showed that it is possible to attribute to the polyethylene a dilatometrically determined (apparent) second-order transition temperature around —21°C. Different transition data for other polyolefins have been recently published.[2,3] Since our data under reference 2 were given as approximate, we wish to report herewith more consistent values we have obtained for the dilatometric isophasic transition temperature of polymers of the first normal α-olefins.

The transition temperatures were determined with capillary dilatometers and a procedure as previously described.[1] The isophasic transition temperature was always taken as that corresponding to the intersection obtained by prolonging the two straight parts of the V_{sp}–T curve. The temperature range explored was in each case about —70° to 0°C. The samples were prepared by melting *in vacuo* and then slow cooling as in the case of polyethylene.[1]

The values of the transition temperatures are listed in Table 1. Essentially the same results are given by both completely amorphous and highly crystalline samples, as well as samples of high and low molecular weight. This is in agreement with the fact that, as already noted,[4,5] in the molten or dilute solution state the properties of isotactic and non-isotactic polymers are the same or differ very little.

In Fig. 1 the average values of the transition temperatures of the different polymers studied are plotted against the number of carbon atoms of the lateral chain. The transition temperature decreases from polyethylene to a minimum value for polypentene and then increases

TABLE I

Sample	$[\eta]$ *(100 cm³ g⁻¹)*	*Crystallinity, %*[a]	*Transition temperature °C*	
			Experimental[b]	*Mean value*
Polypropylene				
A	0·11[c]	amorphous	—34·5	—35
			—35	
B	0·28[c]	80	—35·5	
			—34·5	
			—36	
			—34	
			—34·5	
			—35	
C	0·43[c]	65	—37	
			—37	
D	0·65[c]	50	—34	
			—39	
			—35	
E	0·78[c]	45	—35·5	
			—33·5	
F	0·86[c]	amorphous	—35	
			—36·5	
G	0·96[c]	35	—37	
			—35	
H	2·82[c]	85	—34·5	
I	3·47[c]	75	—36	
			—35	
Polybutene				
J	0·76[c]	amorphous	—48	—45
			—43	
K	2·00[c]	60	—45	
			—44	
Polypentene				
L	—	amorphous	—53	—53
			—51·5	
M	2·65[d]	crystalline	—53	
			—52·5	
			—53	
N	2·96[d]	crystalline	—52	
			—53·5	
Polyhexene				
O	1·99[d]	amorphous[e]	—49	—50
			—51	
P	1·99[d]	amorphous[e]	—51	
			—50	

[a] X-ray determinations, approximate values.
[b] Independent determinations with constant rate of heating or cooling (5°/10 min).
[c] In tetralin at 135°C after annealing by fusion *in vacuo*.
[d] In toluene at 30°C after annealing to a moderate temperature.
[e] At room temperature.

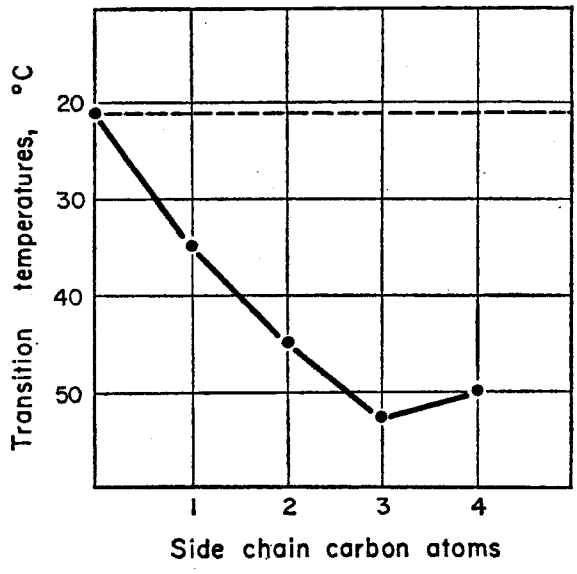


FIG. 1.

again for polyhexene. Therefore, in the amorphous part of the polymer, short side-chains cause a plasticizing effect with regard to the structure corresponding to polyethylene.

The lowering of the dilatometric transition from polyethylene to polypropylene is appreciable, considering that crystal melting temperature of the latter is considerably higher than that of the former. Determinations carried out by us on polypropylenes of high crystallinity (about 85 per cent) have in fact given a crystal melting temperature up to 176°C, while polyethylene samples prepared by us, having a very linear structure without methyl groups detectable by infrared analysis, have given a melting temperature up to 138–139°C. This statement evidently does not support the belief that the ratio of the values of the crystal melting temperature and the glass transition temperature should be constant.

The high crystal melting temperature of polypropylene with regard to polyethylene is not surprising, considering the different arrangement of the chains in the crystal lattice (planar zigzag for polyethylene and helical for polypropylene). On the other hand, the isophasic volume transition considered here is known to be typical of the amorphous (disordered) phase.

The effect of internal plasticizing of the short side-chains is most marked in the case of polypentene, while in polyhexene the cumulative structural effect of the linear lateral chains begins to prevail. In Fig. 1 a horizontal dashed line is drawn corresponding to the value of poly-

ethylene, which also must represent the asymptotic value of the isophasic volume transition temperatures of polyolefins having very long lateral chains.*

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*In this work the transition temperatures were determined on polypropylenes and polybutenes, derived from some investigations on the properties of stereospecific catalysts; these polymer samples later resulted in defective composition. Further measurements on selected samples have permitted us to point out the most reliable values of —12° and —37°C for polypropylene and polybutene.

Consequently the transition temperatures reach a maximum value in correspondence to polypropylene. *Editors Note.*

29

ISOTACTIC POLYMERS*

by G. NATTA

(4 Feb. 1957)

[*Chem. and Ind.* **47**, 1520 (1957)]

First of all I would like to thank the Society of Chemical Industry, its Plastics and Polymer Group, and its London Section for inviting me to lecture on my work on isotactic polymers. It is a great honour for me to be asked to speak on crystalline poly-α-olefins in the country in which the first crystalline polymer of olefins—polyethylene—was discovered.

Other crystalline olefin polymers, belonging to the same family of ethylene, such as polypropylene and polybutene, will shortly be produced commercially and will take their place beside polythene in large-scale industrial production. This is the fruit of a great deal of research carried out in my University laboratory with the help of one of the largest chemical combines of continental Europe, the Montecatini Company.[1]

The subject being very vast, I will limit my lecture here to a short account of the new types of stereospecific catalysis which have permitted us to obtain new classes of stereoisomeric polymers: isotactic polymers, syndiotactic polymers and other new diolefin stereoisomers (for example, the four crystalline butadiene stereoisomers); I will then describe some of the properties of these new polymers.

Before speaking of stereospecific catalysis, I would like to say a few words on the stereoisomerism in the field of macromolecules. The importance of the new processes lies in the possibility of obtaining macromolecules containing a given steric configuration, which are, in general,

*Read before a joint meeting of the Plastics and Polymer Group and the London Section of the Society of Chemical Industry, Belgrave Square, London, on 4 February 1957.

characterized by a high crystallinity. Before the discovery of stereospecific polymerization processes, only a relatively limited number of crystalline synthetic hydrocarbon polymers were known. Those obtained by polyaddition were derived from highly symmetric monomers such as ethylene and vinylidene monomers (isobutene).

All the synthetic polymers of α-olefins and of the vinyl monomers in general, and all the synthetic polymers of diolefins were generally amorphous. The lack of crystallinity depends on the random succession of their constituent units, having different steric structure.[2] Only the molecules of some typical natural polymers, and not those of vinyl polymers, correspond to an architectural model with a predetermined steric arrangement.

To obtain crystalline polymers starting from vinyl monomers or from diolefins, the monomer units should be arranged regularly during polymerization into pre-established and not random configurations, and this was unobtainable synthetically before the discovery of stereoselective or stereospecific polymerization processes.

There are different types of stereoisomers in organic chemistry. The two best-known typical cases are: geometric stereoisomerism, due to *cis* and *trans* configuration (for example, in compounds containing a double bond), and optical stereoisomerism, generally due to the presence of carbon atoms which are linked to four different substituents. Both these cases are important in macromolecular chemistry.

A crystalline polymer can be obtained only when all the monomer units belonging to a long chain have the same configuration, or when opposite configurations follow one another in an orderly way. On the contrary, amorphous polymers are obtained when different configurations, for instance, *cis* and *trans*, or those "left" or "right", follow one another in a disorderly manner.

The new crystalline α-olefin polymers, which we have investigated, and the polypropylene oxides obtained by Price[3] are examples of synthetic stereoisomeric polymers in which the crystallinity is due to the order assumed by the tertiary carbon atom configurations in the chain of each molecule. In the case of polypropylene oxide (Figure 1 of paper 24) and in α-amino acid condensation products, the tertiary carbon atoms are always asymmetric, even in the monomer before polymerization. In the case of poly-α-olefins, they become asymmetric only after polymerization, when the two parts of the chain on the sides of the tertiary atom have a different structure or length.

Figure 1 of paper 19 illustrates molecules, supposedly placed on a

plane, of α-olefin stereoisomeric polymers: the isotactic polymers, in which the tertiary atoms show the same steric configuration, syndiotactic polymers, in which each tertiary atom shows a steric configuration opposite to that of neighbouring tertiary atoms in the chain, atactic polymers, in which the tertiary carbon atoms have configurations randomly distributed in the chain.

In the field of diolefin polymers other stereoisomeric phenomena of a geometric nature appear. Natural polyisoprene stereoisomers with 1,4 linkage are well known, and of these natural rubber has a nearly complete *cis* structure (97 per cent); gutta-percha, instead, is *trans*. Other new stereoisomers of diolefins with 1,2 linkage, not existing in nature, have been synthesized by us in the last few years.[4]

The polymerization processes previously used, most of them using free radicals, are unable to produce chains having a regular steric structure. Only during the last three years, new processes, employing stereospecific catalysts, permitted us to produce different types of stereo-unitary polydiolefins, and also synthetic macromolecules having the same structure as natural rubber and gutta-percha.[5]

In Figure 5 of paper 19, pure polybutadiene isomers, with *cis*-1,4, *trans*-1,4, isotactic-1,2 and syndiotactic-1,2 linkages, which we have prepared synthetically in my laboratory, are shown. The lattice structure has been determined by us for the different stereoisomers.[4, 6]

Isoprene should give, in theory, by polymerization, three types of linkage, namely 1,4, 1,2 and 3,4, each in different stereoisomeric forms. Six stereoisomers can have regular steric structure: two with 1,4 linkage, one *cis*, the other *trans*; two with 3,4 linkage, and two with 1,2 linkage, respectively isotactic and syndiotactic. Only the first two exist in nature. Besides that, two types of amorphous atactic stereoisomers (with 1,2 and 3,4 linkage) and the amorphous 1,4 stereoisomers with random *cis* and *trans* configurations are possible. The two stereoisomers which exist in nature, have now been prepared synthetically in addition to other two new polymers.

The most interesting physical and technological properties of isotactic polymers of α-olefins in the field of plastics and textile fibres, and of some new stereoisomers of diolefins are due to the great linearity of the chain and to the crystallinity of these polymers.

Atactic stereoisomers of α-olefins cannot crystallize and have completely different properties. Their practical interest is limited to very high molecular weight products, which could give particular types of elastomers.

The properties connected with the crystallinity (such as the configuration of the chain in the crystalline state, the relative position of the chains in the crystals, the degree of freedom of rotation of lateral groups, the rate of crystallization, the size, the distribution and the orientation of the crystals, etc.) determine the most interesting technical characteristics of these polymers, namely hardness; the mechanical properties like modulus, ultimate tensile strength and elasticity; the range of the melting temperatures; the moulding properties; and the ability to give high tenacity fibres.

The crystalline structure will be described before discussing the technical properties of these isotactic polymers. Isotactic polypropylene, polystyrene, polybutene, etc., having asymmetric carbon atom sequences with the same configuration, present a characteristic structure. The principle that in a crystal monomer units of a macromolecule must have equivalent positions, referred to the axis of a chain, imposes a helical configuration to the main chain, as in some crystalline proteins. Polypropylene, for instance, has a helical structure with threefold symmetry, which respects the principle of staggered bonds.[7] Polystyrene and the most stable modification of polybutene have an analogous structure, with a small deformation of the angle formed by the linkage of the principal chain (respectively 116° and 114°).[8] Sometimes, steric hindrances may cause the main chain to assume other types of helix structure.

The helix of poly-3-methylbutene-1 has a fourfold symmetry and the helices of α-olefins branched in positions 4 have a sevenfold symmetry. Naturally, in most cases, the symmetry of the chain axis does not correspond to the crystallographic symmetry of the same axis.

The symmetry, the freedom of rotation, the mobility of the side-chain and the steric hindrance have a great influence on the melting temperature of the polymers. Some polymers, having side *iso*propyl or *iso*butyl groups, such as poly-3-methylbutene-1 and poly-4,4-dimethylpentene-1, show very high melting points. Also poly*ortho*-methylstyrene shows a very high melting point (over 300°C).[9]

In isotactic polymers the linkages of the lateral groups with the tertiary carbon atoms of the principal chain are always inclined relatively to the chain axis. In a part of an isotactic chain contained in a crystal all the bonds are inclined in the same sense (isoclined). We can have right-hand and left-hand helices; therefore when we consider the inclination of the lateral groups we find two types of congruent right-handed helices with opposite inclinations (anticlined helices), and two

types of left-handed helices. All four types can be present in the crystals of synthetic polymers which contain racemic mixtures of macromolecules.[7]

In a crystal, two anticlined isomorphous chains occupy about the same space; we consider them capable of being substituted for one another and distributed at random. The symmetry of isotactic synthetic crystals (racemic) agrees with a distribution of helices in such a way that each right helix is facing a left-handed one, and vice versa.

Figures 7 and 9 of paper 24 show how two enantiomorphous chains of isotactic polypropylene and polybutene respectively are associated in a crystal.

CRYSTALLINITY OF ISOTACTIC POLYMERS

Crystallization rate depends on the viscosity of the system which increases with the molecular weight of the polymer. For high molecular weights it is very slow. Even if the crystals are very often smaller than the wavelength of light (in general some hundreds of angström units), the presence of crystallites may, however, be demonstrated by optical methods, as they gather into spherulites, which sometimes are very large, up to a tenth of a millimetre or of the order of a millimetre (polybutene-1). Some very good photographs of spherulites have been taken at the Castellanza laboratories of the Montecatini Company. Figure 12 of paper 29 shows polypropylene spherulites obtained by cooling the melted polymer. In Figure 13 of paper 29 the same spherulites are seen by polarized light.

In certain cases, for example with polybutene-1, the spherulites can be of the order of hundreds and even thousands of microns. Figure 18 of paper 24 shows part of a crystallite examined under the electron microscope in the Novara laboratories of the Montecatini Company.

In the case of polymers having a very low molecular weight it is possible to see crystalline aggregates under the microscope which confirm the symmetry previously seen by X-ray examination.

Isotactic polystyrene aggregates, with a molecular weight of about 10,000, can be seen in Figure 1. Hexagonal lamellae are visible; when these are well oriented they do not seem to be birefringent under polarized light (see also Paper 83).

The formation of spherulites by crystallization of a solution in appropriate solvents is more evident. In this way polybutene spherul-

ites are very well developed. The presence of small quantities of amorphous products of low molecular weight, which reduce the viscosity of the raw polymer and occupy the intercrystalline spaces, facilitates the formation of large spherulites separated one from another and easily distinguishable under the microscope.

STEREOSPECIFIC PROCESSES OF CATALYSIS

In these last few years a great deal of work has been done by us on stereospecific catalysis and a great number and variety of catalysts have been found that can be used to obtain given steric configurations in macromolecules of polyolefins. These catalysts contain compounds of strongly electropositive transition metals having valency inferior to maximum value and act in the presence of organometallic compounds, preferably belonging to the first, second and third group of the periodic system. From the possible combinations of the various transition metals and metal-alkyl compounds which are also highly electropositive (lithium, beryllium, aluminium, magnesium, zinc, etc.) we can obtain a great number and variety of catalysts to which we attribute a polymerization mechanism of anionic type.[10] These catalysts derive from the important research on organometallic compounds carried out by Prof. Ziegler.[11] The numerous catalysts described by Ziegler can be used in ethylene polymerization, but only a few of them, prepared under particular conditions, can be employed practically in polymerizing the higher α-olefins. In general, however, they are not really stereospecific, because they produce complex mixtures containing various mostly atactic, stereoisomers and in certain cases a limited quantity of only partly crystallizable stereoisomers.[12]

Our research has not only established conditions for the polymerization of propylene and other α-olefins (styrene and other aromatic vinyl hydrocarbons) to high molecular weight linear polymers. We have also found really stereoselective catalysts for the production of highly isotactic polymers having high crystallinity, and other catalysts for the production of completely atactic polymers, i.e. completely amorphous.[13]

It is interesting to observe that the completely amorphous products obtained by these new processes differ from the poly-α-olefins previously known. This is due to the fact that the new processes (even when not stereospecific) can produce high molecular weight polymers, which are completely linear, head-to-tail, without long branchings.

In the case of ethylene, polymerization already takes place with

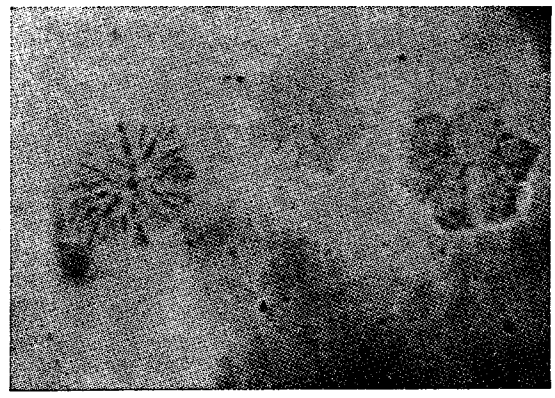


FIG. 1. Isotactic polystyrene aggregates.

aluminium alkyl or lithium alkyl alone, and the addition of small quantitites of transition metal compounds, that give complexes with the organometallic compound, causes the formation of very high polymers.

In order to obtain crystalline polymers from other α-olefins, it is necessary that an asymmetric metal alkyl complex is located on the surface of a solid catalyst and imparts a particular orientation to the reacting monomer units. The monomer inserts itself in the metal alkyl link, polarized in the sense of an electropositive metallic cation and of an electronegative carbon ion ($\overline{CH_2}$). Our recent research on a large class of monomers has enabled us to better understand the nature of these complexes and the cause of their catalytic activity.

One of the most interesting characteristics of some of the highly stereospecific polymerization processes is the simplicity of their kinetic mechanism. Some catalysts obtained from V, Ti, etc., dichloride or trichloride are characterized by the presence of a crystalline support consisting of a lattice in which metal atom layers alternate with chlorine atom layers. The fact that one plane of metal and two of chlorine follow one another along the axis in the crystals explains the easy cleavage of the crystals, which takes place during polymerization as a result of the mechanical strains induced by the growing chains. These catalysts, after an initial settling period, are characterized by a very regular type of kinetics. The catalytic activity remains constant for hundreds of hours provided that the polymer produced does not prevent the diffusion of the monomer towards the surface of the catalyst.[14]

In some laboratory tests employing small quantities of catalyst in the presence of considerable quantities of solvents, thousands of grammes of polymers were obtained for each gramme of solid catalyst and polymerization ended only when the reaction vessel was completely filled by the polymer.

Figures 2–5 show some curves of polymerization rate. The reaction

rate is proportional to the partial pressure of the monomer, to the weight (and therefore to the surface of the solid catalyst) and it is independent of the concentration of metal alkyl compound over a wide concentration interval. The crystallinity of the polymer, its molecular weight, and therefore also the stereospecificity of the catalyst, are practically independent of the quantity of polymer produced if one excludes a brief initial period in which the molecular weight increases. The activation heat is about 12,000–15,000 cal.

The kinetics of polymerization using another type of freshly prepared $TiCl_3$ is given in Fig. 6. In this case, during the settling period the activity is higher.

The study of this and other catalysts obtained by changing the transition metal compounds and the organometallic compounds leads us to attribute to the polymerization an anionic mechanism based on the introduction of a molecule of a monomer through the polarized bond between a metal atom and the growing chain.

This conclusion was reached after a series of experiments which have shown us that:

1. The molecules of the polymer produced at first, contain a terminal group which was bound initially to the organometallic component of the catalyst.[10]

2. Using aluminium triphenyl as a catalyst, a phenyl end group is bound to a tertiary carbon atom of some polymer chains.

3. Using catalysts prepared from titanium di*cyclo*pentadienyldiethyl and aluminium triphenyl in ethylene polymerization, we have observed the presence of phenyl groups in the polymer, whilst they are absent when the polymer is obtained from titanium di*cyclo*pentadienyldiphenyl and aluminium triethyl. Therefore, we think that in the last cases mentioned the growing chain is bound to the aluminium and not to the transition metal.[15]

4. The unsaturated end groups are almost always merely vinylidene groups.[10]

This is in agreement with the hypothesis that the reaction mechanism is of the anionic type. The molecule reacts as if it were polarized in the sense that the CH_2 carbon atom is negative and the CH carbon atom positive, and said molecule settles between the electropositive aluminium atom belonging to a bimetallic complex and the growing chain in which the terminal CH_2 group, bound to the aluminium, is negatively polarized. The most active catalysts for the polymerization of α-olefins seem all to belong to this type.

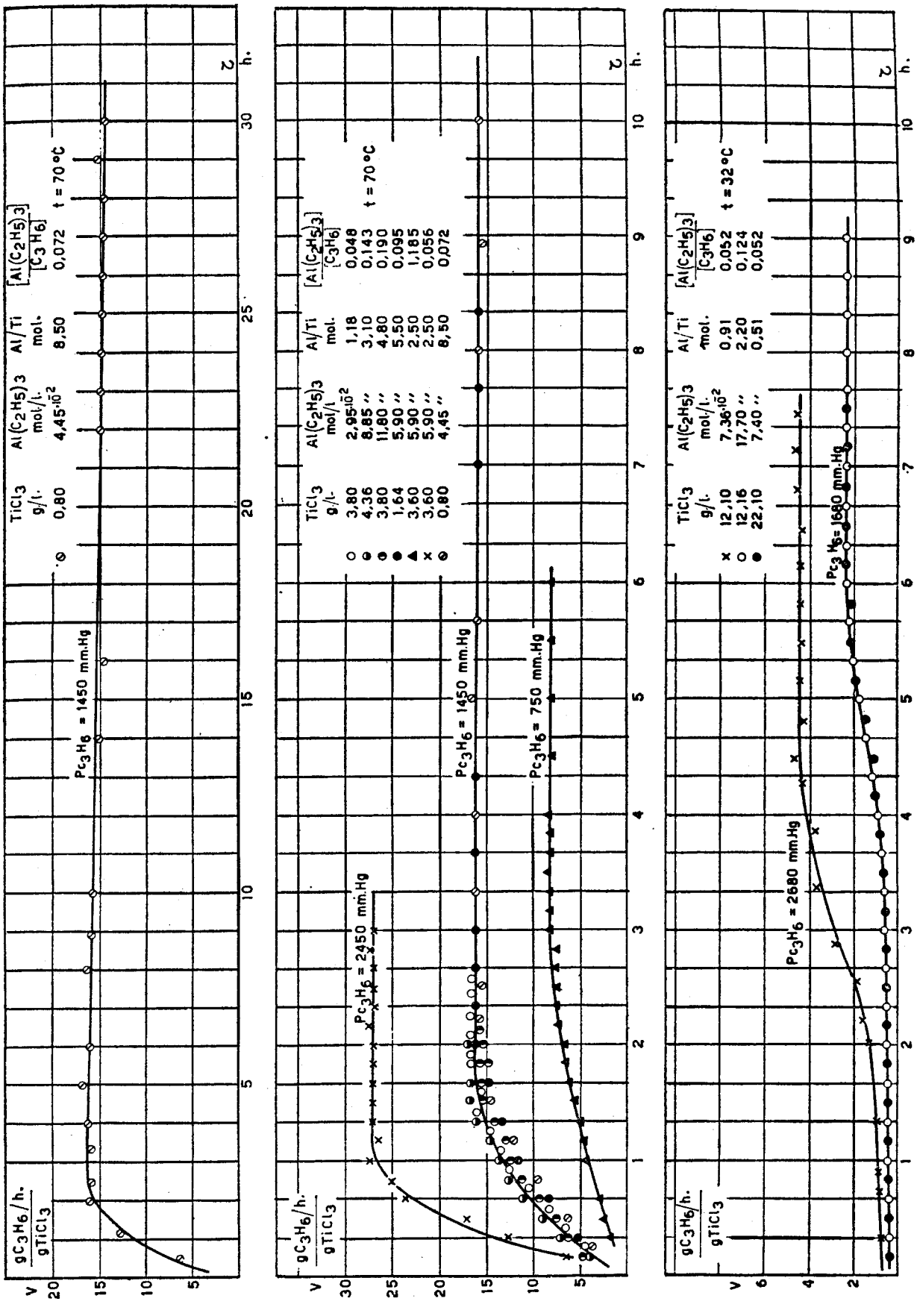


FIG. 2. Rate of propylene polymerization versus time (in hours) for various monomer pressures and catalyst concentrations.

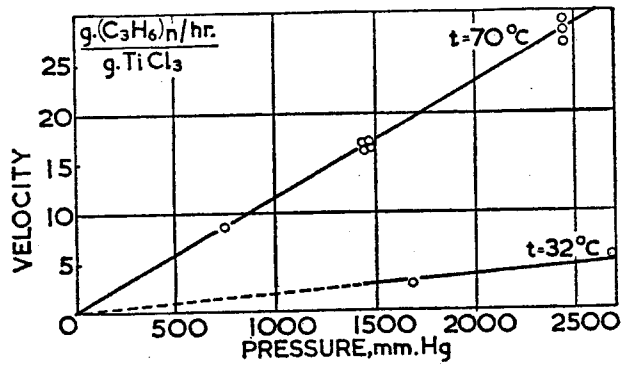


FIG. 3. Rate of propylene polymerization versus monomer pressure—at two temperatures.

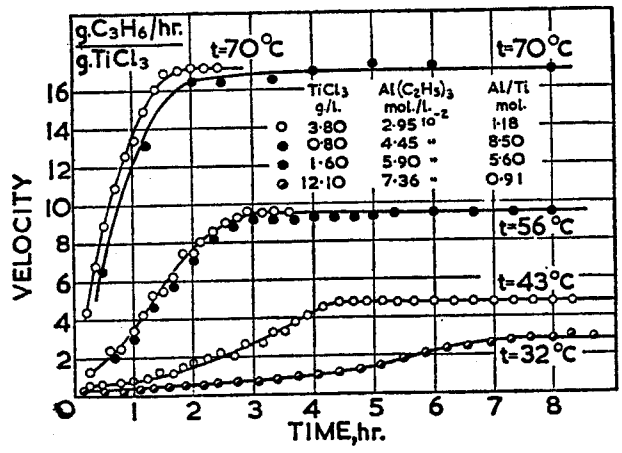


FIG. 4. Rate of propylene polymerization versus time for various catalyst compositions and temperatures.

One of the most important problems was that of molecular weight control and it has been solved by means of several different methods. Hydrogen pressure reduces the molecular weight and produces saturated polymers.

One process based on the use of hydrogen was elaborated independently and nearly at the same time in the U.S. and in Italy—at least, so it would appear from the dates of the patent applications.[16]

Temperature has very little influence on the molecular weight at low temperatures, but its effect is greatly increased over 100°C, at which stereospecificity is also reduced.

Molecular weight increases and stereospecificity decreases the higher the polarizability of the metal alkyl link. The ability to give organometallic complexes of the type described is dependent on the presence of metal cations of small diameter. Catalysts acting with anionic mechanism and containing large diameter metals, for example alkali metals with atomic weight greater than that of lithium, characterized

by atomic radius exceeding 1 Å, cannot give stereospecific catalysts. Organometallic compounds of lithium, beryllium, aluminium, whose metallic ions have a very small radius (less than 0·8 Å), are best used for preparation of catalysts acting stereospecifically with anionic mechanism.

It is interesting to note that the only catalysts having a certain stereospecificity in vinyl ether polymerization and acting with cationic mechanism, are, according to Schildknecht, boron fluoride compounds, and these also contain small diameter atoms. We could demonstrate that crystalline polymers obtained with these catalysts have isotactic structure.[17]

The processes controlling the molecular weight of polymers are of different types:

1. Dissociation into hydride ion and olefin with formation of vinylidene terminal groups.

2. A chain termination process of first order in regard to the concentration of the monomer, which may be considered to be like a chain

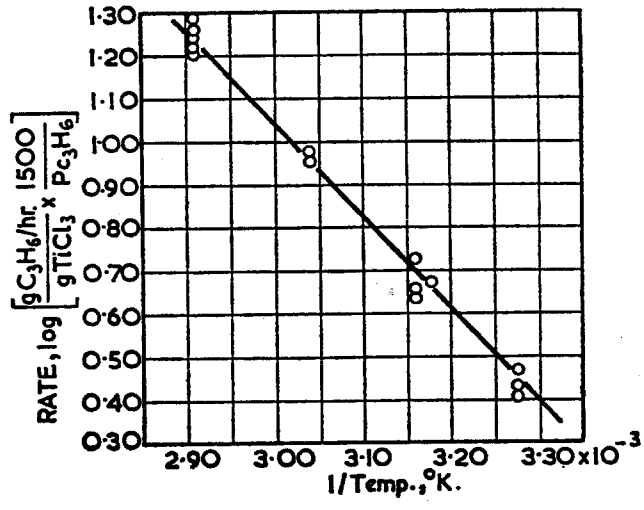


FIG. 5. Arrhenius plot for propylene polymerization.

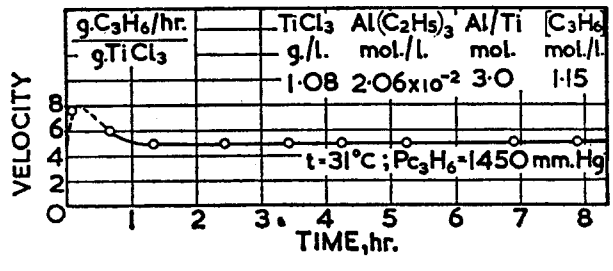


FIG. 6. Rate of propylene polymerization versus time curve for catalyst showing high initial activity.

transfer with monomer. This is the cause of propyl terminal groups in prolonged polymerization of propylene.

3. Chain exchange between dissolved organometallic compounds and catalytic complexes.

The first process predominates only at higher temperatures.

The above-mentioned mechanism does not explain the stereospecificity of catalysts. Catalysts acting in the above way can produce crystalline or amorphous polymers. The cause of the stereospecificity is not to be attributed to the chemical mechanism of polymerization, but to the monomer molecule orientation during polymerization.

One of our first observations in 1954 was that the catalysts obtained from crystalline compounds of transition metals, insoluble in the solvent used, produce crystalline polymers, while dispersed catalysts, not revealing crystallinity under X-rays, produce generally amorphous polymers.[13] The concept of crystallinity must here be extended to the limit of X-ray or infrared sensitivity. X-ray examination in general reveals crystal dimensions over 50 Å. Hexagonal titanium trichloride in crystals having a layer lattice and dimensions microscopically visible (from 1 to 10 microns) produces highly crystalline polymers. Titanium trichloride obtained by reducing one molecule of titanium tetrachloride with one molecule of aluminium triethyl is crystalline by X-rays, but not under the microscope and generally shows a different crystal structure. It is less stereospecific giving only 60 per cent of insoluble polymers in boiling heptane.

The catalyst obtained by reducing titanium tetrachloride with a greater quantity of triethyl aluminium shows lesser crystallinity under X-rays than the trichloride previously described. It is also less stereospecific, giving only 35 to 40 per cent of polymer insoluble in boiling heptane.

Catalysts obtained from chloro-alkoxides are not crystalline, neither are they stereospecific in general.

ATACTIC AND BLOCK POLYMERS

The new polymerization processes have allowed us to produce, using stereospecific catalysts, not only linear crystalline α-olefin polymers having uniform steric structure, but also, using non-stereospecific catalysts, amorphous polymers. These have also a linear main chain without long branching and can be obtained with very high molecular weights.

Perfectly linear aliphatic olefin polymers, having a molecular weight of some hundreds of thousands, were hitherto unknown except for vinylidene monomers. In fact, all the processes previously employed were unsuitable for the production of linear α-olefin polymers. Because of frequent chain transfers during polymerization, these processes produced polymers having, in general, a low molecular weight or else long branched chains.

The comparison between the properties of amorphous α-olefin polymers in the aliphatic series, having a linear structure, which we call atactic, and those of crystalline isotactic polymers emphasizes the enormous influence that stereoisomeric phenomena exercise on the physical properties of macromolecular substances. The visco-elastic properties are more influenced than the others by the regular or irregular steric structure of the chains. So much so that low molecular weight isotactic polymers, composed for example of some dozens of monomer units, are already high melting-point crystalline solids, whereas atactic polymers with the same molecular weight are still liquid. Their viscosity increases with the increase in molecular weight, and when the latter reaches values of some hundreds of thousands, they show the visco-elastic properties of nonvulcanized rubber. They can still be considered as highly viscous liquids, and can be transformed into true elastomers when cross-linkages prevent viscous flow.

High molecular weight polypropylene, polybutene and polyhexene can be made vulcanizable, for example by sulphochlorination, and then vulcanized using polyvalent bases. They yield rubbers with high reversible deformation values. In certain respects, their technical properties seem to be far superior to those of sulphochlorinated polyethylene. Actually, the production of Hypalon (Du Pont sulphochlorinated polyethylene) requires the introduction, in a disorderly manner, of considerable quantities of chlorine (25–40 per cent) in order to destroy the original crystallinity. If, on the contrary, the starting material is an originally amorphous α-olefin polymer (propylene, n-butene, etc.) it is not necessary to use great quantities of chlorine. A small quantity of sulphur, less than 1 per cent, plus a small quantity of chlorine necessary for sulphochlorination, will be sufficient to transform the polymer into a vulcanizable material, and the latter into vulcanized products which generally have elastic properties which are superior, and densities which are inferior to those of sulphochlorinated polyethylene (Hypalon).

We have therefore found a class of saturated elastomers[18] which

have improved properties, even in respect of elastic hysteresis, over those of the known saturated rubbers obtained from vinylidenic olefins (butyl rubber) or from Hypalon.

Besides crystalline isotactic and amorphous atactic polymers there is a range of intermediate products consisting of polymers the chains of which are composed of a succession of isotactic blocks with inversions of the isotactic order at the ends.[19]

According to the frequency with which inversion of the isotactic order along the chain takes place, the polymers show elastomeric properties to a greater or lesser extent.

In practice, low frequency of such inversions in the isotactic chain of very high molecular weight causes only a slight lowering of the melting point and a small increase in elastic elongation, but the yield point and ultimate tensile strength are more or less the same. The properties of these polymers are not very different from those of completely isotactic polymers, when they have a sufficiently high molecular weight. In an analogous way, the presence of very small isotactic parts in an atactic chain does not alter appreciably the properties of the atactic polymer. New and interesting characteristics appear only if the iso-

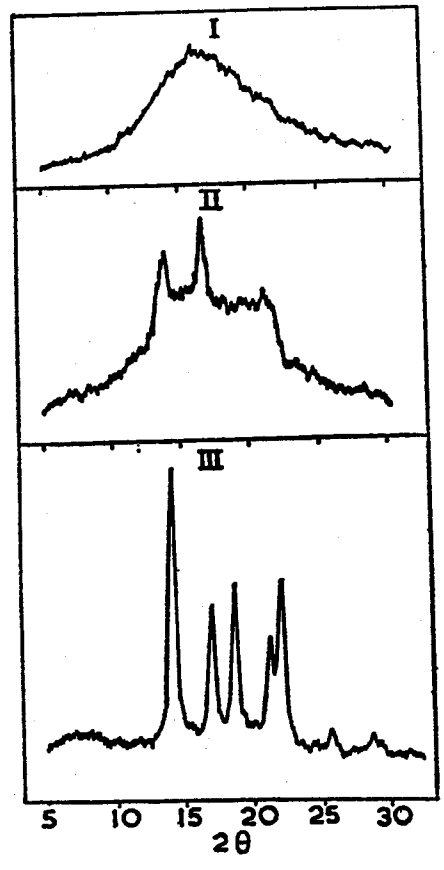


FIG. 7. Geiger diagram comparing amorphous (I), crystalline (III) and a stereoblock polymer (II).

tactic blocks are sufficiently large, giving the property of crystallizing partially. In Fig. 7, Geiger X-ray diagrams of amorphous and crystalline polymers are compared with that of a stereoblock polymer. In general, block polymers compared with crystalline polymers are characterized by higher solubility and lower melting point, as can be foreseen theoretically.

The theories developed by various authors, and in particular by Prof. Flory, on the lowering of the melting point of a copolymer, due to the presence in the chain of chemically different monomer units, can be applied to the case of linear homopolymers, where structural irregularities are due to different steric configurations of chemically identical monomer units.

The fact that parts of the molecule are constituents of crystalline systems, gives to the oriented materials properties similar to those due to physical vulcanization; for instance, like those produced by the rapid stretching of natural rubber.

These block polymers, when pure (not vulcanized) and after stretching in a given direction, present a reversible elongation in the same direction of the value of 50–100 per cent or more. Furthermore, they present ultimate tensile strengths which are superior to those of the most vulcanized rubbers.

In Fig. 21 of paper 24 curve I shows mechanical properties of a pure isotactic polypropylene, and curve II of an isotactic polymer containing a small number of stereoblocks; curves III and IV show polymers containing only stereoblocks and the last a high molecular weight amorphous polymer. The vulcanizing effect of crystallinity alone, found in block homopolymers, differs from that produced by chemical bonds in that it disappears when the material is heated beyond the melting point of the crystals and reappears when it is cooled and stretched.

PROPERTIES OF MIXTURES OF STEREOISOMERS

It is possible to obtain widely different types of products from α-olefin polymerization, the properties of which depend on many factors: the quality and the quantity of the different stereoisomers present, that is the percentage of crystallizable isotactic polymers; the percentage of stereoblock polymers and the type of blocks; the percentage of atactic polymers, and the distribution of the molecular weight of the various stereoisomers.

Hence it is possible to obtain a great variety of products. Those having great practical interest in the plastics field are very rich in isotactic polymers and these, in turn, rich in very high molecular weight blocks, but lacking in completely atactic low molecular weight molecules.

The simplest methods for the characterization of the different raw products are:

1. Crystallinity determined by means of X-rays or density measurements.
2. Contents of the three types of stereoisomers (isotactic, atactic, stereoblock polymer) determined by extraction with solvents.
3. Average viscometric molecular weight of the different fractions.

Many physical properties (like density and melting point) vary slightly with the change of the molecular weight above a certain limit (over 50,000), but in the melted state the viscosity varies considerably thus influencing the use of particular processes for extrusion and injection.

Raw products with high molecular weight (80,000–200,000), good crystallinity (over 60 per cent) and poor in completely atactic parts can be obtained directly by polymerization. These products have good mechanical properties differing slightly from pure steric polymers. The presence of a small quantity of block polymers with very high molecular weights increases the elastic elongation.

We give, in Tables 1 and 2 of this paper and Table 4 of paper 24, data relating to the raw products obtained by polymerization. It is probable that they will correspond to the products which will be put on the market in the near future by Montecatini's Ferrara plant. We think that, at the beginning, the greatest practical interest will be focused on the cheapest types which in the raw and unfractionated state, already have technically satisfactory characteristics for many practical uses.

Wide applications of the new crystalline polymers are expected in the field of textile fibres. Before the discovery of the new isotactic polymers, it was believed that the presence of macromolecules containing groups capable of association was necessary to prevent viscous flow and to obtain textile fibres with good mechanical properties. The high tensile strength of nylon is attributed to association forces due to the hydrogen bonds. In other cases, where such bonds do not exist, the associative forces between chains are attributed to the presence of polar groups (e.g. Orlon and Terylene). The discovery of isotactic poly-

TABLE I
MECHANICAL PROPERTIES OF POLYPROPYLENE, POLYBUTENE AND OTHER PLASTIC FILMS

	Polypropylene crystallinity: 60–65%	*Polybutene crystallinity: 40–50%*	*Rotene*	*Polyethylene Marlex 50*[1]	*Fertene*	*Cellophane*
Tensile strength:						
Machine direction p.s.i.	5000—6000	5000—6000	3500	3800	2800	4300—18,000
Transverse direction p.s.i.	4000—5000	4000—5000	3500	3400	2600	—
Elongation:						
Machine direction %	700—750	200—230	800	200	280	15—40
Transverse direction %	730—750	300—320	770	75	235	—
Tear strength:[2]						
Machine direction g/mil	410—490	260—280	330	460	220	51—230
Transverse direction g/mil	360—410	260—280	290	450	190	—

[1] From "Properties of Marlex 50" presented before the division of Petroleum Chemistry—Dallas Meeting, 8-13 April 1956.
[2] *A.S.T.M.* D1004—49T.

mers showed us that it is possible to obtain high-tenacity synthetic fibres, corresponding to the best so far known, from polyolefin without hydrogen links and polar groups. It is essential, however, that the polymers have a perfectly linear structure and a very high molecular veight, for example of about 40,000–50,000 for polypropylene, corresponding to about 1000 monomer units.

It is interesting to observe that polypropylene fibres have tensile strength and elasticity far superior to that of the best new types of linear polythenes. In practice, it is easy to obtain isotactic polypropylene fibres having a tenacity of 5 to 8 g/den and very high reversible elongation.

Polypropylene fibres have a density (0·91–0·92) lower than that of any other known fibre. They can be melt-spun, without the use of solvents or plasticizers, like nylon. The low melting point (175° for completely isotactic polymers and generally 165–170° for raw polymers) facilitates spinning. Polypropylene fibres have very good electrical and thermal insulating properties, and excellent mechanical characteristics—in particular, outstanding elastic capacity for absorbing high quantities of

deformation energy. Furthermore the raw material—propylene—is available in practically unlimited quantities and is very cheap. At present no other monomer can be obtained at a cheaper price (about 3 centis per pound in the U.S.A.). Polymerization gives very high yields, espec ally when the monomer is in a very pure state. The raw product, after the removal of traces of catalyst, can be woven directly.

In Table 3 the main mechanical properties of polypropylene fibres are illustrated, and in Fig. 22 of paper 24 these are compared with other synthetic fibres.

DIOLEFIN STEREOISOMERIC POLYMERS

A field, in which stereospecific polymerization processes present a particular interest, is that of the simple aliphatic diolefin polymers. The most interesting properties of diolefin polymers, from a practical point of view, are their viscoelastic characteristics which are related to the stereoisomeric structure of the chain of the polymer.

In nature there are two polymers of isoprene with a definite steric structure, namely, gutta-percha and Hevea rubber. All synthetic polymers produced before 1953 by diolefin polymerization had disordered and irregular structures due to the presence of 1,4 linkage with both *cis*- and *trans*-double bond configurations and of 1,2 linkage with the two possible configurations of tertiary carbon atoms. These structural irregularities are the principal cause of the poorer properties of conventional synthetic rubber. Practically all types of synthetic rubber obtained from hydrocarbons before 1953 show inferior mechanical properties and, particularly, too high elastic hysteresis.

By the addition of considerable quantities of finely dispersed substances, in particular carbon black, hardness and tensile strength are improved but elastic hysteresis impaired. In the case of tyres the old types of synthetic rubber absorb irreversibly a great part of the deformation energy. Because of this they heat excessively during use and therefore they are not suitable for very thick tyres.

The application of stereospecific processes has allowed us to obtain the two butadiene stereoisomeric polymers with 1,4 linkage (*cis* and *trans*) and the stereoisomers with 1,2 linkage (isotactic and syndiotatic) in the crystalline state, besides the 1,4 and 1,2 amorphous polymers.[4,5,6] Each crystalline stereoisomer presents a typical crystalline structure and particular physical properties. Amorphous polymers with 1,4 link-

TABLE 2. PHYSICAL PROPERTIES OF ISOTACTIC POLYMERS

	Polypropylene			*Polybutylene-1*	
Intrinsic viscosity[1] 10^2 cm^3/g	2·66	5·25	1·84	1·12	2.64
Residue from:					
n-heptane extr. %	89	91	100	—	—
ethyl ether extr. %	—	—	—	72	91
Yield strength p.s.i.	5150	5400	5700	—	—
Ultimate tensile strength p.s.i.	5500	5850	5700	2150	5200
Elongation at break %	320	670	100	165	320
Stiffness p.s.i.	121,000	117,000	143,000	18,500	24,000
Hardness, Brinell p.s.i.[2]	27,000	22,000	28,000	—	—
Hardness, Shore "A"	—	—	—	95	97
Vicat softening point					
(load 1 kg) °F	—	—	—	212	265
(load 5 kg) °F	210	210	235	—	—

[1] In tetrahydronaphthalene at 135° C.

[2] D $^1/_2$ in., 1 min, 70 lb.

age present very slight hysteresis during elastic deformation, less than that of polymers with 1,2 linkage.

Some of the characteristics determined for certain crystalline stereoisomers of polybutadiene are indicated in Table 7 of paper 24.

Melting point of *cis*-1,4-polybutadiene is not indicated, because it is strongly dependent on the stereoisomeric purity and on the stress.

We have also obtained crystalline polymers from other diolefins (isoprene, piperylene, etc.). The lattice structure of 1,4 crystalline polyisoprene stereoisomers is the same as that of the natural products. The synthesis of the isoprene stereoisomers, which needs very pure monomer, was principally studied in the United States.[20] In Europe most of the work was performed in the synthesis of the pure butadiene stereoisomers.

For a number of the new polymers we have determined the crystal structure and chain configuration. The isotactic 1,2 butadiene polymer has, in the crystalline state, a helix chain structure like other isotactic polymers; actually, it can be regarded as a vinyl polymer. Its principal chain is structurally the same as that of isotactic polybutylene where lateral chains are formed by ethyl groups instead of vinyl groups.

The structure of syndiotactic 1,2 polybutadiene is very different. It is the first synthetic polymer in which monomer units with opposite

TABLE 3. MECHANICAL PROPERTIES OF RELATIVELY LOW MOLECULAR WEIGHT POLYPROPYLENE FIBRE: $[\eta] = 1$

Standard tenacity (20°C, 65% relative humidity)	6—7 g/den
Wet tenacity (20°C, in water)	6—7 g/den
Knot tenacity	5—6 g/den
Loop tenacity	5—6 g/den
Elongation at break (20°C, 65% relative humidity)	30—40 %
Elongation at break (20°C, in water)	30—40 %
Average stiffness	17 g/den
Average toughness	12 g/den
Initial modulus	35—45 g/den
Elastic recovery	100% at 7% elongation
Shrinkage at 100°C	1—2%

steric configuration alternate regularly. The principal chain has a nearly planar form and each monomer unit can be brought to cover its neighbour by means of a translation on the longitudinal axis of the chain of one half the identity period ($\frac{1}{2}$ c) accompanied by specular reflection.

The structure of *cis*-1,4 polybutadiene is characterized by an identity period containing 2 monomer units. Their arrangement is such that it is possible to pass from one to another by a displacement of $\frac{1}{2}$ c accompanied by specular reflection (as in syndiotactic polymers). The segment of the chain corresponding to the identity period has a symmetry centre, and consequently only one type of chain is present in the system.

A great amount of work has been done in connection with copolymers, which have many interesting possibilities once the difficulty of obtaining homogeneous products has been overcome.

Also for diolefin polymers we can have amorphous copolymers of sterically different units and stereoblock polymers.

Naturally, high melting-point, crystalline diolefin polymers are not, in the pure state and at room temperature, real rubber as usually understood. They become rubber at high temperatures and when their crystallinity is reduced.

Excellent elastic properties can be obtained when the relative mobility of the group of the main chain containing unsaturated links (like those of 1,4 diolefin polymers) is accompanied by low melting temperatures and low melting entropies.

The field of rubbers having very low elastic hysteresis at room temperature is still confined to diolefin polymers but is certainly no longer restricted to natural rubber.

The results obtained by the new discoveries of the stereospecific polymerization processes can lead to further developments. Numerous research chemists are actively working on, improving stereospecific processes and extending these to other classes of monomers.

The synthesis of crystalline high melting-point polymers of other vinyl monomers (vinyl chloride, acrylonitrile, vinyl ethers, vinyl esters, etc.) will be the next stage in stereospecific polymerizations. This aim will, perhaps, be more difficult to achieve, but it certainly will be interesting both from a scientific and a practical point of view.

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KINETICS OF THE STEREOSPECIFIC POLYMERIZATION OF PROPYLENE TO ISOTACTIC POLYMERS

by G. NATTA, I. PASQUON and E. GIACHETTI

(8 Feb. 1957)

[*Angew. Chemie* **69**, 213 (1957)]

ABSTRACT

The kinetics of the polymerization of propylene to an isotactic polymer was studied with a heterogeneous catalytic system prepared from α-$TiCl_3$ (violet modification characterized by a layer lattice) and Al $(C_2H_5)_3$ in n-heptane.

The catalytic system adopted here possesses a good stereospecificity.

In runs carried out at constant temperature and pressure of olefin, the polymerization rate kept constant even for several tens of hours. The catalytic activity was also unaltered when the catalyst was kept under different operating (or not operating) conditions and subsequently brought back to its original starting conditions.

The polymerization rate was first order with respect to the partial pressure of the olefin, and with respect to the amount of α-$TiCl_3$ present in the system, while it was independent of the ratio of $Al(C_2H_5)_3$ to $TiCl_3$, and of the concentration of the $Al(C_2H_5)_3$.

The apparent activation energy of the overall polymerization process, measured between 30° and 70°C, was about 14,000 cal/mol (referred to the concentration of the olefin in the liquid phase).

The results obtained demonstrate that the polymerization process of propylene is really catalytic with respect to $TiCl_3$. This differentiates this type of polymerization from the polymerization processes characterized by a free radical mechanism. In these last processes the initiator is not actually a true catalyst, because, at the end of the polymerization it is found bound to the polymeric chains.

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ISOTACTIC AND STEREOBLOCK POLYMERS OF PROPYLENE

by G. NATTA, G. MAZZANTI, G. CRESPI and G. MORAGLIO

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SUMMARY

New high linear polymers of α-olefins are described, characterized by the presence in the same macromolecule of chain segments having different steric configuration, namely by segments having crystalline isotactic structure and segments having irregular steric structure and therefore non-crystallizable. Macromolecules of this kind are defined by the authors as stereoblock polymers. These polymers differ from the well-known block copolymers because the former are obtained by polymerization of a single monomer.

Methods for the separation of stereoblock polypropylenes from atactic and isotactic polypropylenes are described. While the latter, when free from stereoblocks, have a melting temperature of about 175 °C and high crystallinity, stereoblock polypropylenes have lower melting temperatures (generally between 100 and 170°C) and lower crystallinity the lower are melting temperatures.

Stereoblock polymers of α-olefins, of low crystallinity, show peculiar mechanical properties: high elastic elongation in the oriented state (100–200 per cent) and low initial elastic moduli. They represent a new interesting class of elastomers which, in the oriented state, behave as if they were vulcanized in a thermolabile way. This must be attributed to the presence of microcrystalline regions, in which isotactic chain segments of different macromolecules are arranged. Their lattice energy hinders the viscous flow of the amorphous parts of the same macromolecules inserted between the isotactic portions.

I. STEREOISOMERY ASPECTS IN THE LINEAR CHAINS OF POLYPROPYLENE

In a communication [1] presented before the "Accademia dei Lincei" in 1954, and in previous patents[2] and subsequent articles,[3] we described the synthesis of α-olefin polymers having a high crystallinity and

high melting temperature. We had also foreseen important practical applications of these polymers. Their crystallinity is due to the exceptional regularity of their structures which are characterized by the fact that their linear chains, at least for long segments, consist of regular sequences of monomeric units having tertiary carbon atoms with the same steric configuration. One of us gave the term "isotactic" to the chains with such a steric structure; thus polymers containing such a chain were also called "isotactic".[1] This regularity of structure is lacking in the chains of non-crystallizable polymers, where opposite steric configurations of tertiary carbon atoms show irregular sequences (atactic structure).

These new crystalline polymers were obtained through particular heterogeneous catalytic processes, using special catalysts containing transition metals and metal alkyl compounds.[4] The raw polymers obtained at the very beginning of our investigation were generally rather heterogeneous, being formed of mixtures of linear polymers containing different stereoisomers; some of them were crystallizable, others, though linear and having a regular head-to-tail enchainment of the monomeric units, were not.

By changing the catalyst and the polymerization conditions it was possible to vary the relative ratios of the different types of polymers which were present in the raw polymerization products.[2c,5] In fact, using catalytic systems obtained from crystalline compounds which were insoluble in hydrocarbons, such as $TiCl_3$, $TiCl_2$, VCl_3, and which possessed a low valence of the transition metal, we obtained prevailingly isotactic propylene polymers. On the contrary, using other catalysts, obtained from soluble compounds of transition metals, which when mixed with metallorganic compounds gave extremely dispersed catalytic systems, we obtained practically all linear atactic polymers.

The structures of the isotactic polymers were described in detail in a recent work.[6] It appears that every chain in the polymer takes up a spiral configuration characterized by a tertiary symmetry and by 6·8 Å pitch corresponding to 3 monomeric units. An elaborate study on the symmetry of the crystals and also a study on the structure, demonstrated that there are two types of chains facing each other; one type formed of right-handed helices and the other of left-handed ones. For each type of helix two kinds of chains (defined as "anticlined") are possible: their difference consists in the inclination of the methyl groups, and on the steric configuration of the tertiary carbon atoms.

Thus a single isotactic chain may exhibit four different structures.

In Fig. 19 of paper 24 are shown: a left-handed chain with isotactic structure (I); a left-handed chain formed of two parts differing from each other because of the different steric configurations of the tertiary carbon atoms (II); and one of the foreseen structures, having the lowest potential energy of the various possible types of atactic chains (III).

The methods we employed for the separation of crystalline polymers from the amorphous ones are based on the solubility difference existing between the crystalline and amorphous stereoisomers. Thus, for instance, we separated propylene polymers of high crystallinity from the completely amorphous polymers and from those of low crystallinity, by the fractional extraction of the mixture either with boiling n-heptane or with other hydrocarbons used at temperatures lower than the melting point of the highly crystalline polymer. Fractions having a high degree of crystallinity, contrary to the amorphous ones and to those of low crystallinity, were not extractable in those solvents. Therefore, the determination of the extraction residue may be considered a practical method to evaluate the amount of isotactic polymers existing in polypropylene.[7]

A more accurate separation of stereoisomers present in some α-olefin polymers with several suitable solvents, enabled us to obtain intermediate fractions whose properties greatly differ from both the isotactic and the completely atactic polymers.[8] These fractions exibit low isotactic crystallinity and cannot be resolved with physical methods into amorphous or highly crystalline fractions. When one compares them with previously described isotactic polymers, which have a higher degree of crystallinity, they are characterized, in the solid state, by a lower melting temperature and by different viscous-elastic properties.

The peculiarities of these fractions have been connected with a particular structure of their macromolecules, characterized by the fact that only some chain segments exhibit an ordered steric structure. In fact, chain segments having an isotactic structure, hence crystallizable, are interposed among non-crystallizable segments. The reason why these fractions are not crystallizable could be either ascribed to their atactic structure, or to the succession of short segments of isotactic chains having an opposite steric configuration. These stereoisomers, therefore, may be considered as stereoblock homopolymers. They differ from the usual block copolymers because each block does not derive from the copolymerization of chemically different monomers, but instead it consists of stereoisomeric units derived from the same monomer.

II. SEPARATION AND CHARACTERIZATION OF STEREOBLOCK POLYMERS OF PROPYLENE

(*a*) *Methods used to Separate Stereoblock Polymers from the Highly Isotactic and Amorphous Ones*

We performed the separation of the different stereoisomers preferably on the raw polymer; either in the powdered form or in the small granules, after having removed the inorganic constituent of the catalyst.

The raw polymer so obtained in the usual conditions (i.e. at the temperature of 80°–90°C) was already partly crystalline: its crystallinity increased very little after further annealing at higher temperatures. Even if it was necessary, in order to obtain a good fractionation, to use a product having its crystallizable stereoisomers in the form of crystals, in most cases the annealing process seemed superfluous. On the contrary the annealing is necessary when the products to be fractionated had been obtained from a melted or dissolved product by rapid cooling at low temperature, as the isotactic parts might still remain prevailingly amorphous and thus they would have exhibited a greater solubility than the products crystallized by annealing.

The raw propylene polymers which we examined most frequently were those containing block stereoisomers having an intrinsic viscosity in tetralin at 135°C higher than 0·3.

The separation of the various stereoisomers was carried out by subsequent extractions. At first, using suitable solvents, the amorphous stereoisomers were extracted (i.e. with acetone we extracted the amorphous, oil-like products having a low molecular weight; then, with ether, we extracted the amorphous, solid rubber-like polymers having a higher molecular weight); then fractions, having a gradually-increasing crystallinity, were separated by subsequent extractions with liquids having increasingly better solvent properties, or by means of a single solvent operating at various temperatures.

A certain amount of crystallinity (15 per cent), was present in the usually amorphous fraction extracted by ether only when the extraction was carried out on stereoblock polypropylenes of low molecular weight (with an intrinsic viscosity lower than 0·25). In the experimental part it is described how those polymers were prepared.

A suitable laboratory fractionation system consists in employing various homologous solvents (in the case of polypropylene, aliphatic hydrocarbons), in the order of their increasing boiling point, and by

TABLE I. FRACTIONATION OF POLYPROPYLENES OBTAINED WITH DIFFERENT CATALYSTS BY HOT SOLVENT EXTRACTION

Fractions	*Partially stereospecific polymerizations*						*Highly stereospecific polymerizations*					
	I. Polypropylene from $TiCl_4$ and $Al(C_2H_5)_3$; $R = 2{\cdot}5$; $T = 90°C$; initial $P = 21$ atm			*II. Polypropylene from $TiCl_4$ and $Al(C_2H_5)_3$; $R = 2{\cdot}8$; $T = 35°C$; constant $P = 3{\cdot}3$ atm*			*III. Polypropylene from $TiCl_3$ and $Al(C_2H_5)_2Cl$; $R = 3$; $T = 70°C$; initial $P = 21$ atm*			*IV. Polypropylene from $TiCl_3$ and $Al(C_2H_5)_3$; $R = 2{\cdot}5$; $T = 80°C$; constant $P = 6$ atm*		
	%	$[\eta]$ 100 cm^3/g	*crystallinity* %	%	$[\eta]$ 100 cm^3/g	*crystallinity* %	%	$[\eta]$ 100 cm^3/g	*crystallinity* %	%	$[\eta]$ 100 cm^3/g	*crystallinity* %
acetonic extract	15·4	—	—	6·6	—	—	2·10	—	—	1·50	—	—
ether extract	41·8	0·46	0	38·7	0·67	0	8·90	0·50	0	6·53	0·42	0
n-pentane extract	2·23	0·51	27	4·2	1·12	11	1·50	0·35	15	1·38	0·48	27
n-hexane extract	9·42	0·61	37	5·1	1·13	29	1·90	0·67	25	2·60	0·55	36
n-heptane extract	7·45	0·68	54	10·2	0·92	41	1·90	0·90	41	3·29	0·63	52
ethylhexane extract	13·60	1·22	64	17·4	1·01	52	2·30	1·12	53	17·98	0·86	62
n-octane extract	10·10	2·08	68	17·8	3·11	60	12·80	1·63	62	16·22	1·32	64
residue	—	—	—	—	—	—	68·60	3·50	64	50·50	2·97	66

R = molar ratio of alkylaluminum to titanium halide.
$[\eta]$ = intrinsic viscosity at 135°C in tetralin.

carrying out every extraction at the boiling temperature of the solvent.

In Table 1, for instance, are tabulated the results obtained from subsequent extractions using acetone, ether, n-pentane, n-hexane, n-heptane, 2-ethylhexane and n-octane. The corresponding fractions which were thus separated exhibited an increasing degree of crystallinity.

It is of interest to point out that in most cases when we tried to further fractionate the previous fractions, it was not possible to separate those intermediate fractions (which we believed as formed of stereoblocks) in completely amorphous and crystalline fractions. At most we obtained a further separation of the single fractions in other fractions having slightly different degrees of crystallinity.

(*b*) *Crystallinity of Block Polymers*

Quantitative determinations of crystallinity were performed, by an X-ray method developed at this Institute,[9] on several fractions, isolated by means of solvent extraction.

Figure 1 shows the data obtained (on polymer IV of Table 1) with a Geiger counter concerning the intensity of X-rays diffraction (copper anticathode) of a series of fractions with an increasing crystallinity.

It appears that the crystallinity increases with the increase of the temperature extraction; such an increase corresponds to an increase of the amount and of the length of the isotactic fractions in a single macromolecule.

However, even if the crystallinity, measured with X-ray methods is a very useful parameter for the study of stereoblock polymers, it is not a suitable criterion to determine, in an exact quantitative way, the isotacticity, unless it is applied to mixtures of stereoisomeric polymers having not a high molecular weight and a small amount of very short isotactic fragments.

The complete crystallization of the isotactic polymers becomes more and more difficult when this molecular weight increases, due to the fact that the viscosity of the system increases.

When the single molecules have a length which is longer than the *c* axis of the single crystals (whose length generally does not exceed some hundred angstroms) they can only crystallize partially.

If one compares some corresponding fractions, obtained using the

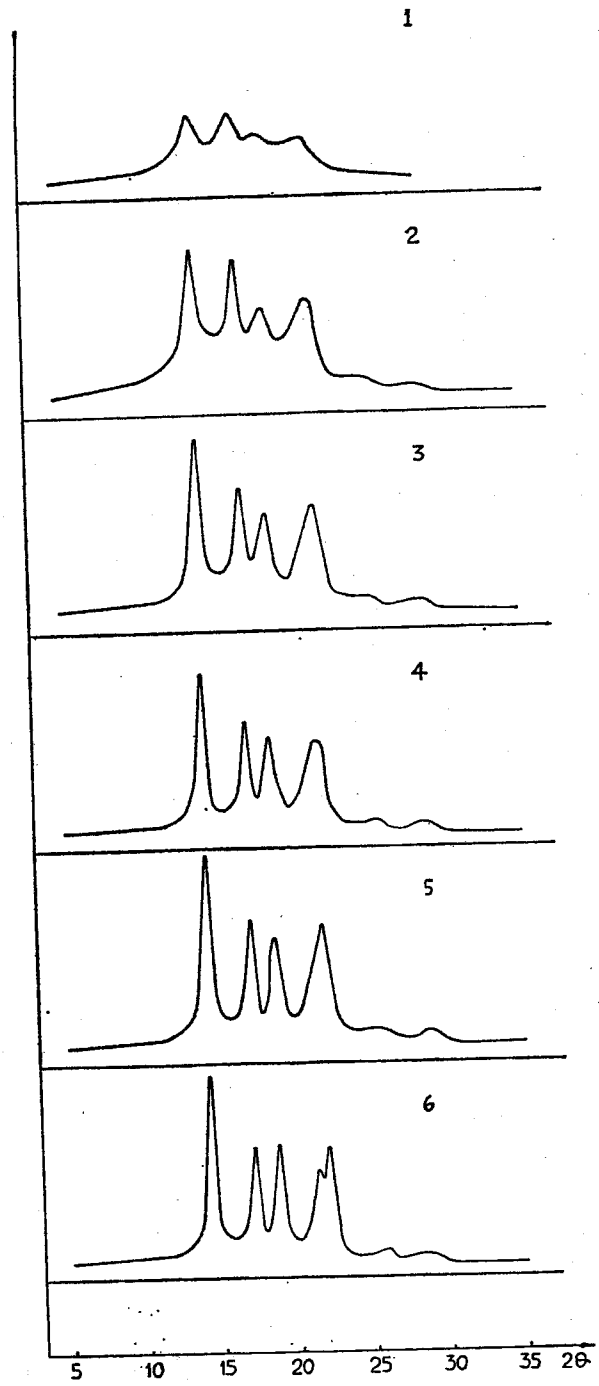


FIG. 1. Intensity of the diffractions (observed by X-ray methods) of different polypropylene fractions with increasing crystallinity (polymer IV is fractionated, as is shown in Table 1).

same solvent, but starting from products of different molecular weight, it can be observed (Table 2) that for intrinsic viscosities higher than one, the crystallinity decreases with an increase of the molecular weight. A single molecule can then belong to different crystals or to different parts of the same crystal, thus the isotactic parts of the molecule can be interposed between two different crystalline parts, and remain amorphous.

TABLE 2. CRYSTALLINITY OF DIFFERENT MOLECULAR WEIGHT POLYPROPYLENES, LEFT AS RESIDUE OF THE n-HEPTANE EXTRACTION

$[\eta]$ 100 cm^3/g	% *crystallinity by X-rays*
1·3	82
1·9	78
2·1	73
2·5	65

TABLE 3. MELTING TEMPERATURES OF MIXTURES OF AMORPHOUS POLYPROPYLENE (ETHER EXTRACT, $[\eta] = 0{\cdot}59$) AND OF ISOTACTIC POLYPROPYLENE (ETHYLHEXANE RESIDUE, $[\eta] = 3{\cdot}52$)

% isotatic sample	*Crystallinity %*		*Melting temperature °C*
	calculated for the mixture	*determined by X-rays*	
100	67·7	67·7	174
87·5	59·3	60·3	173
75·8	51·4	49·8	172—173
60	40·6	40·2	171—172

The considerations about crystallinity could also be extended to other properties directly derived from crystallinity, such as density. Therefore, with some stereoblock polymers of low molecular weight, it is possible, in some cases, to obtain by X-ray method, higher values of crystallanity, and they may even have higher density values than other polymers having a very high molecular weight and a greater amount of isotactic parts.

One must also remember that the X-ray methods allow just to detect crystals whose dimensions are bigger than 50 Å; and for this reason the X-rays crystallinity is generally lower than the one determined with I.R. or N.M.R. methods.

The study done on block polymers has also demonstrated that by only measuring the crystallinity, it is impossible to determine the stereoisomeric composition of a raw polymer. In fact, it is possible that the same percent crystallinity can be found for a certain type of block stereoisomers and for a heterogeneous mixture of isotactic and atactic stereoisomers, respectively (Table 3).

(c) *Melting Temperature of Stereoblock Polymers*

It is well known that polymers having a very regular structure and therefore, a high degree of crystallinity (such as a polymethylene free from branchings), have melting temperatures which increase asyntotically with the increase of their molecular weight until they assume a practically constant value when the chain length exceeds some thousands of monomer units.[10]

In block polymers the temperature at which the crystallinity disappears (temperature of complete melting), depends mostly on the length of the segments of the crystallizable chain. With regard to stereoblock polymers, the presence of a large or a small amount of atactic segments, exerts a double influence on the melting points of the isotactic crystallizable parts which are present; the principal cause is derived from the reduction of length of the isotactic segments; the secondary one is due to the lowering of the melting temperature, according to the laws of cryoscopy, which are of the same nature as the ones observed in the mechanical mixtures of the isotactic and atactic polymers.

With regards to crystallizable stereoisomers of polypropylene, the accurate determination of the melting curve (for instance by dilatometric methods), or of the variation of crystallinity with the temperature, furnishes data which can be used to evaluate the length of the isotactic segments present in the stereoblock chains.

The stereoblock polymers which we have separated, show, in fact, a melting temperature which is remarkably lower than the one of the completely isotactic stereoisomers. This agrees with what has been foreseen theoretically for copolymers, provided, as we have already observed, stereoblock homopolymers are considered as block copolymers of different monomeric units. From the examination of artificial mixtures of isotactic and amorphous polymers having both high molecular weight, it results that the crystallinity is proportionally lowered and the melting temperature is very little affected (Table 3).

On the contrary, fractions consisting of block polymers show much lower melting points. In Table 4 are reported the melting temperatures of different fractions having an increasing crystallinity. These fractions were isolated by means of subsequent extractions from raw polymers of polypropylene prepared by different ways.

It is of interest to notice that, with regard to polypropylene obtained with highly stereospecific catalysts (such as those containing titanium

TABLE 4. MELTING TEMPERATURE AND CRYSTALLINITY OF SOME POLYPROPYLENES HAVING A DIFFERENT STEREOISOMERIC COMPOSITION

Solvent used for the extraction	*I. Polypropylene fractions obtained with catalysts formed by $TiCl_4$ and $Al(C_2H_6)_3$; $R = 2{\cdot}5$; $T = 90°C$; Initial $P = 21$ atm*			*II. Polyproylene fractions obtained with catalysts formed by $TiCl_4$ and $Al(C_2H_5)_3$; $R = 2{\cdot}8$; $T = 35°C$; Constant $P = 3{\cdot}3$ atm*			*III. Polypropylene fractions obtained with catalysts formed by $TiCl_3$ and $Al(C_2H_5)_2Cl$; $R = 3$; $T = 70°C$; Initial $P = 21$ atm*			*IV. Polypropylene fractions obtained with catalysts formed by $TiCl_3$ and $Al(C_2H_5)_3$; $R = 2{\cdot}5$; $T = 80°C$; Constant $P = 6$ atm*		
	[η] 100 cm^3/g	*crystallinity*	*melting T °C*	*[η] 100 cm^3/g*	*crystallinity %*	*melting T °C*	*[η] 100 cm^3/g*	*crystallinity %*	*melting T °C*	*[η] 100 cm^3/g*	*crystallinity %*	*melting T °C*
pentane	0·51	27	114	1·12	11	114	0·35	15	106	0·42	27	110
hexane	0·61	37	130	1·13	29	135	0·67	25	110	0·55	36	127
heptane	0·68	54	159	0·92	41	159	0·90	41	147	0·63	52	159
2-ethylhexane	1·22	64	170	1·01	52	168	1·12	53	168	0·86	62	170
octane	2·08	68	174	3·11	60	174	1·63	62	174	1·32	64	174·5
residue	—	—	—	—	—	—	3·50	64	174	2·97	66	174·5

TABLE 5. FRACTIONATION OF POLYPROPYLENES OBTAINED WITH CATALYSTS FORMED BY $TiCl_4$ BY DIRECT SOLVENT EXTRACTION

Solvent used	*Residue %*	*[η] 100 cm³/g*	*Crystallinity %*	*Melting temperature °C*
V. ethylhexane	72	1·95	75	174·5
VI. n-octane	79	2·17	66	175
P. trichloroethylene	80	1·80	85	175

Samples V and VI were obtained in the laboratory (see experimental part), while sample P corresponds to a product obtained at the Montecatini pilot plant in Ferrara.

trichloride), the melting temperature of the residue, after the extraction with 2-ethylhexane, was practically identical with that of the polymer isolated as a residue from the subsequent extraction with n-octane. Considering that by the extraction with n-octane, the resulting fraction has a lower molecular weight which corresponds to about 1/4 of the residue of the preceding 2-ethylhexane extraction, and also considering that, no increase of the melting temperature of the residue was observed, one could conclude that the fraction which is not extractable in boiling 2-ethylhexane is wholly formed of equally isotactic polymers, practically free from stereoblock.

The same high melting temperature was also observed for the residue obtained from direct extraction of the raw polymer with boiling n-octane, as shown in Table 5, and for the residue of other highly crystalline polypropylenes extracted with trichloroethylene. It is of interest to notice that also the samples with a very high crystallinity (85 per cent), possess the same ultimate melting temperature.

According to what has been stated above and to the results shown in Tables 4 and 5, it is here suggested that a temperature of 175°C may be considered as the melting point of the pure isotactic polypropylene having a very high molecular weight.

(*d*) *Mechanical Properties of Stereoblock Polymers*

The mechanical properties of stereoblock polymers confirm their typical structure. In particular very significant characteristics can be observed when one examines block polymers having a degree of crystallinity of 15–30 per cent (as measured by X-ray methods). In fact, in

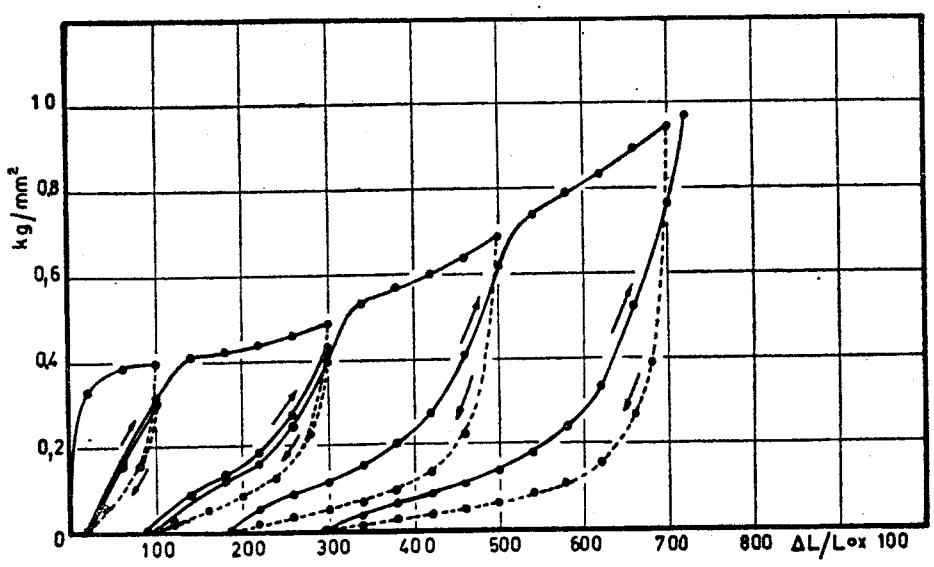


FIG. 2. Stress–strain plot of a stereoblock polymer, having an intrinsic viscosity of about 1.

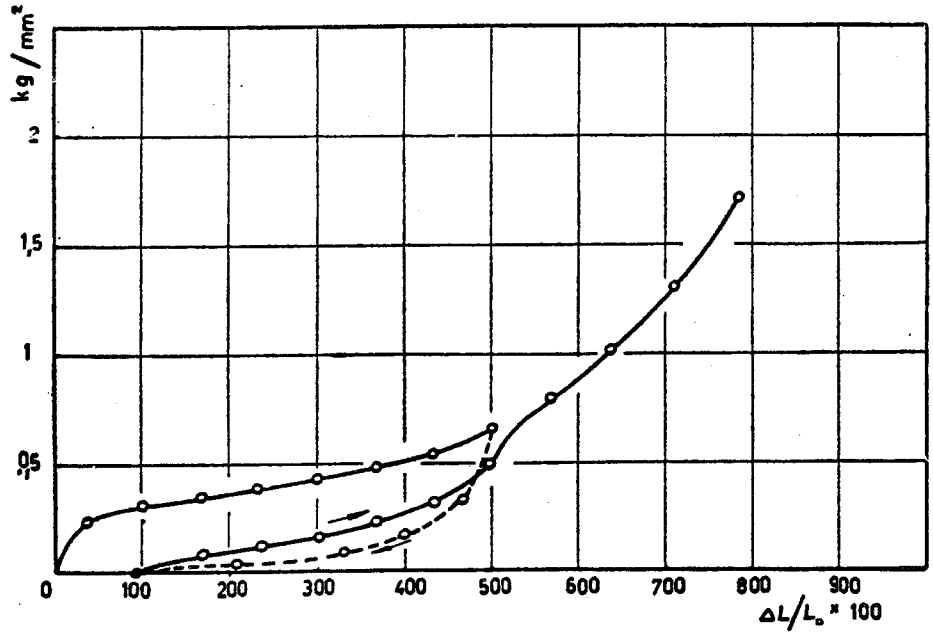


FIG. 3. Stress–strain plot of a stereoblock polymer, having an intrinsic viscosity of about 1·5.

the stress–strain diagrams, it can be observed that the initial elastic moduli are not very high, especially when they are compared with those of the highly isotactic polypropylene. Furthermore, the stresses increase with the increase of the elongation, contrary to what happens to the physical mixtures of the two amorphous and isotactic stereoisomers, which tend to be deformed under an almost constant stress.

High elasticity is the property which makes block polymers particularly interesting. The reversible elongation, with regards to block

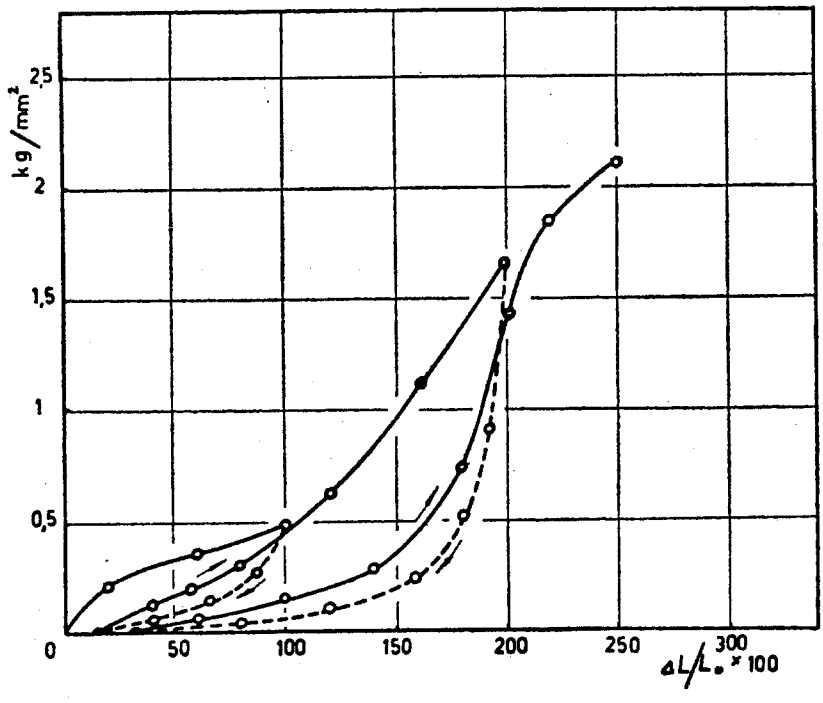


FIG. 4. Stress–strain plot of a stereoblock polymer, with an intrinsic viscosity of 1, previously and temporarily stretched to 700 per cent and afterwards relaxed.

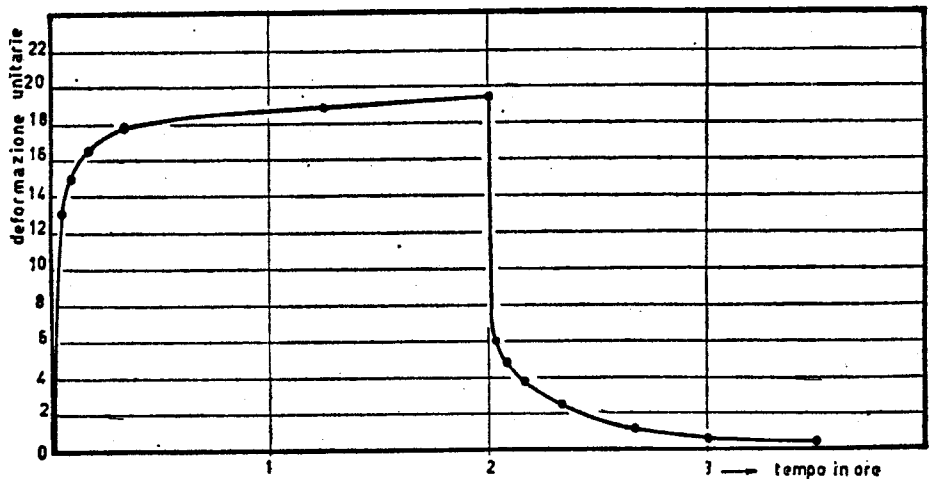


FIG. 5. Deformation under a constant stress, and relaxation diagram of a stereoblock polymer previously stretched to 700 per cent.

polymers having a crystallinity of about 25 per cent, reaches values ranging from 100 per cent (see Fig. 2, concerning stereoblocks with an intrinsic viscosity of about 1) to 200 per cent (see Fig. 3 concerning the stereoblocks with intrinsic viscosities of about 1·5).

From this view-point some stereoblock polymers of propylene may be considered as real elastomers. Their elastomer-like behaviour becomes more evident if one examines the stress–strain plot of a stereoblock polymer, which had previously been subjected to a temporary stretching of 700 per cent (Fig. 4).

The diagram shows that these polymers initially have low elastic moduli, elongations which are almost completely reversible even for stresses which are very close to the maximum tensile strength, and a fairly high maximum tensile strength. Even the plot which indicates the deformation under constant stress, as function of time, of a stereoblock polymer, previously stretched by 700 per cent (Fig. 5), shows a behaviour very similar to the one exhibited by vulcanized elastomers. The viscous flow appears to be of a very limited range for those products with a very high molecular weight. This can be ascribed to the fact that, in the oriented products, the isotactic chain segments tend to have an orientation parallel to the direction of stretching, by associating themselves in crystals, whose lattice energy hinders the chain flow, thus exercising an action which is similar to that of crystallinity in the rapidly stretched natural rubber. Its effect may be compared with that of a thermolabile vulcanization.

Unlike the articles which are manufactured with common elastomers, vulcanized by chemical agents, those obtained from unvulcanized stereoblock polymers may be melted and shaped at a temperature higher than their melting point. This material, if it is employed again, keeps unaltered its mechanical properties, its capacity to be oriented and its ability to be crystallized under stretching.

On the other hand, stereoblock polymers of high crystallinity (40–50 per cent), show higher initial elastic moduli, higher maximum tensile strength and, generally, a reversible elasticity which is rather low (of the order of the 10–20 per cent).

It is possible to have a continuous variation of the mechanical properties going from block polymers of low crystallinity to highly crystalline isotactic polymers.

The initial elastic modulus under stress, the maximum tensile strength, the surface hardness and the residual deformation after breaking increase with the increase of crystallinity; whereas, the reversible elastic elongation decreases.

III. EXPERIMENTAL PART

(*a*) *Preparation of Polymers to be Fractionated*

The polymers to be fractionally extracted were prepared with systems described in previous patents[2] and in other papers dealing with the synthesis of polypropylene.[3,5]

The samples, whose fractions are shown in Tables 1, 3 and 4, were prepared in the following way:

I (Table 1). The catalyst was prepared by adding a solution of 0·02 moles of $TiCl_4$ in 50 cm³ of n-heptane in a 1-l. pressure vessel containing a solution of 0·05 moles of triethylaluminium in 250 cm³ of n-heptane and 182 g of propylene kept at a temperature of 80°C.

The polymerization was carried out at a temperature of about 90°C and it was stopped after about 4 hr. By using the procedure already described in other papers, we isolated 112 g of raw polymer.

II (Table 1). In a 1-l. rocking pressure-vessel containing a solution of 0·013 moles of triethylaluminium in 100 cm³ of n-heptane thermostatized at 35°C, was injected a solution of 0·00455 moles of $TiCl_4$ in 50 cm³ of n-heptane. Two minutes later, propylene was introduced and the pressure was then maintained at 3·3 atm for 30 min. In this way 18 g of polymer were obtained.

III (Table 1). In a 2-l. rocking pressure-vessel containing 0·008 moles of powdered titanium trichloride and a solution of 0·024 moles of diethylaluminium monochloride in 300 cm³ of n-heptane, 190 g of propylene was introduced at 70°C. The polymerization was carried out at 70°C and was stopped after 15 min; doing this 155 g of propylene were obtained.

IV (Table 1). In a 1-l. rocking pressure-vessel, containing 0.008 moles of titanium trichloride and a solution of 0·020 moles of triethylaluminium in 250 cm³ of n-heptane, maintained at 80°C, propylene was added until a pressure of 6 atm was reached. The flow of propylene was regulated to maintain the constant pressure of 6 atm. The reaction was stopped after 5 hr, and 41 g of propylene were thus obtained.

V (Table 5). In a 2-l. rocking pressure-vessel, containing 0·01 moles of titanium trichloride and a solution of 0·02 moles of triethylaluminium in 400 cm³ of n-heptane, maintained at 90°C, propylene was added until a pressure of 6 atm was reached. The flow of propylene was regulated to maintain a constant pressure of 6 atm. The reaction was stopped after about 8 hr and 74 g of polypropylene were thus obtained.

VI (Table 5). In 1-l. rocking pressure-vessel, containing 0·008 moles of titanium trichloride and a solution of 0·024 moles of diethylaluminium monochloride in 250 cm³ of heptane, kept at 80°C, propylene was added until a pressure of 6 atm was reached. The flow of propylene was regulated to maintain a constant pressure of 6 atm. Polymerization was interrupted after about 7 hr, and 40 g of polypropylene were thus obtained.

VII *Polymerization at high temperature* with formation of stereoblock polymers with low molecular weight ($[\eta] < 0 \cdot 3$).

In a 1-l. rocking pressure-vessel containing a suspension of 0·90 g of $TiCl_3$ in 450 cm^3 of n-heptane and thermostatized at 144°C, we introduced propylene until a pressure of 9·5 atm was reached. Five minutes later, a solution of 4·2 g of triethylaluminium in 50 cm^3 of n-heptane was injected.

The pressure of 9·5 atm was kept constant, with subsequent introductions of propylene, for a period of about 90 min.

The product so obtained was fractionated by extraction with boiling solvents, employing successively: acetone, ether, n-heptane. By operating at the above-mentioned conditions, a fraction, extractable in ether, and corresponding to the 15·2 per cent of the polymer, with an intrinsic viscosity of 0·24 and with a degree of crystallinity of 17 per cent was obtained.

By using the same conditions we have just described, but carrying out the polymerization at 163°C, we obtained a polymer with a fraction extractable in ether, corresponding to the 13·2 per cent of the original polymer and with an intrinsic viscosity of 0·20 and a degree of crystallinity of 17 per cent.

(*b*) *Equipment and Technique Employed in Carrying out Fractionations by Extraction*

The fractionation of the raw polypropylene has been accomplished by warm extraction using Kumagawa extractors, which allow the sample, which is to be extracted, to be maintained at the boiling temperature of the employed solvent. The extractors could use thimbles of 33 per 94 mm size. The frequency of the solvent drainage from the thimble was about 15–20 times per hour.

The extraction with a particular solvent was interrupted when a 10 cm^3 aliquot, after being evaporated, did not leave any residue of the polymer. (The time for the extraction with a certain solvent was generally 35-40 hr.) The extracted polymer fractions were successively isolated by the evaporation of the solvent at a reduced pressure.

The residue was then dried on a steam bath at a pressure of 20 mm, until a constant weight was reached.

A detailed description of an extraction carried out with different solvents using polypropylene obtained with a catalyst of titanium trichloride and triethylaluminium, is described here. See Table 1 (run IV).

A sample of 13·07 g of powder of polypropylene, previously dried at a pressure of 20 mm, and at 80°C, was introduced in an extraction thimble of 33 per 94 mm size. The thimble was previously dried at reduced pressure and at 100°C until a constant weight was obtained.

First the extraction with acetone, covering about 12 hr, was started. Afterwards, having observed that, from the evaporation of a 10 cm^3 aliquot, no residue was left, the extraction was stopped. The solvent employed was then removed by heating *in vacuo*, while the thimble was dried on a steam bath at a pressure of 20 mm. The decrease in weight of the polymer after the extraction was 0·19 g.

The polymer which was left in the thimble was subjected to a further extraction with ether for about 40 hr. After that time we operated in the same way which has been previously described and we isolated 0·86 g of polymer.

Following the extraction with n-pentane, carried out for about 40 hr, and the evaporation of the solvent, 0·18 g of extract was isolated.

Then the extraction with n-hexane was carried out for the same length of time as the others, and 0·34 g of extracted fraction was isolated.

The polymer was finally extracted with n-heptane. The extracted fraction weighed 0·43 g. All these values were confirmed by the loss in weight of the residual polymer.

Operating at analogous conditions as previously described, an extraction with 2-ethylhexane and then with n-octane were also performed. The fraction extracted from 2-ethylhexane weighed 2·35 g, while the fraction extracted from n-octane weighed 2·12 g. The final residual polymer, following the n-octane extraction, was 6·6 g.

The result of the extractions was generally evaluated by considering the weight variations of the polymer after each extraction. Generally, we observed a very good agreement between the values thus determined and the values resulting from the weight of the extracted fractions.

(*c*) *Physical Measurements Performed on Different Extracts of Polypropylene*

I. *Intrinsic viscosities.* The intrinsic viscosities of polypropylene were determined in tetralin, using slightly modified viscosimeters of the DESREUX–BISCHOFF type.[11]

The solvent employed to carry out the measurements had been previously distilled under an inert atmosphere, and in the presence of hydroquinone. The volume of the solvent needed for the preparation

of the solutions was measured at room temperature. The intrinsic viscosity is expressed in 100 cm^3/g.

II. *Melting temperatures.* The melting temperatures were determined with a Leitz polarizing microscope equipped with a heating stage. The polymer, placed between two small glasses, at the temperature of about 200°C, was shaped under pressure to a thin lamina, then it was slowly cooled until a spherulite layer was formed. By heating slowly, with a maximum speed of 0·25–0·3°C/min, the melting temperatures were determined.

We considered as melting temperature, the point at which the spherulite birefraction disappeared.

With heating rates lower or equal to the above-mentioned ones, we found values which were in a very good agreement with those obtained by dilatometric methods.

(*d*) *Determination of the Mechanical Properties of Stereoblock Polypropylenes*

The samples which were subjected to the mechanical test, were prepared according to the ASTM D 412/51 T rules from small plates which were obtained by press-forging at 165–175°C in a press with parallel plates.

The traction test was carried out by means of an Amsler traction machine having a moving rate from the terminals of 50 mm per minute.

CONCLUSIONS

The extraction, by means of suitable solvents, of raw polypropylenes obtained with catalysts prepared from transition metals, and from metal alkyls of electropositive metals, allowed the separation of polymer fractions from isotactic and atactic stereoisomers. The polymers thus separated are chemically homopolymers as they are produced by a single monomer.

However, they consist of a succession of blocks of different steric structure; some of them consist of short-chain segments having a regular steric structure. The authors, therefore, called these polymers "stereoblock polymers".

An analytical method was developed to separate the isotactic polymers from the amorphous and from the stereoblock ones.

Using catalysts which do not have a very high stereospecificity,

heterogeneous products were obtained which contained a remarkable percentage of fractions constituted of stereoblocks, besides atactic macromolecules (non-crystallizable), and isotactic ones. With more stereospecific catalysts, it was possible to obtain products which prevailingly consisted of isotactic polypropylenes.

With catalysts obtained from titanium halides and aluminium alkyls it was possible to separate fractions of high molecular weight having a melting temperature of about 175°C, which did not vary even after further fractionation. Due to their high crystallinity in relation to their high molecular weight, one could attribute a highly isotactic structure to those fractions, which must be considered as practically free from stereoblocks.

The crystallinity of the isotactic polymers, which for polymers having an intrinsic viscosity lower than 2, may reach values of 80–90 per cent generally appeared lowered for these polymers having a much higher molecular weight, but the same melting temperature.

The statement of Schildknecht, [12] that no stereospecific polymerization process may give fractions constituted of molecules with a completely regular structure must therefore be limited to the catalytic processes used by Schildknecht and others, but cannot be extended to our systems.

Stereoblock polypropylenes having an intrinsic viscosity higher than 0·25, have melting points ranging between 100 and 170°C, which are lower than those of the highly isotactic polymers and than those of the mechanical mixtures of isotactic and of atactic polymers with high molecular weight.

The separation of fractions just consisting of stereoblock polypropylenes permitted us to find some particular mechanical properties, depending on the crystallinity and, therefore, on the proportion of segments of isotactic chains and on the molecular weight.

Stereoblock polypropylenes having a degree of crystallinity of about 25 per cent, and high molecular weights ($[\eta] > 1$), form a new class of elastomers, which, in their oriented state, exhibit high reversible elongations, and in some cases, ($[\eta] > 1{\cdot}5$), is higher than the 150 per cent.

For these polymers the crystallinity factor acts in the same way as the thermolabile vulcanization.

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A CRYSTALLIZABLE ORGANOMETALLIC COMPLEX CONTAINING TITANIUM AND ALUMINIUM

by G. NATTA, P. PINO, G. MAZZANTI and U. GIANNINI

(18 Feb. 1957)

[*J. Amer. Chem. Soc.* **79,** 2975 (1957)]

Following our previous researches[1] concerning the nature of the catalytic agent promoting the α-olefin polymerization, we have isolated a crystallizable compound containing titanium, aluminium and organometallic bonds, which causes the polymerization of ethylene.

By treating 0·01 mole of bis-(cyclopentadienyl)-titanium dichloride[2] suspended in 50 ml of n-heptane with 0·025 mole of triethylaluminium at 70°, in the absence of air and of moisture, a slow gas evolution takes place, the titanium compound is dissolved and the solution becomes dark blue. By cooling the solution at —50°, a blue crystalline solid has been obtained in good yield.

The macroscopic blue needles of the compound, recrystallized four times from n-heptane, melt at 126–130° without appreciable decomposition.

The blue compound contains titanium, aluminium, chlorine and organic groups; from the elementary quantitative analysis a ratio Ti:Al:Cl = 1:1:2 has been found.

The values 331 and 339 have been calculated for the molecular weight of the blue compound from two different cryoscopic measurements in benzene.

By treating the blue product with 2-ethylhexanol, ethane is evolved; a quantitative gas volumetric determination shows that two moles of ethane are evolved per mole of compound.

By treating the product with anhydrous hydrochloric acid in ether solution bis-(cyclopentadienyl)-titanium dichloride is formed in almost quantitative yield (more than 90 per cent).

The analytical data and the chemical behaviour agree very well with a formula $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$, as shown in the table.

	Calcd. for $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$	*Found*	
Cl, %	21·22	21·02*	21·78*
Al, %	8·073	7·92	8·90**
Ti, %	14·33	14·33	14·55**
$-C_2H_5$, %	17·40	16·07	17·67***
Mol. weight	334	331	339****

It seems probable that, in the complex, both C_5H_5-groups are bound to the titanium atom and that both C_2H_5-groups are bound to the aluminium atom.

By polymerizing ethylene in heptane solution in the presence of 0·6 g of the Ti–Al complex at 40 atm and 95° after a reaction time of 20 hr, 8·4 g of white polymer has been obtained, which has been fractionated by boiling solvent extraction (acetone extractable fraction 10·1 per cent; ether extractable fraction 1·8 per cent, carbon tetrachloride extractable fraction 17·20 per cent, residue 70·9 per cent having intrinsic viscosity in tetralin at 135° = 1·55 × 100 ml/g).

As it is reported in the next table, $(C_5H_5)_2TiCl_2$ alone is completely inactive for the ethylene polymerization; $Al(C_2H_5)_3$, according to previously published data,[3] does not give solid polyethylene in the reaction conditions, but only low molecular weight oily polymers. Comparative experiments were carried out at 95° and 40 atm.

Although the complex is a catalyst for the ethylene polymerization, less active than the catalyst prepared from $TiCl_4$ and $Al(C_2H_5)_3$, the composition of the complex strongly supports the hypothesis that the Ziegler type catalysts[4] for the polymerization of ethylene are, generally bimetallic complexes containing organometallic bonds.

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* Decomposition of the complex by Na_2O_2; chlorine has been determined by the Volhard titration.

** Decomposition of the complex by H_2SO_4 5 per cent; titanium has been determined as titanium cupferrate, aluminium as 8-oxyquinolinate, chlorine by gravimetric determination (I. Ubaldini and F. Capizzi, *Chimica e Industria*, **37** 779 (1955)).

*** By gas volumetric determination.

**** By cryoscopic determination in benzene solution.

Soluble catalyst		*Solvent*		*Reaction time, hours*	*Crystalline polyethylene, g*	*Oily polymers g*
Type	*Mole*	*Type*	*Cc.*			
$(C_6H_5)_2TiCl_2$	0·005	Benzene	100	20	0	0
$Al(C_2H_5)_3$	0·05	n-Heptane	300	8	0	11·07*
$(C_5H_5)_2TiCl_2$ $Al(C_2H_4)_2$	0·003	n-Heptane	40	8	7	0·4

* 66 per cent of the product consists of hydrocarbons lower than decane.

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33

STEREOSPECIFIC POLYMERIZATION OF α-OLEFINS. NOTE I

by G. NATTA, P. PINO and G. MAZZANTI

(6 Mar. 1957)

[*Gazz. Chim. It.* **87**, 528 (1957)]

ABSTRACT

This paper represents a preface to a series of papers on the stereospecific polymerization of olefins, diolefins and of a number of other vinyl monomers. The conditions that are essential for the obtainment of a sterically ordered macromolecular chain of a vinyl polymer are here discussed.

Two stereoisomeric structures, the isotactic and the syndiotactic one, are foreseen for a mono-olefin of the vinyl type $CH_2 = CH–R$, depending on the particular steric position of the —R— group. The authors first discuss whether it is possible to encounter the phenomenon of optical activity, due to the presence of asymmetric tertiary carbon atoms in the stereo-ordered macromolecules, which are derived from the polymerization of monomers of the type $CH_2 = CH–R$.

They have also examined the requirements for stereospecific syntheses of polymers, namely the conditions which are required to enable the monomeric units to be linked together in an orderly fashion and not only along the chain axis, but also in space. It was concluded that a head-to-tail linear polymerization of a vinyl monomer can yield stereoregular macromolecules, provided the entering position of the monomer with respect to the growing chain is constant.

Isotactic or syndiotactic macromolecules depending on the entering position of the monomer and on the mechanism of the addition to the double bond can be obtained.

Following the theoretical discussion, the authors described the procedure adopted for the synthesis and fractionation of stereoisomeric macromolecules starting from some α-olefins: propylene, butene-1, pentene-1 and 3-methylbutene-1.

From the polymers thus obtained, the fractions consisting of highly stereoregular macromolecules were easily separated from the "atactic" fractions by taking advantage of their lower solubility in some organic solvents. Following the same method of fractional extraction, it was also possible to separate fractions having a different degree of steric order or a different type of steric structure.

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STEREOSPECIFIC POLYMERIZATION OF α-OLEFINS. NOTE II. THE FIRST SYNTHESES OF LINEAR, ISOTACTIC AND NON-ISOTACTIC POLYMERS OF PROPYLENE

by G. NATTA, P. PINO, G. MAZZANTI and P. LONGI

(6 Mar. 1957)

[*Gazz. Chim. It.* **87**, 549 (1957)]

ABSTRACT

A study is reported of the polymerization of propylene in the presence of a catalyst obtained by reacting triethylaluminium and titanium tetrachloride in anhydrous hydrocarbon solvents and under an inert atmosphere.

It was found that both the composition and the activity of the catalyst, as well as the properties of the resulting polymer, depend on some factors, such as: the mole ratio of triethylaluminium per titanium tetrachloride; the time elapsed from the moment in which the above-said compounds are mixed together to the moment in which the catalyst is used in the polymerization of propylene (or in any case when it is decomposed and analysed). More precisely, it has been shown that when one increases the molar ratio of the $Al(C_2H_5)_3$ to $TiCl_4$ from 1 to 8, a marked increase of the catalytic activity occurs, up to a ratio value of about 2; then it decreases up to a value of 5 and at last keeps practically constant for higher values.

It has also been observed along with the high catalytic activity noticed for molar ratios, $Al(C_2H_5)_3/TiCl_4 = 2$, a marked decrease of the stereospecificity of the catalyst (measured on the percent basis of the highly isotactic polypropylene, obtained from the raw polymer by

extraction with boiling n-heptane), and also an appreciable decrease of the degree of polymerization.

With regard to the composition of the catalyst, a constant decrease of the chlorine content (ratio Cl/Ti), and a continuous increase of the Al content (Al/Ti ratio) up to a molar ratio of $Al(C_2H_5)_3/TiCl_4 = 3$, was observed.

The composition of the catalyst varies markedly with time, measured from the moment in which $Al(C_2H_5)_3$ and $TiCl_4$ are mixed together. This "ageing" has been observed not only by the constant decrease of the chlorine content and by the increase of the aluminium content, but, more evidently, by the decrease of the catalytic activity. It has been suggested that the decrease of the catalytic activity is independent of the fact that the catalyst, during ageing, is or is not used in the polymerization of propylene.

The polypropylenes obtained with the aid of a catalyst prepared from Al $(C_2H_5)_3$ and $TiCl_4$ were fractionated by subsequent extraction with the following set of solvents, at their boiling temperature: acetone, ether, n-heptane.

The fraction soluble in boiling acetone which was oily, and the one soluble in boiling ethyl ether which was gum-like, consisted of atactic polypropylene; the one soluble in boiling n-heptane was a solid product consisting of macromolecules of isotactic stereoblock polypropylene. The fraction insoluble in boiling n-heptane appeared as a water-white powder, and consisted of macromolecules of isotactic polypropylene, with a high regularity of steric structure and a melting temperature of 173—175°C.

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STEREOSPECIFIC POLYMERIZATION OF α-OLEFINS, NOTE III. POLYMERIZATION OF PROPYLENE WITH CATALYSTS HAVING A DIFFERENT DEGREE OF STEREOSPECIFICITY

by G. NATTA, P. PINO, G. MAZZANTI and P. LONGI

(15 Mar. 1957)

[*Gazz. Chim. It.* **87**, 570 (1957)]

ABSTRACT

A study of the polymerization of propylene with the aid of catalysts prepared from triethylaluminium and halides, alcoholates or chloro-alcoholates of tetravalent titanium, as well as from trivalent or bivalent titanium chlorides, is here described.

The catalytic activity and, in particular, the stereospecificity of these polymers are markedly different, depending on the valence of the titanium halide used. For instance, in the preparation of the catalyst, when titanium tri- or dichloride is used instead of titanium tetrachloride, it is possible to increase the n-heptane insoluble fraction of polypropylene from 35 to over 90 per cent.

The rate of polimerization shows a quite different behaviour, depending on whether the catalysts are prepared from titanium tetrachloride, or from solid tri- or dichloride titanium chlorides that are insoluble in the hydrocarbon solvents employed.

In fact the activity of the catalysts prepared from $TiCl_3$ and $TiCl_2$ is initially much lower than that shown by catalysts prepared from $TiCl_4$; but whereas the latter rapidly loose their activity, the catalysts prepared from $TiCl_3$ keep their catalytic activity almost constant for a long time.

The properties of the catalysts prepared from titanium chloro-

alcoholates are so much more similar to those of the catalysts prepared from $TiCl_4$, as the number of the chlorine atoms present in chloro-alcoholate gets nearer to four.

In case of a complete absence of halogens, as in the case of titanium tetra-alcoholate, the catalyst obtained from it proved to be practically unable to yield both atactic and isotactic polymers of propylene. The authors believe that this can be related with the fact that this catalyst is the only one (with respect to those which use titanium compounds, halogenated at least partially) which is formed in a very dispersed and unfilterable product. This hypothesis was confirmed, by the obtainment of a considerable increase of the catalytic activity and, to a lower extent, of the stereospecificity, when the catalyst obtained from $Al(C_2H_5)_3$ and $Ti(i\ O\ C_3H_7)_4$ was supported on alumina, silica or mixtures of the two.

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NEW SYNTHETIC ELASTOMERS*

by G. NATTA

(26 Mar. 1957)

[*The Rubber and Plastics Age*, **38**, No. 6 (1957)]

[*Chimica e Industria* **39**, 653 (1957)]

Our research on anionic polymerization processes in the presence of metallorganic compounds and on stereospecific syntheses, particularly of isotactic polymers, has already been the object of several publications.[1] Recently, they were partially summarized in a lecture held in London under the auspices of The Society of Chemical Industry.[2]

In that lecture I dealt principally with the results obtained in the field of highly crystalline poly-α-olefins, such as isotactic polypropylene, polybutene and polystyrene, which are of interest mainly in the field of plastic materials and textile fibres. In the present lecture I shall limit myself to recalling the principal results obtained by the Milan school in the specific field of the new elastomers in these last 3 to 4 years, a period which probably will be considered revolutionary in the history of synthetic rubber.

Our research in the field of elastomers has been carried out on two main lines:

1) The production of particular stereoisomers of polydiolefins having definite steric configurations
(2) The production of elastomers from linear olefin polymers and copolymers having very high molecular weight and improved resilience.

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* Lecture held at the International Synthetic Rubber Symposium, London, 26 March 1957.

G. NATTA

NEW STEREOISOMERS OF POLYDIOLEFINS

Whilst the research in my laboratory in the field of stereospecific polymerization was chiefly concerned with the new olefin polymers, we had started since 1953 the study of diolefin polymerization and this in close relation to the polymerization of ethylene with organic aluminium compounds. At the beginning of 1954, in parallel with the synthesis of isotactic and atactic poly-α-olefins by the use of a catalyst containing transition metals, we succeeded in polymerizing diolefins into polymers having prevailingly 1–4 structure.[3]

As isoprene was not available in Europe and we had to prepare and purify it ourselves, we concentrated our researches chiefly on butadiene.

A thorough investigation of the possible mechanisms of the new polymerization processes led to the discovery of different catalytic systems, which enabled us to obtain selectively not only diolefin polymers with substantially 1–4 arrangement or with substantially 1–2 arrangement, but also to reach a high degree of stereospecificity in the polymerization reactions.

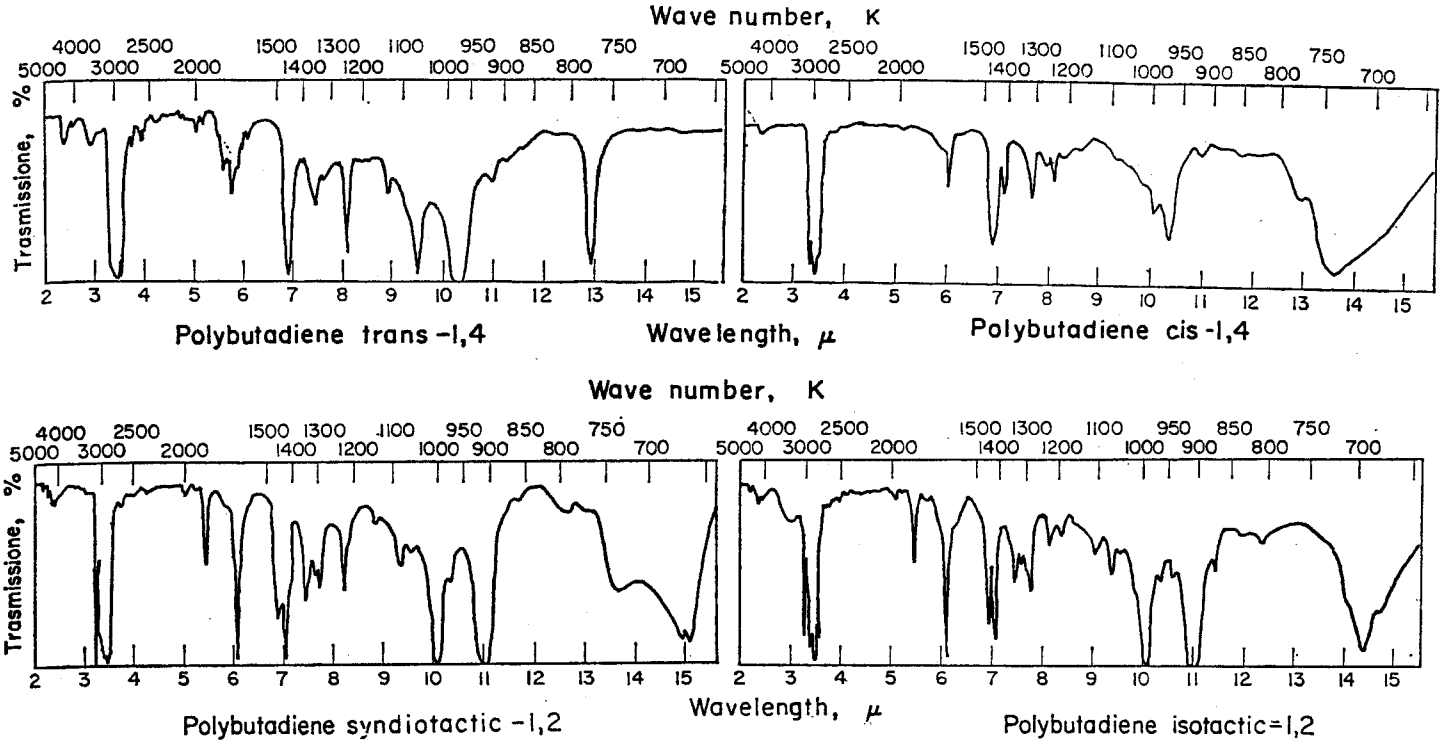
In fact, we succeeded in synthesizing many different stereoisomers of linear polybutadiene with a different crystalline structure, and four of them with a high crystallinity (Table 1). The most interesting are:

(1) crystalline *trans*-1,4 stereoisomers with more than 98 per cent purity, M.P. higher than 145°C.

TABLE 1. ROENTGENOGRAPHIC DATA ON CRYSTALLINE POLYBUTADIENE—STEREOISOMERS

Polymer	*Space group*	*Number of monomer per unit cell*	*Cell dimensions Å*		*Chain axis c*	α	β	γ	*X-ray density*	*X-ray melting point*
			a	*b*						
trans-1,4	(pseudohexagonal)	(1)	(4·54 Å)		4·9Å				1·02	148°C
cis-1,4	*C*2/*c* (monoclinic)	4	4·60	9·50	8·60	90°	109°	90°	1·01	(*)
syndiotactic-1,2	*Pacm* (rhombic)	4	10·98	6·60	5·14	90°	90°	90°	0·96	155°C
isotactic-1,2	*R*3*c* (hexagonal)	18	17·3	17·3	6·50	90°	90°	120°	0·96	125°C

(*) The melting temperature of pure *cis*-1,4 polymer is not known. The impure polymers have melting temperatures depending on composition and stress.



FIGS. 1-4. Infrared spectra of average samples of the four different crystallizable polybutadienes.

(2) *cis*-1,4 stereoisomers sufficiently pure to be slightly crystalline, their crystallinity strongly increasing on stretching at room temperature.

(3) amorphous or slightly crystalline *cis-trans*-1,4 copolymers.

(4) crystalline syndiotactic 1,2 stereoisomers, M.P. higher than 155°C.[4]

(5) crystalline isotactic 1,2 stereoisomers, M.P. higher than 125° C.[5]

(6) amorphous atactic 1,2 polymers.[4]

The infrared spectra of average samples of the four different crystallizable polybutadienes are given in Figs. 1–4.

In Fig. 5 the Geiger registrations of the X-ray spectra of the different stereoisomers are shown. The structure of said polymers in the crystalline state are indicated in the following figures.

A model of the structure found by us for crystalline *cis*-1,4 polybutadiene[6] is shown in Fig. 6.

The value found by us for the identity period (8·60 Å) is less than that (8·75 Å) indicated by Aries in a lecture held at Atlantic City.[7] The identity period indicated by him apparently corresponds to the approximate value foreseeable for a complete planar chain.

The hypothesis that the main chain should be planar, and hence should differ in the length from that found for *cis*-1,4 polyisoprene,

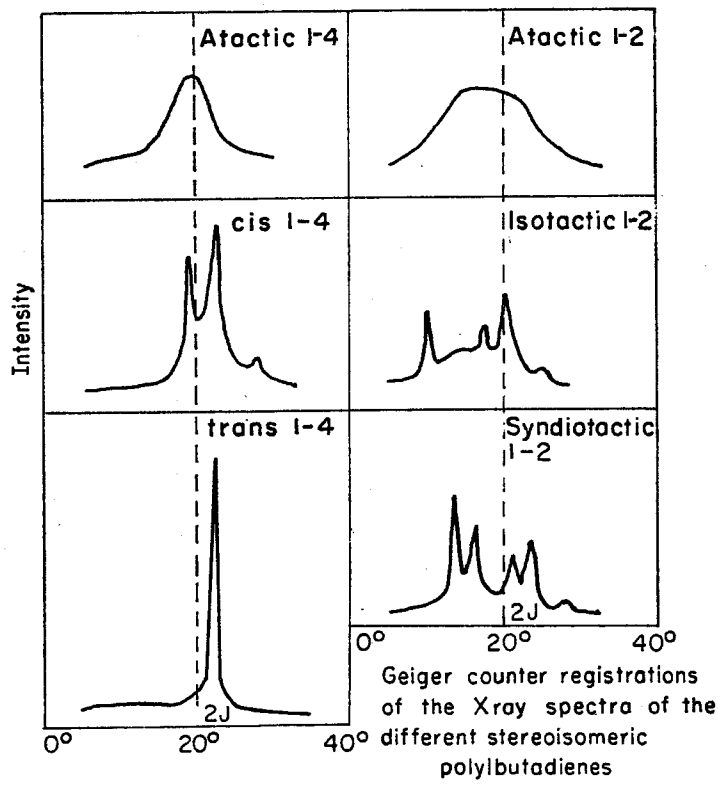


FIG. 5. Geiger registrations of X-ray spectra of different stereoisomers of polybutadiene.

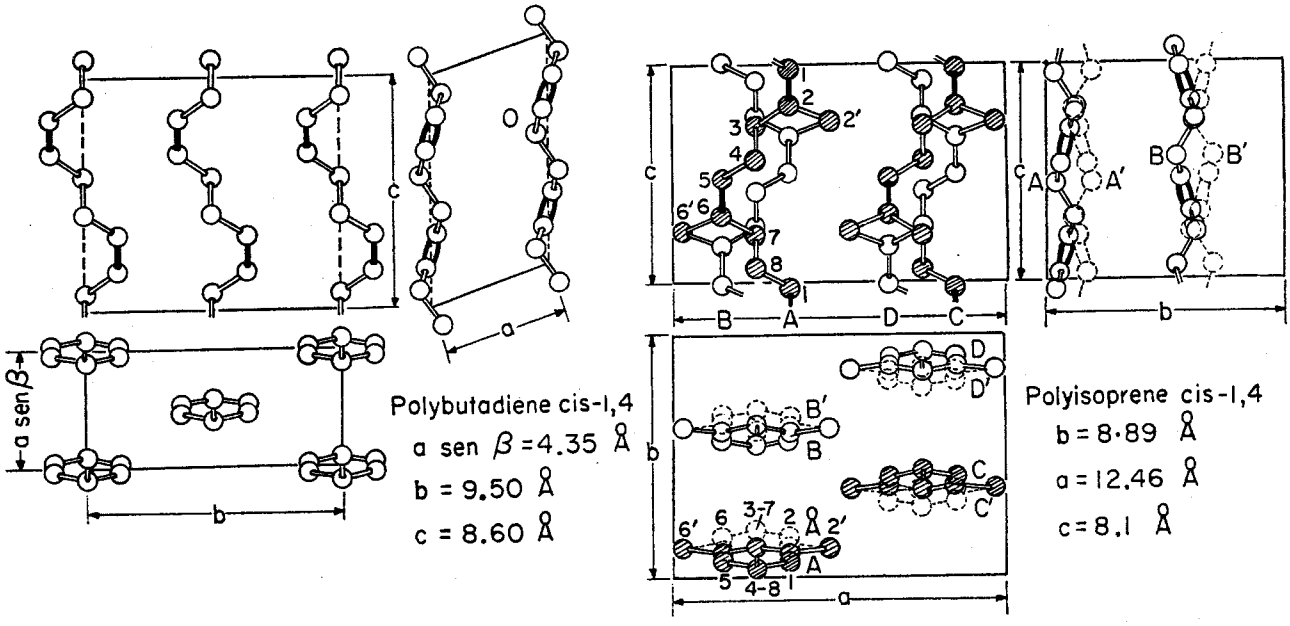


FIG. 7. Comparison of structure of *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene.

appears to be justified by the absence of lateral methyl groups. Due to unsuitable methyl contacts it is most likely that the said methyl groups present steric hindrance to the planarity of the chain,

this being probably only one of the reasons which cause the polyisoprene chain to deviate from planarity.

Actually, as already supposed by Bunn, there is a tendency for the C–C single bonds to stagger and therefore a staggered saturated portion of the chain cannot lie in the same plane with an adjacent double bond. Actually in the chain of crystalline *cis*-1,4 polybutadiene the succeeding monomeric units are contained in planes which are parallel but not coincident. The staggering is not, however, complete owing to the repulsion between two approaching hydrogens of the methylenic groups. Thence, the identity period actually found (8·6 Å) is greater than the one which could be expected from a perfect staggering of single bonds.

The structure of *cis*-1,4 polybutadiene and of *cis*-1,4 polyisoprene are compared in Fig. 7.

The crystalline polyisoprene structure proposed by us was in fact very similar to that suggested by Nyburg,[8] the only difference stressed by us being the statistical distribution of the successive layers of differently orientated chains.

In the case of the other stereoisomeric crystalline polybutadienes no steric factor hinders the staggering of single bonds, and in fact the staggering is found to be perfect (Fig. 8). In Fig. 9 models of the structures found by us for isotactic and syndiotactic polybutadienes, are shown. Isotactic polybutadiene shows a helicoidal chain configuration,[9] with threefold symmetry similar to that of poly-α-butene.[10] The relating projection normal to the chain axis is shown in Fig. 10. The electron density maxima show a statistical distribution of up and down molecules in the same lattice sites (Fig. 11).

Syndiotactic polybutadiene has a chain along which enantiomorphic units alternate[11] (Fig. 12).

The pure high-melting-point crystalline stereoisomers are not elasto-

TABLE 2. REBOUND (*) OF SOME CURED POLYBUTADIENES (SUBSTANTIALLY AMORPHOUS AFTER CURING)

	Rebound at	
	20°C %	*90°C* %
trans-1,4 ...	75—80	90—93
prevailingly *cis*-1,4	88—90	92—95
1-2	45—55	90—92

(*) ASTM D 1054-49T.

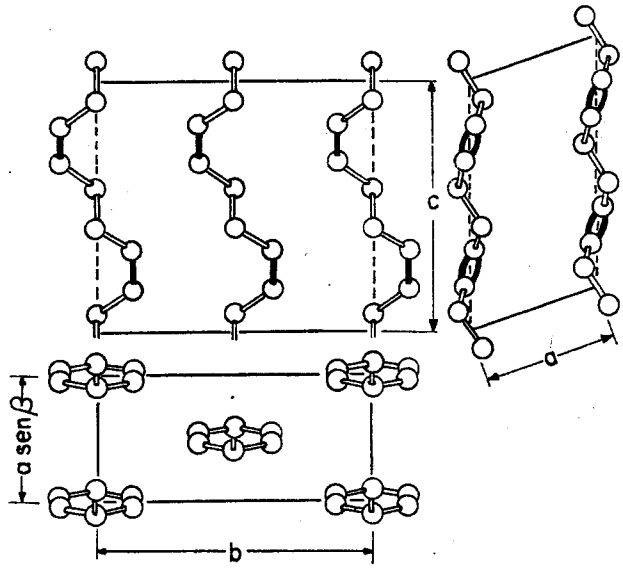


FIG. 6. Model of structure for crystalline *cis*-1,4-polybutadiene.

mers at room temperature, unless their crystallinity is considerably reduced.

(*cis* or *trans*) 1,4 products have, in the amorphous state, excellent resilience.

Amorphous 1,2 polymers have lower resilience than amorphous 1,4 polymers because of lesser flexibility of the saturated main chain, which does not contain the more freely rotating single bonds adjacent to double bonds (Table 2).

It is interesting to note that the resilience of atactic 1,2 polybutadiene, which increases rapidly as the temperature goes up, is much higher than that of atactic poly-α-butene also at room temperature; 1,2 polymers, because of their vinyl side groups, are very reactive and this can favour their use even outside the field of elastomers.

Among 1,4 butadiene polymers, those possessing a *trans* structure (*trans* double bonds $>$ 98 per cent of total) are highly crystalline[12] and have a very high melting point (140–148°). They can be used for the production of hard rubber characterized by a high modulus only if the crystallinity is reduced. If suitably cured, they have good resilience values, even at room temperature.

The presence of small quantities of *cis*-1,4 monomeric units in the mainly *trans*-1,4 polymer lowers its crystallinity considerably and also its melting point, and 1–4 polymers, rich in the *trans* form, which melt at lower temperatures (even below 100°) are easily obtainable.

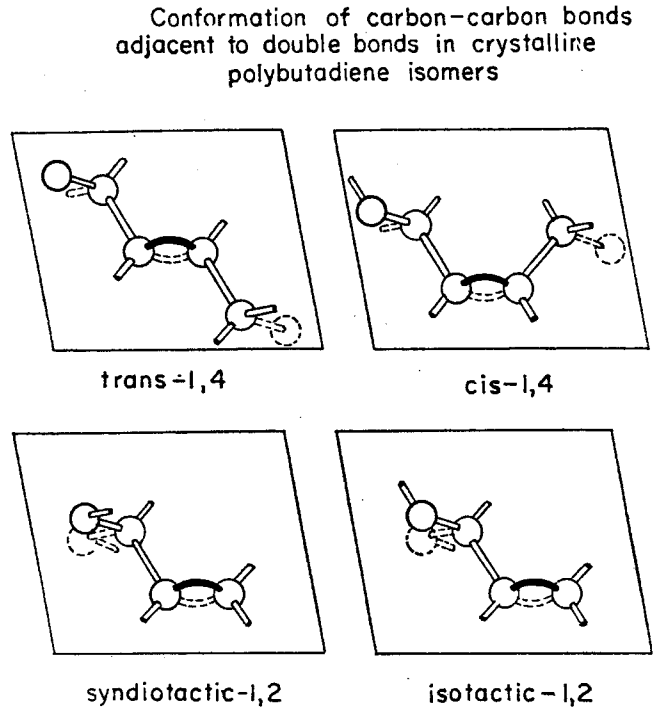


FIG. 8. Staggering of single bonds in stereoisomeric crystalline polybutadienes.

The resilience of *cis*-1,4-polybutadiene is very near to that of *cis*-1,4 polyisoprene. The mechanical and particularly the elastic properties of *cis*-1,4 polybutadiene depend obviously on its steric purity, and in fact impure not crystallizable polymers have a stress-strain diagram

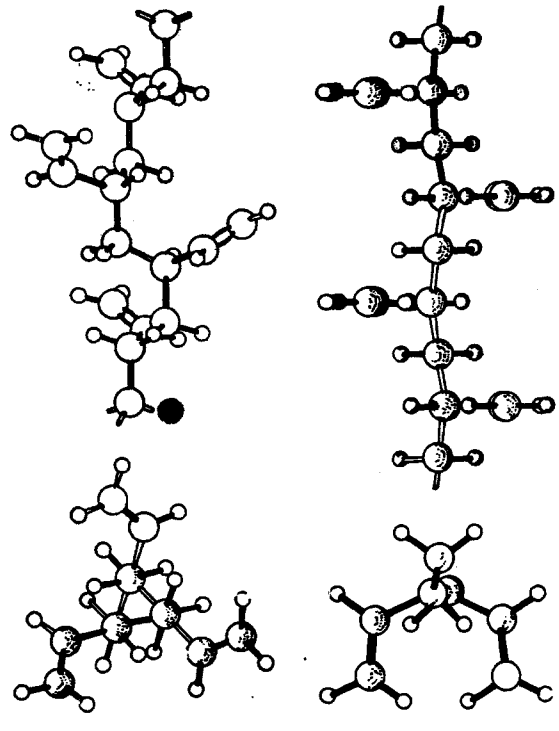


FIG. 9. Model of structures for isotactic and syndiotactic polybutadienes.

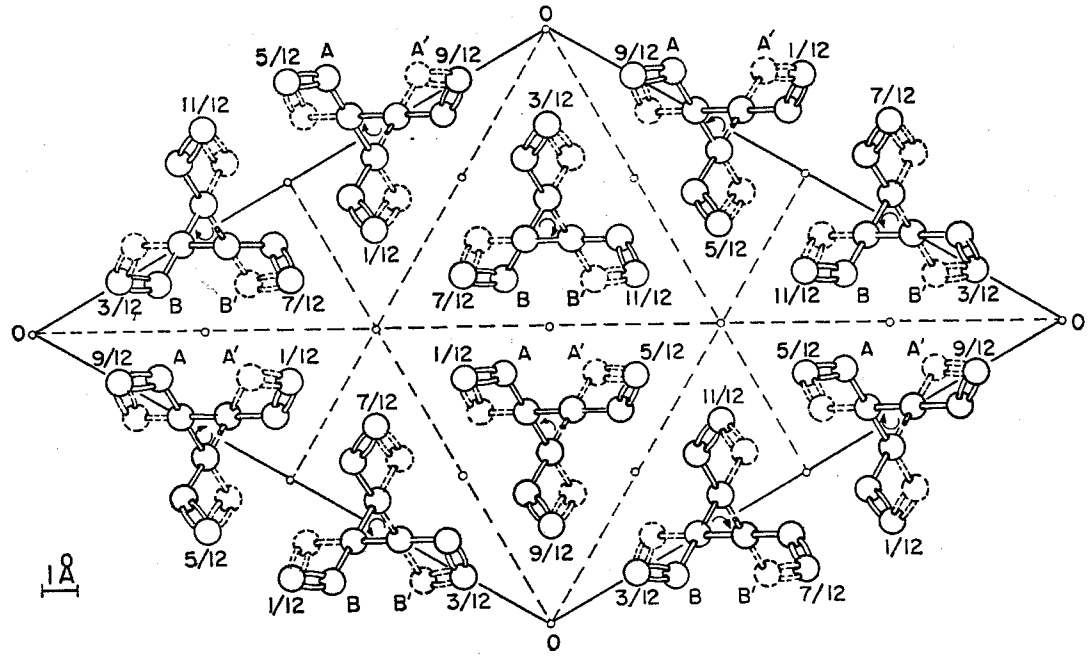


FIG. 10. Projection normal to chain axis of isotactic 1,2-polybutadienes.

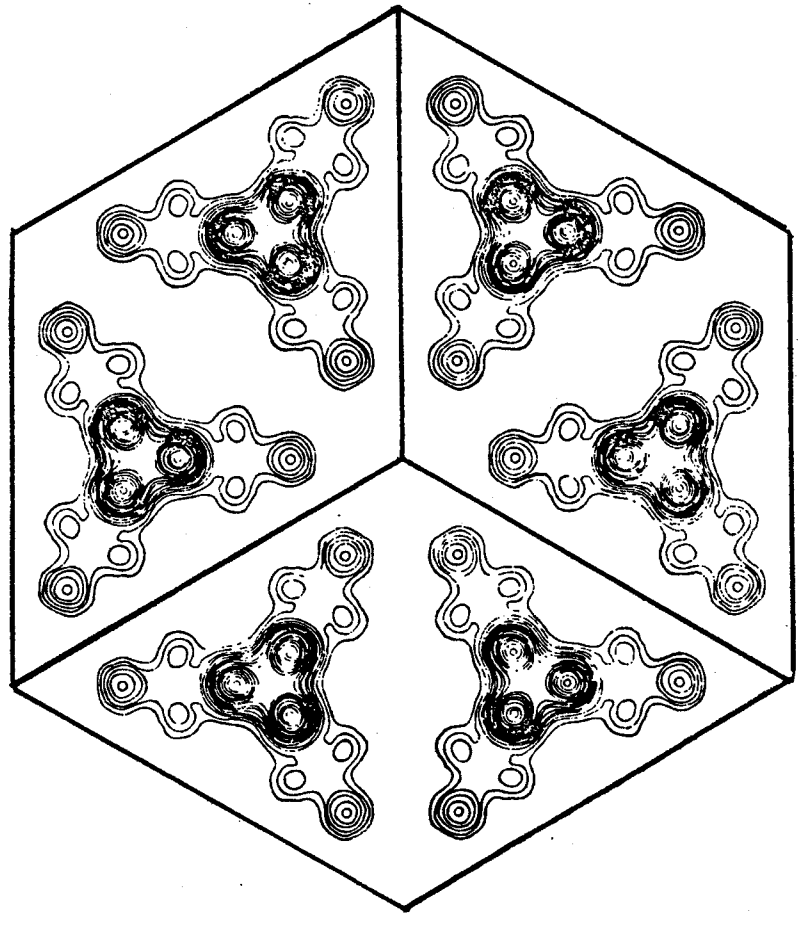


FIG. 11. Statistical distribution of up and down molecules in same lattice site (isotactic poly-α-butene).

which differs considerably from typical diagrams of rubbers which crystallize under stretching.

The preparation, with high yield, of the pure linear *cis*-1,4 stereoisomer, free of cross-links, and with a molecularweight exceeding 200,000, presents more difficulties than the preparation of the other stereoisomers, although recently great progress has been made.

Figure 13 shows a comparison between two X-ray spectra of relaxed and stretched samples of polybutadiene, cured with standard recipe containing ZnO as activator. They show the crystallization under stretching of the *cis*-1,4 isomer. Fig. 14 reproduces the spectra of a *cis*-1,4 polybutadiene cured in the absence of ZnO activator.

The properties of the polymers with 1–4 arrangement containing both the *cis* and *trans* forms, depend on the way the monomeric units, having different steric configurations, are distributed along the chains. The properties of a polymer constituted by macromolecules having a random distribution around a certain average value of *cis* and *trans* double bonds differ considerably from those of polymers having the same average stereoisomeric composition, but constituted by mixtures

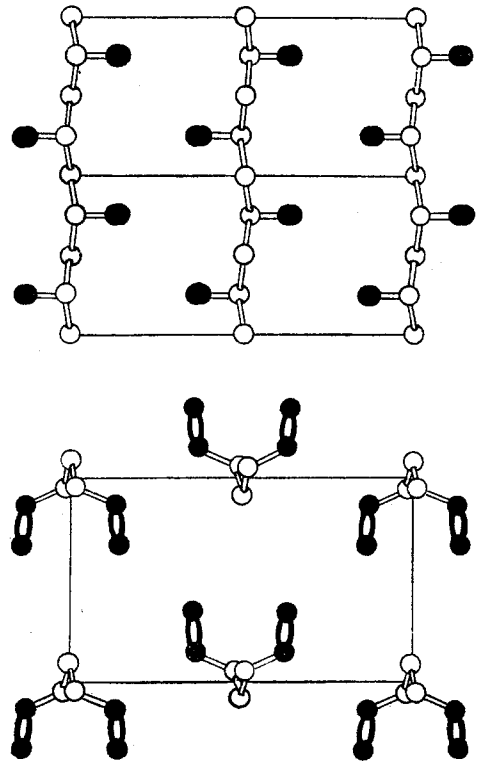


FIG. 12. Alternating enantiomorphic units along syndiotactic polybutadiene chain.

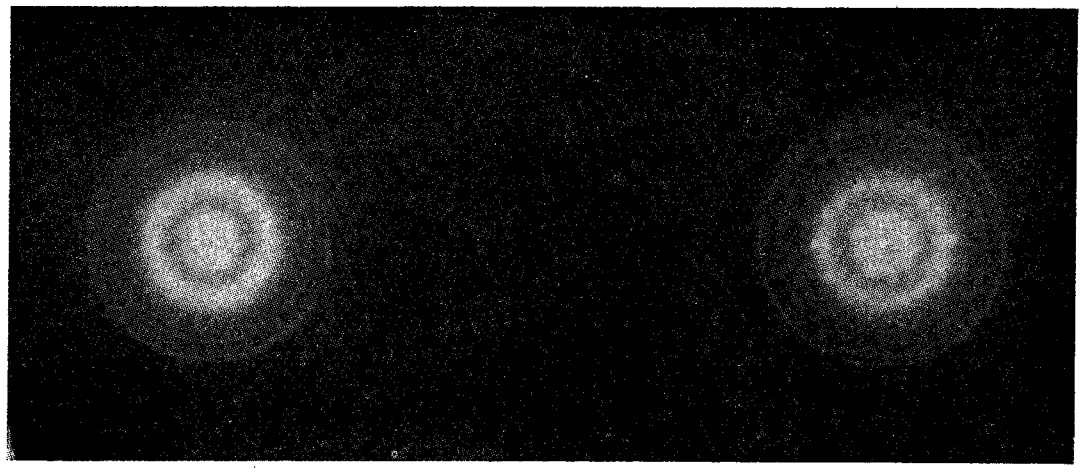


FIG. 13. X-ray spectra of relaxed and stretched polybutadiene cured with standard recipe containing zinc oxide.

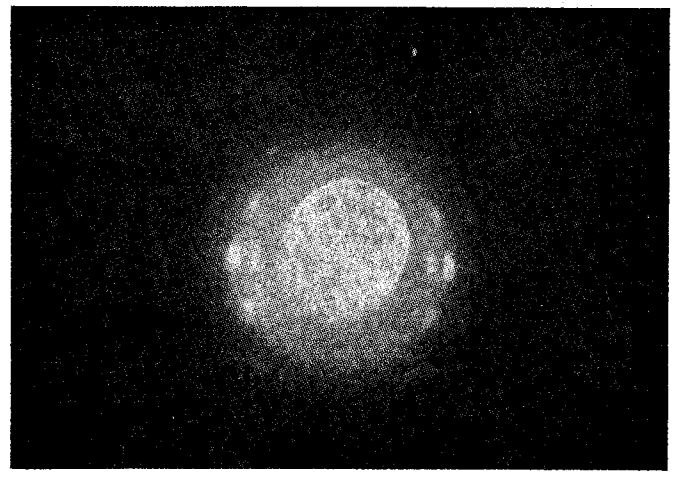


FIG. 14. Spectrum of *cis*-1,4 polybutadiene cured in absence of zinc oxide.

of macromolecules widely different from each other in the steric composition.

The possibility therefore clearly emerges of obtaining a large number of different products with different properties, and I believe that further extensive research will be necessary for a thorough study of the properties of the new stereoisomeric polydiolefins.

The stereoisomeric purity is not the only factor which determines the properties of a polymer. The way the impurities are distributed is of enormous importance. A limited percentage of sterically different and random distributed units should be in theory sufficient to destroy the X-ray crystallinity of a 1–4 stereoisomer of a diolefin, whilst products of every composition are crystalline when the sterically different units are distributed in blocks.

One cannot therefore relate properties with stereoisomeric composi-

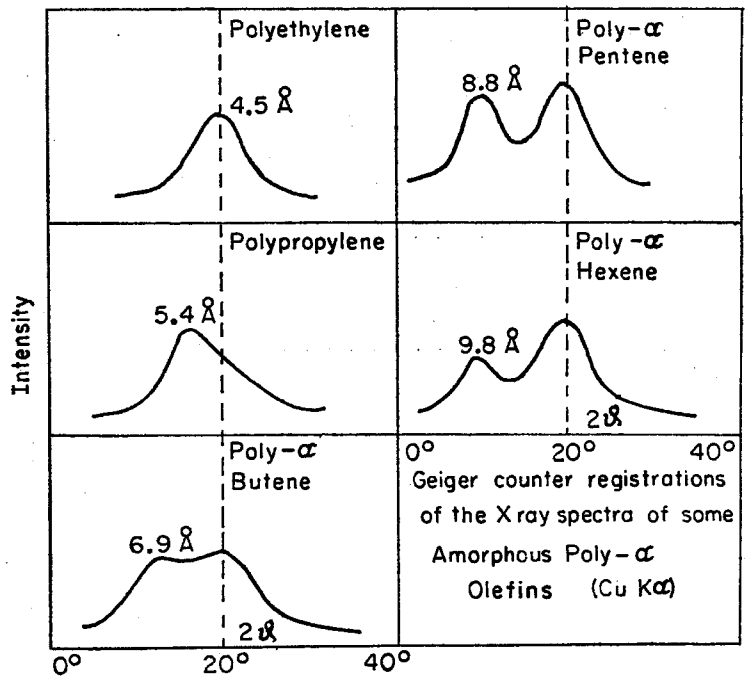


FIG. 15. X-ray spectra of some amorphous linear poly-α-olefins.

tion unless, besides this, the way in which the stereoisomeric units are distributed is known. This is the principal reason for our so cautiously describing the properties of the new products and in particular the mechanical properties which especially depend on the way in which the stereoisomeric units are distributed in the individual chains.

α-OLEFIN POLYMERS

One may estimate the costs of the different olefins (propylene, ethylene, butylene) to range between 1/3–1/5 of that of butadiene, whilst the cost of the pure commercial isoprene is expected to be higher than that of butadiene. We are therefore of the opinion that due to the low cost of the raw materials the new olefinic rubbers are worthy of considerable attention.

Already during our researches on α-olefin polymerization with the new anionic processes at the beginning of 1954, we found that stereospecificity and activity of the catalyst are two independent properties and that it is possible by using certain types of catalysts, to obtain crystalline polymers (isotactic), whilst with other types, amorphous polymers (atactic) are obtained.[13]

We had also found that said atactic polymers greatly differ from α-olefin polymers obtained by conventional processes (which act by means of cationic or radical mechanism). Further researches enable

us to obtain very high molecular weight polymers (over 100,000) with linear structure, practically without branchings, and with a random distribution of *d* and *l* monomer units.[14]

Most of the chains are of the following type:

$CH_2 = CR–CH_2–CHR \ldots\ldots\ldots\ldots CH_2–CHR–CH_2CH_2R$

In the case of propylene:

$CH_2=CHCH_3–CH_2–CHCH_3 \ldots\ldots\ldots CHCH_3–CH_2CH_2CH_3$

This implies that they contain vinylidene terminal groups and n-propyl, n-butyl, etc., terminal groups according to the monomer taken into consideration. The presence of long branches cannot be made apparent by conventional methods.

Poly-α-olefins known beforehand, obtained by cationic polymerization, have completely different structures, with vinyl and isopropyl terminal groups, branchings and irregularities of different types.

The atactic polymers with linear structure produced by us have properties of unvulcanized elastomers when the molecular weight is sufficiently high. In Fig. 15 the X-ray spectra of some amorphous, linear poly-α-olefins are shown and they can be related with the linearity of the main chain. Indeed, the amorphous maximum is shifted to low angles as a function of the bulkiness of the side groups, and therefore of the distance between the main chains.

Before our findings only two types of aliphatic olefins having highly linear structure and high molecular weight were known: polymethylene and polyisobutylene.

The first is not an elastomer, at least at room temperature, being a high-melting crystalline polymer. The second can give elastomers but has the drawback of low resilience at room temperature.

The advantage of the new amorphous poly-α-olefins is that they behave like elastomers whose chains, at temperatures far from the transition temperature, are more flexible than those of polyisobutylene. Actually, the steric hindrances to the rotation around the C–C single bonds in the main chain, owing to the presence of only one side group bound to a tertiary carbon atom, are smaller than those observed when two side groups are bound to a quaternary carbon atom in the chain.

The comparison between the elastic properties of rubber obtained from different α-olefins indicates that resilience at room temperature increases with an increase in the length of the side-chains. This is in relation also with the variation of the transition temperature, which

TABLE III. REBOUND (*) OF SOME COPOLYMERS, HAVING A HIGH OLEFIN CONTENT

	Rebound at	
	20°C %	*90°C %*
Ethylene-propylene (35–65% C_2H_4)	55–65	65–80
Ethylene-propylene-isoprene (< 10% C_5H_8)	50–65	65–80
Propylene-isoprene (< 10% C_5H_8)	18–20	55–65
Butyl rubber	16–21	55–60

(*)ASTM D 1054-49 T.

decreases as the length of the linear side groups increases (from C_1 to C_4).

Alpha-olefin copolymers show, in general, lower transition temperatures than the corresponding homopolymers, and higher resilience.

Ethylene-propylene copolymers, and in particular those very rich in ethylene, show very high resilience value although they are saturated macromolecules (Table 3).

The causes are to be found in:

(1) Increase in chain flexibility because of reduced steric hindrance to rotation around the $-CH_2-CH_2-$bond, compared with the $-CH_2-$CHR-bond.

(2) Lower second order transition temperature of the copolymer, compared with amorphous polypropylene.

(3) Hindered crystallization of the unstretched polyethylene chain due to the random distribution of propylene units in the chain.

The best values of the elastic properties are obtained with the lowest propylene percentages (Fig. 16), which are sufficient to prevent the crystallization of polyethylene in the unstretched state. Theoretically very small propylene percentages should be sufficient for this purpose as long as they are randomly distributed and not concentrated in some of the macromolecules or in certain parts of each of them. At the beginning we have met some difficulties in obtaining homogeneous copolymers free of homopolymers or of mixtures of copolymers of very different composition and also in obtaining high molecular weight polymers. It is to be emphasized that the properties of the crude polymers are very different, depending on the way they have been prepared, and on their degree of heterogeneity.

These difficulties have been overcome by using suitable catalytic systems[15], by means of which the ratio between the growth rates of the chains of each monomer remains constant with time and is not sensibly

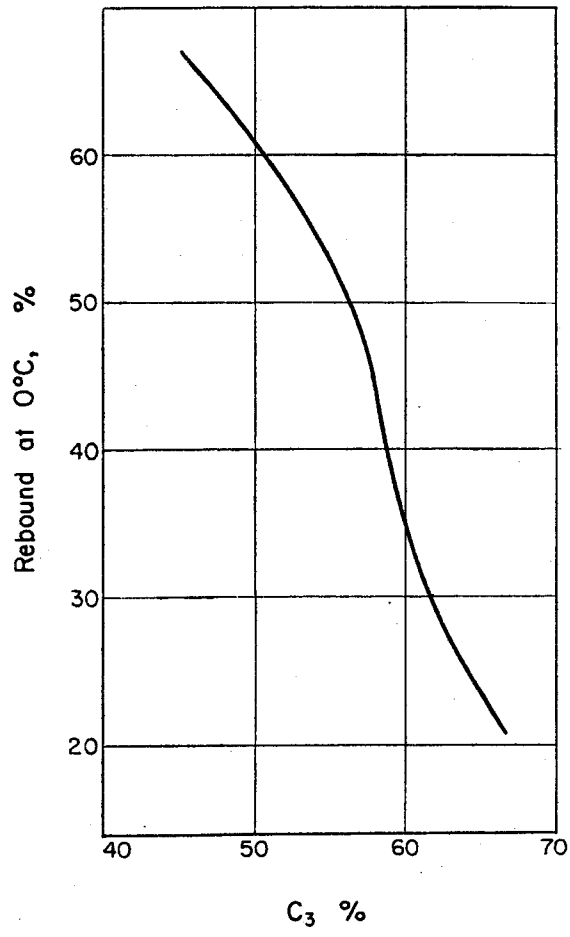


FIG. 16. Elastic properties of ethylene-propylene copolymers. Best values at lower propylene percentages.

modified by the nature of the last monomer unit linked with the growing chain. This last condition must be fulfilled if random distribution is desired and the formation of blocks is to be avoided.

Uncured atactic polyolefins and amorphous olefin copolymers, also with molecular weight of the order of hundreds of thousands, still have considerable creep properties under prolonged stress.

The problem of avoiding creep has been solved by us in different ways.

(a) By chemical vulcanization processes which lead to formation of bridges between the chains, and some of which are known to be used for other elastomers.

(*b*) By processes which we consider as physical vulcanization processes in which the forces opposing creep depend on the binding energy in crystalline microelements.

Many chemical methods have been used successfully by us, and we would like to mention only the most practical ones:

(1) Random copolymerization with small quantities of diolefins and other monomers with reactive groups, as for butyl rubber.

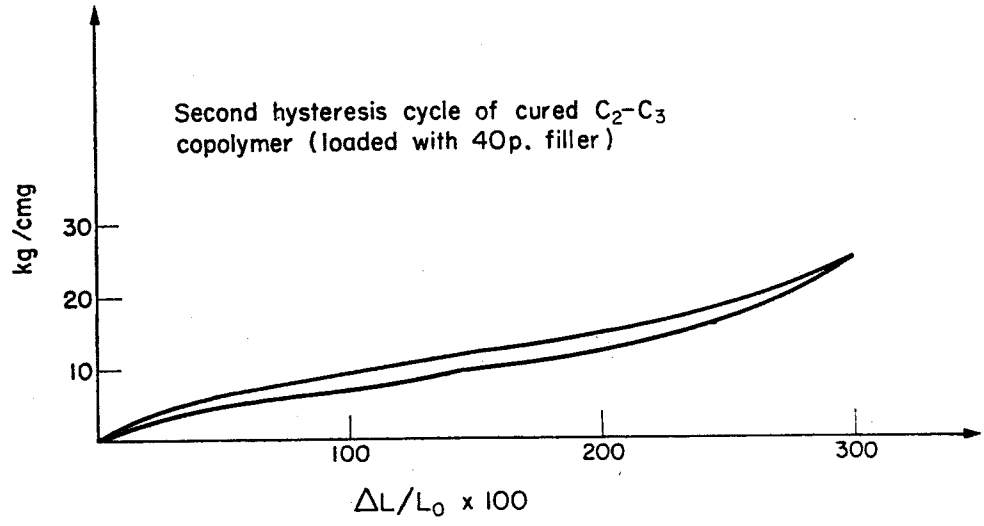


FIG. 17. Second hysteresis cycle of cured C_2—C_3 copolymer (loaded with 40 parts filler).

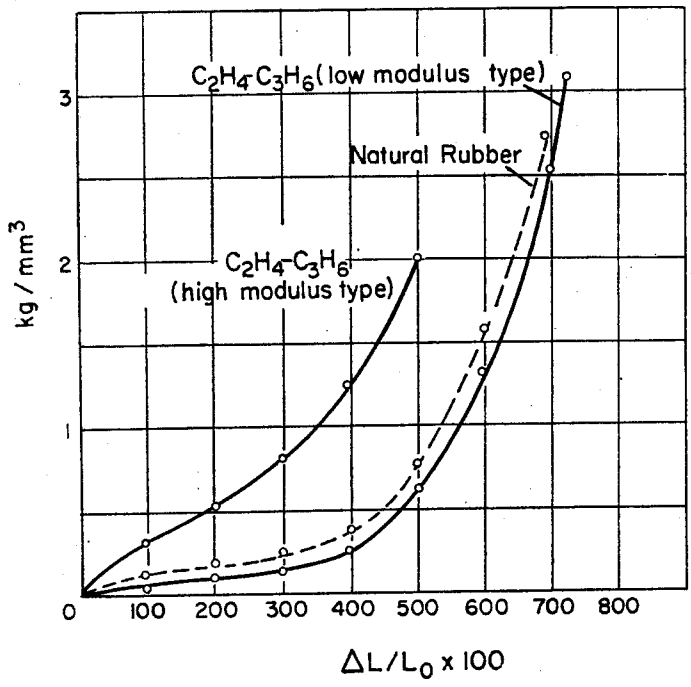


FIG. 18. Stress–strain curves of ethylene-propylene copolymers.

(2) Introduction into the macromolecules of acidic groups (e.g. SO_3H, SO_3Cl, COOH, etc.), or basic groups with the formation of polyvalent acids or bases respectively.

(3) Other methods based on the great reactivity of the tertiary carbon atom, causing cross-links between the chains.

In Figs. 17 and 18 are shown some characteristics of rubber obtained with ethylene-propylene copolymers. The polymers have stress–strain curves characterized by very low initial elastic moduli and by very high tensile strength and reversible elongation, without reinforcing

fillers, like polymers which crystallize under stretching. This is probably due to portions of chains having regular structure and being constituted of methylene sequences.

Rebound properties are somewhat inferior to those of natural rubber and *cis*-1,4 polybutadiene; however, they are fairly good, better than GR-S rubber.

We think that ethylene-propylene copolymers will prove to be of great practical interest.

In respect of what we consider physical vulcanization processes, we have observed properties like vulcanized products in some ethylene copolymers and also in linear α-olefin homopolymers, when these are built up by stereoblocks giving very low crystallinity. In the case of poly-α-olefins, stereoblock macromolecules are characterized by the fact that they contain ordered chain portions with ordered structures which are of short length, compared with the total length of the macromolecules.[16]

A plausible model of a stereoblock macromolecule may be given for instance by a chain built up by portions of variable lengths, each of these portions being constituted of monomeric units with the same steric configuration, alternating with portions in which the monomeric units have opposite configurations.

Elastomeric properties are observed when short portions of isotactic chains, sufficiently long to crystallize, alternate with large portions which are not crystallizable (Fig. 19).

These stereoblock polymers have a melting point which is remarkably lower than that of pure isotactic polymers. For example, in the case of polypropylene, polymers having 15–25 per cent crystallinity melt completely at 110–120°, but, notwithstanding the fact that they contain microcrystals, they maintain elastomeric properties even below room temperature.

Elastomeric properties are evident in products which have been restretched (e.g. a fibre or a sheet pre-stretched in one direction up to a temporary elongation of about 700 per cent).

The stress–strain graphs (Fig. 20) of these stereoblock polymers are characterized by initial elastic moduli which are not very high, by elastic elongations of about 100–200 per cent (increasing with molecular weight and decreasing with crystallinity), and by very high tensile strength. In the case of very high molecular weight polymers creep is very limited.

An interesting characteristic of the stereoblock polymers is that,

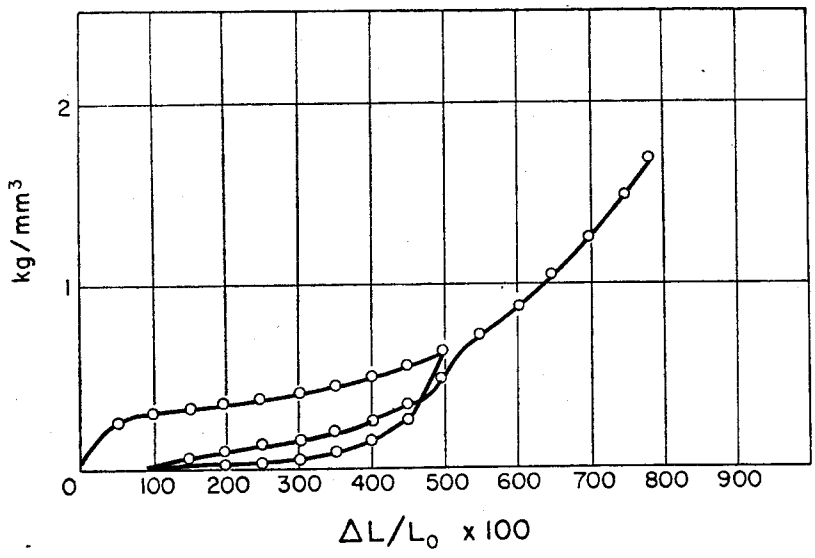


FIG. 19. Elastomeric properties of stereoblock macromolecules when short portions of isotactic chains alternate with non- crystallizable large portions.

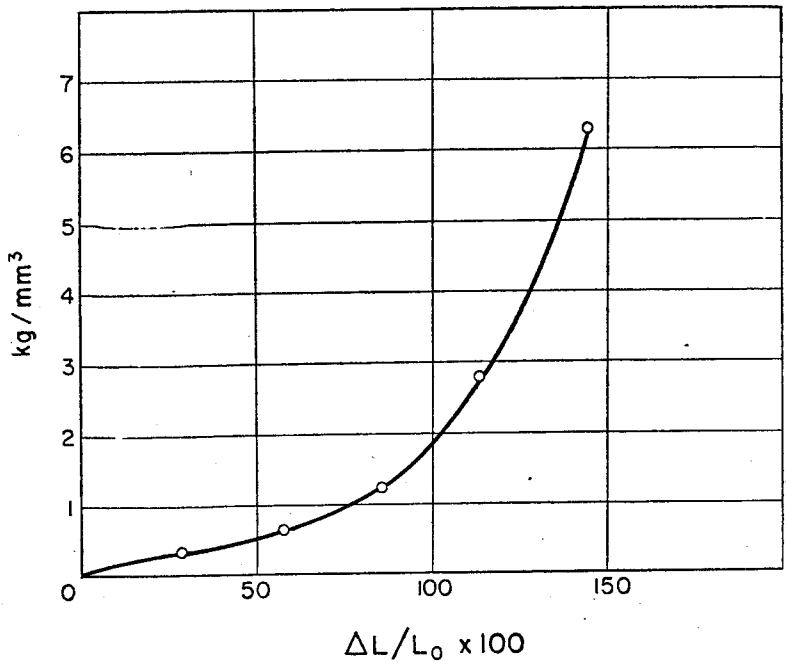


FIG. 20. Stress–strain curves of pre-stretched stereoblock polymers

contrary to the chemically vulcanized elastomers, they can be melted and moulded again at temperatures above the melting point, because the material keeps unchanged its thermoplastic properties as well as the property of orientating itself and of crystallizing under stretching.

CONCLUSIONS

From the points briefly set out above we can conclude that the new polymerization processes have allowed us to obtain new classes of very high molecular weight, and substantially linear macromolecules, and

to isolate, in the case of diolefins and α-olefins, new crystalline and amorphous stereoisomers.

Not only is the field of plastic materials interested in this evolution of macromolecular chemistry, but we can foresee consequences and important developments also in the field of synthetic rubber.

Although recent literature has pointed out that the American industry is strongly interested in synthetic polyisoprene obtained from costly isoprene, I would say that interest should be devoted also to rubbers from special butadiene stereoisomers and particularly to rubbers obtained from the very much cheaper α-olefin copolymers.

Although their low temperature resilience is not so high as that of natural rubber or of *cis*-1,4 polybutadiene, ethylene–propylene copolymers have sufficiently good resilience values and high mechanical strength. Their chemical and ageing resistance is far superior to those of the known synthetic unsaturated rubbers.

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DISCUSSION

Dr. W. Cooper — (Dunlop Research Centre):

Q.—I wonder whether Professor Natta could comment on the conditions where the 1,2 structure groups in polybutadiene do not act as olefins to cause the polymerization to form branched molecules.

A.—We use a catalyst which cannot polymerize α-olefins. Of course, if you employ a catalyst which can also polymerize α-olefins you can obtain a branched polymer, but if you employ a catalyst which cannot polymerize α-olefins it is possible to obtain linear 1,2 polymers.

Dr. G. Kraus—(Phillips Petroleum):

Q.—Do you disclose in which way the low modulus and high modulus ethylene/propylene copolymers differ? What gives you high modulus in the one instance and low modulus rubber in the other?

A.—We use different curing conditions.

Q.—Is this in each case chemical vulcanization?

A.—Yes.

L. R. Mernagh—(Firestone—Great Britain);

Q.—What is the maximum *cis*-1,4 content of any polybutadiene polymer produced to date?

A.—It is difficult to say because we had no 100 per cent *cis*-1,4 polybutadiene available to determine exactly the I.R. absorption co-

efficients. One can estimate between 80 to 90 per cent, but the analytical methods must be controlled.

One sample of polybutadiene rich in *cis*-1,4 units is shown in Fig. 2.

Dr. W. Cooper:

Q.—In the case of polybutadiene polymerization, do you find it possible to go to very high conversions? Can you continue to polymerize until all the butadiene has been polymerized without any sacrifice in physical properties of the polymer?

A.—That depends on a number of factors, like concentration, etc. It is very variable: it depends on catalyst and operating conditions. In dilute solutions it is possible to obtain very high conversion, but generally it seems preferable to stop the polymerization at about 50 per cent conversion.

37

THE NATURE OF SOME SOLUBLE CATALYSTS FOR LOW-PRESSURE POLYMERIZATION OF ETHYLENE

by G. NATTA, P. PINO, G. MAZZANTI, U. GIANNINI, E. MANTICA and M. PERALDO

(28 March 1957)

[*J. Polymer Sci.* **26,** 120 (1957)]

Letter to the Editor

For the substantial contents:

SEE PAPER 27, P. 181.

38

KINETICS OF CHAIN GROWTH AND TERMINATION PROCESSES IN THE STEREOSPECIFIC POLYMERIZATION OF PROPYLENE

by G. NATTA, I. PASQUON and E. GIACHETTI

(3 July 1957)

[*Makromol. Chemie*, **24**, 258 (1957)]

ABSTRACT

This is a study of different factors which exert an influence on the molecular weight and on the steric purity of isotactic polypropylene obtained with a catalytic system prepared from α-$TiCl_3$ (violet modification) and $Al(C_2H_5)_3$.

The $\alpha TiCl_3$ was previously ground. When using these catalytic systems, the apparent energy of the overall polymerization process, (referred to the olefin in the diluted phase) was equal to 11,000–12,000 cal/mol.

It has been observed that the molecular weight of the polypropylene obtained, decreased with the increase of both the concentration of alkyl aluminium and of the amount of $TiCl_3$ present in the system, whereas it slightly depended on the partial pressure of propylene (when operating at partial pressures above some hundreds of mm Hg). When the temperature was lowered, a slight increase of the molecular weight occurred.

The results obtained were interpreted by assuming that the polymerization process of propylene, with the catalytic system used, was related to the following termination processes of the polymeric chains (which must be distinguished from the termination processes of the kinetic chains):

— A process which can be compared with a monomer chain transfer.

— A process of alkyl exchange between growing polymeric chains and organometallic compounds in solution.

— A dissociation of the active chains into an active hydride. None of these processes gives rise to the termination of the kinetic chains.

The activation energy of the quantitatively most important termination processes of the polymeric chains (monomer transfer and alkyl exchange with the organometallic compounds in solution) are slightly different from the activation energy of the propagation process of the polymeric chains.

The kinetic mechanisms of the formation of different stereoisomeric types of polymer are of the same type, independently of the steric phenomena concerning the polymers.

In this field, the stereoisomeric composition of the crude polypropylenes, obtained at a given temperature, depends slightly on the pressure, on the ratio $Al(C_2H_5)_3$ to $TiCl_3$, and on the concentration of the triethyl aluminium.

39

DILATOMETRIC PROPERTIES AND STRUCTURE OF THE ISOMERIC POLYMERS OF ETHYLENE AND OF α-OLEFINS

by F. DANUSSO, G. MORAGLIO and G. NATTA

(July 1957)

[*Industrie des Plastique Modernes*, **10**, 40 (1958)]

ABSTRACT

The specific volumes of various polyethylenes and of amorphous or crystalline stereoisomeric polymers of propylene and of butene-1 have been determined as a function of temperature. With regard to crystalline polymers, the shape of the dilatometric curves in the fusion interval and the value of the terminal melting temperature show evident correlations with the structure of the polymer. The glass transition temperatures have also been determined by measurements of specific volumes at low temperature.

By means of all the experimental data, a method has been established which allows the rapid determination of the degree of crystallinity within a few percents of the three types of polyolefins from a single measure of density. The principles for this procedure, based on the additivity of the volumes of ordered and amorphous regions, are explained in detail. Nomographs are also given.

40

COPOLYMERIZATION OF ETHYLENE WITH ALIPHATIC α-OLEFINS. NOTE I: PRELIMINARY STUDIES ON THE COPOLYMERIZATION OF ETHYLENE WITH PROPYLENE

by G. NATTA, G. MAZZANTI, A. VALVASSORI and G. PAJARO

(July 1957)

[*Chimica e Industria*, **39**, 733 (1957)]

ABSTRACT

In previous papers published in the above journal, we have described the polymerization of α-olefins to linear polymers, having different stereoisomeric constitution. The present paper initiates a series of investigations carried out by the authors in the field of copolymerization.

Notwithstanding the difficulties involved in the production of homogeneous copolymers by anionic polymerization processes, and in particular by heterogeneous catalysis, the problem of the obtainment of very high molecular weight linear copolymers has been solved by using particular highly-dispersed catalytic systems, and by operating under such conditions as to keep the composition of the monomer mixture in the liquid phase constant.

This paper describes the characterization and the preparation of the ethylene–propylene copolymers with aluminium-trihexyl/vanadium oxychloride as catalytic system. These polymers are amorphous in a large range of compositions and show characteristic I.R. and X-ray spectra. They possess peculiar mechanical properties, which are similar to those of non-vulcanized elastomers, but very different from those of the

mixture of the corresponding homopolymers. These polymers have a solubility different from that of the two homopolymers.

The methods adopted to establish the composition of the copolymers are either based on the radiochemical analysis, using ^{14}C labelled ethylene, or on the I.R. spectrographic analysis, by the evaluation of the propylene content measured by the intensity of the absorption band at 7·25 μ. The two methods of analysis agree quite well with one another.

The copolymerization tests were carried out in the presence of n-heptane and at a temperature of 25°C.

The monomer mixture was circulated in a continuous way through the reactor at high space velocity, so as to have a low conversion of each monomer for each passage.

The ethylene–propylene copolymer composition is independent of catalyst concentration, reaction time, the time elapsed between the preparation of the catalyst and its use and aluminium to vanadium molar ratio used in the preparation of the catalyst.

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COPOLYMERIZATION OF ETHYLENE WITH ALIPHATIC α-OLEFINS. NOTE II. THE COPOLYMERIZATION REACTIVITY RATIOS WITH CATALYSTS OBTAINED FROM VANADIUM OXYCHLORIDE AND ALKYLALUMINIUMS

by G. MAZZANTI, A. VALVASSORI and G. PAJARO

(July 1957)

[*Chimica e Industria* **39**, 743 (1957)]

ABSTRACT

The high reactivity of ethylene with respect to propylene, in their copolymerization, is the cause of a marked difference between the composition of the copolymers and of the starting monomer mixture.

The kinetic determination of the reactivity ratios of the two monomers is essential for the theoretical interpretation of the results and for the establishment of optimum conditions for a given composition of the copolymers.

The systematic study of the influence of the composition of the monomer mixture on the composition of the copolymers was carried out in the presence of a catalytic system obtained from $VOCl_3$ and $Al(C_6H_{13})_3$.

The results of this study, reported in the present paper, confirm the ionic mechanism of this copolymerization and introduce the possibility to obtain copolymers of any preferred average composition.

By applying the copolymerization equation to the results obtained, we have determined the ethylene and propylene reactivity ratios. They are, respectively: $r_{C_2H_4} = 17{\cdot}95$ and $r_{C_3H_6} = 0{\cdot}065$.

42

STEREOSPECIFIC CATALYSIS AND STEREOISOMERIC POLYMERS. PREPARATION OF FIBRES, PLASTICS AND NEW ELASTOMERS

by G. NATTA

(18 July 1957)

[*Experientia* Suppl. VII, 21 (1957)]
[*Materie Plastiche*, **24**, 3 (1958)]

INTRODUCTION

First of all I wish to thank Prof. Delaby and the Committee of the 16th International Congress of Pure and Applied Chemistry for having invited me to deliver the inaugural lecture.

I am going to speak on a subject on which my co-workers and I have concentrated our efforts for the past few years.

I think that the field of stereospecific catalysis is nowadays of a particular importance, and it will be of interest to a great number of scientists, in almost all branches of pure and applied chemistry. The stereospecific polymerization processes are of interest because one can obtain long linear chains by polyaddition of vinyl monomers. These chains consist of sequences of monomeric units with tertiary carbon atoms with the same steric configuration.[1-4]

The macromolecules which contain these units crystallize, while those in which the monomeric units of different steric configuration are arranged at random, do not crystallize.

Figure 1 of paper 19 shows the chain structures of three types of stereoisomeric vinyl polymers, arbitrarily stretched on a plane.

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* Inaugural lecture delivered by Prof. Natta at the 16th International Congress of Pure and Applied Chemistry.

The discovery of the processes of stereospecific catalysis has brought a revolutionary impetus [5] in macromolecular chemistry: it is still too soon to evaluate the significance of these new discoveries, but they certainly represent a fundamental step in the history of macromolecular chemistry.

Before 1954, it had not been possible to obtain synthetically hydrocarbon polymers with a regular structure.

This possibility was limited, in the case of vinyl and vinylidene polymers, to products obtained from monomers containing two symmetry planes in their molecule.

Nature, on the other hand, offers various examples of crystalline macromolecules with a regular steric structure; namely, natural rubber, gutta-percha, crystalline proteins, wool, silk, cellulose. The regular repetition of units with the same steric configuration is the cause of the crystallinity of these natural products and of their technological properties.

In the case of diolefins, the newly-discovered processes of stereospecific polymerization not only made possible by synthesis the obtainment of crystalline polymers corresponding to two types of geometric stereoisomery, which are present in natural rubber and gutta-percha, [6-10] but also have led to other stereoisomers, which do not exist in nature, such as the isotactic and syndiotactic polymers, derived from the 1,2- and 3,4-arrangement of the monomeric units of conjugated diolefins.[11-12]

It may be of interest, from a historical point of view, to describe the evolutionary process of thinking which has led to the discovery in Italy of these new classes of macromolecules (isotactic and syndiotactic crystalline polymers) and to the determination of their structure, and, almost at the same time in the United States and in Europe, to the synthesis of polydiolefins similar to natural products, such as elastic rubber and gutta-percha.

It had been known for a long time that most vinyl polymers [13] and synthetic polydiolefins could not crystallize due to the randomness of the monomeric units in the succession of steric configurations within the polymer.

Already at Freiburg in 1933, when I was studying the interferences of electron rays, after ten years of experience in the structural field by using X-ray methods, I was captivated by the brilliant research work of Staudinger on macromolecules, and of Mayer and Mark [14-15] on the crystalline structure of natural high polymers.

I then started the electron rays examination of a number of vinyl polymers, supplied to me by Staudinger.

However, all these examined vinyl polymers appeared to be essentially amorphous. I had only observed the presence of crystalline parts, which were very small, (probably due to a syndiotactic structure) in very thin laminae (10^{-6} cm thick) of a sample of polystyrene, which we did not succeed in reproducing any more.[16]

A high degree of crystallinity in a polymer obtained starting from a $CH_2=CHR$ monomer requires a high regularity of structure and above all a chemical regularity, that is a linear head-to-tail arrangement, without branchings longer than R, and consequently the use of processes which do not give rise to either chain transfer processes or the formation of copolymers between the monomer and its low polymers, as well as a great regularity of steric structure. The solution of the problem was only possible when catalytic processes became available which showed, also chemically, a more regular behaviour than the polymerization processes of radical and cationic nature.

We began our studies on the polymerization of olefins [17] with the aid of heterogeneous catalysts and on polyaddition reaction kinetics [18] in 1939–1945, but the history of our research on the α-olefin polymerization starts in 1952.

At Frankfurt, listening to a lecture by Ziegler on organometallic compounds, I was impressed by two facts which were very surprising to me: the possibility of dimerizing olefins obtaining a pure dimer, while in general, the cationic polymerization processes yield mixtures of isomers, and the possibility of obtaining, starting from ethylene, perfectly linear polymers with a molecular weight of some thousands.[19]

In 1953, with the firm belief that this field could afford remarkable developments, my co-workers and I started the kinetic study of the ethylene polymerization reactions, in order to examine the possibility of increasing the rate of growing and decreasing the termination rate.[20]

It is well known, however, that, in general, the catalysts which polymerize ethylene do not polymerize α-olefins at all, or polymerize them only to low molecular weight polymers. This appeared in fact to hold also for the Ziegler catalysts which we had first examined.[21] This notwithstanding, we went deeply into the study of α-olefin polymerization.

The very first α-olefin polymers we obtained, showed in the raw

state, an evident crystallinity when examined by X-ray diffraction methods.[22]

The first attempts at fractionating the crude polymers by extraction with various solvents led however to surprising results, that is, to the separation of amorphous fractions with a rather high molecular weight (20,000–30,000) from nearly insoluble fractions having in general, but sometimes only slightly, higher molecular weight. The melting temperature of these last fractions, which were crystalline, was very high.

Since the properties of polymers vary in general continuously with molecular weight (*natura non facit saltus*) I immediately thought that the difference in solubility was to be attributed not to the slight difference in molecular weight, but to a different chain structure.

This was then confirmed by the fact that by depolymerization (and later also by direct synthesis) nearly insoluble crystalline polymers of propylene having a molecular weight of only a few thousands and very soluble amorphous polymers with a molecular weight of even 100,000 could be obtained.

We immediately attributed the insolubility to the crystallinity caused by a regular succession of the tertiary carbon atom configurations; it was, however, necessary to identify the type of regularity.

From X-ray studies of fibres, oriented by stretching, it appeared that each portion of the chain of certain crystalline α-olefin polymers, corresponding to an identity period of 6·5 Å, contained three monomeric units.[23]

The odd number of monomeric units excluded a succession of monomeric units of opposite configuration and thus we came to the conclusion that the monomeric units were all identical and therefore had the same steric configuration. We called these polymers "isotactic polymers."[1]

The simplest operation (as Pauling has already observed for proteins) to convert an asymmetric element into an identical equivalent element (which is not its mirror image) is rotation around an axis, combined with a translation along this axis. For polypropylene and polystyrene this displacement is of 2·15–2·20 Å and the rotation of 120°.

By a more careful examination, both by X-rays and by Fourier's analysis (Fig. 2), we succeeded in determining the structural type of the chain of several isotactic polymers and also their arrangement and the positions of all the atoms present.

For the completely interpreted structures (polybutene, polystyrene

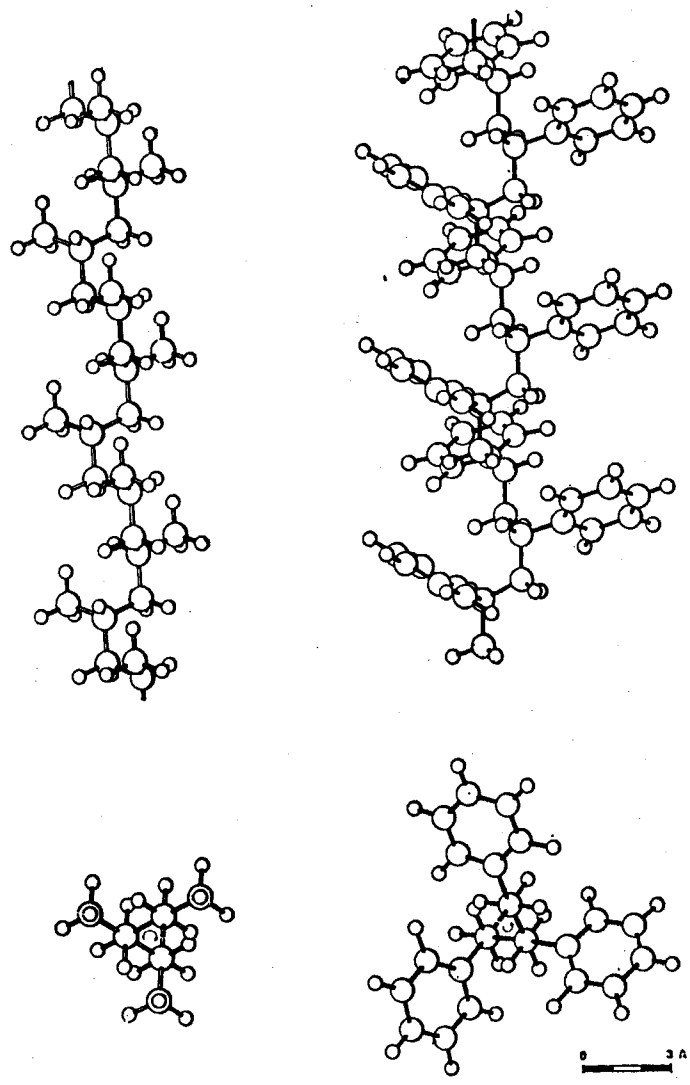


FIG. 1. Conformation of chains of isotactic polypropylene and polystyrene in the crystalline state (side and end views).

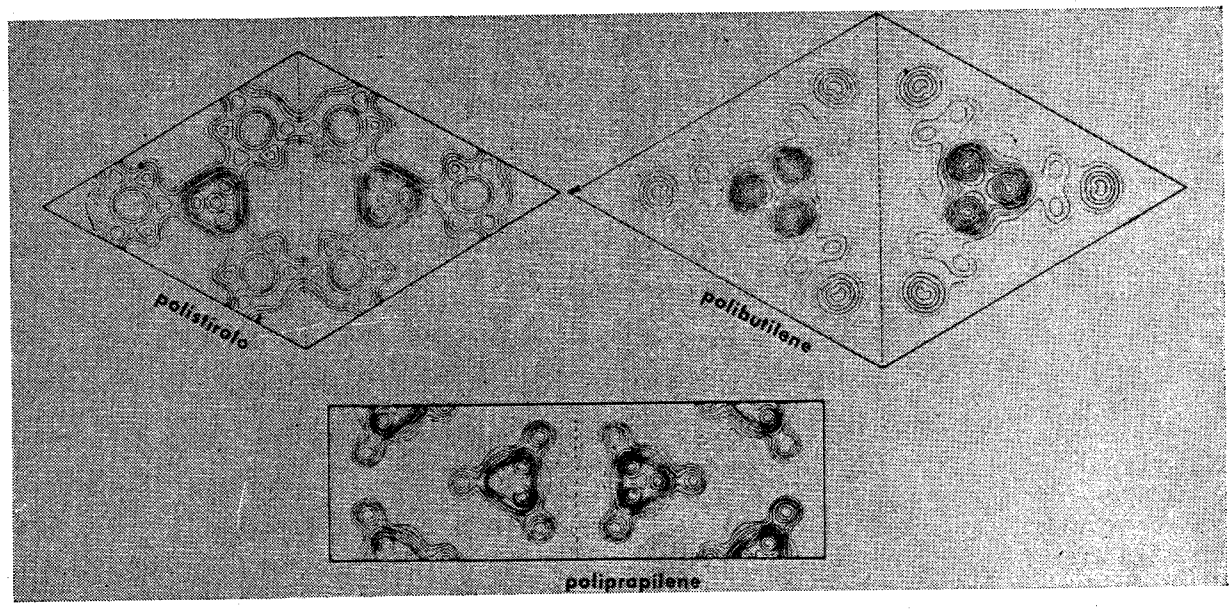


FIG. 2. Projection of electronic density on a plane normal to the fibre axis, for isotactic polypropylene, polybutylene and polystyrene crystals.

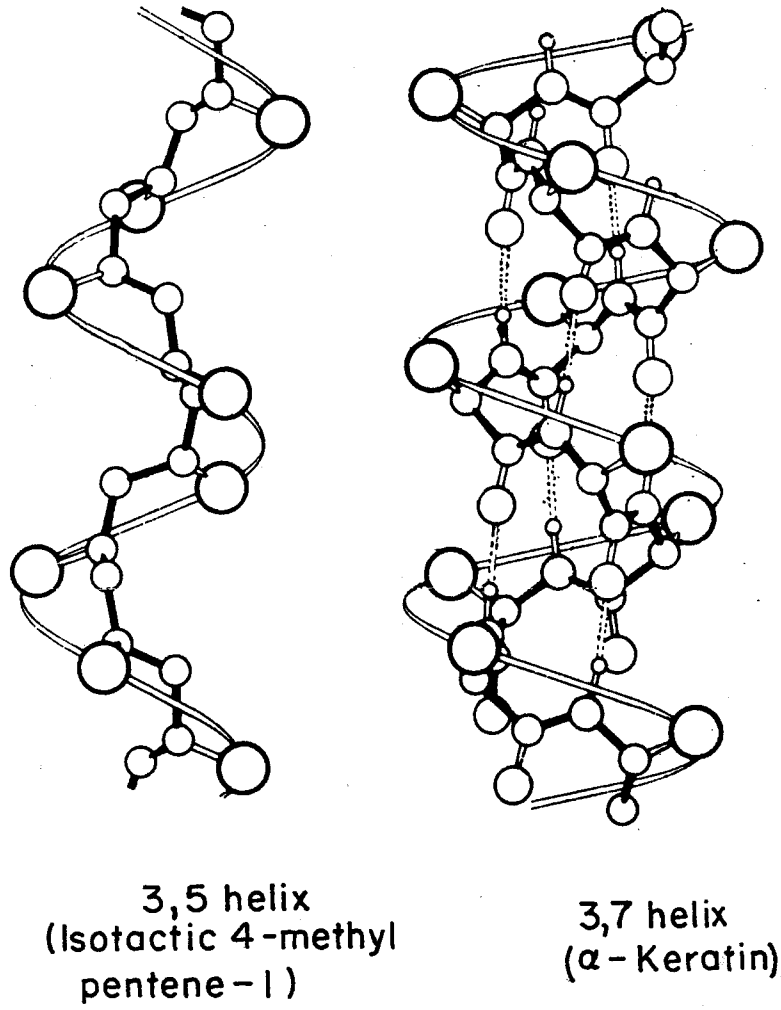


FIG. 3. Comparison between the helix structure of α-keratin (Pauling-Corey) and the isotactic poly-4-methyl-pentene (Natta-Corradini).

and polypropylene) a very extraordinary accordance between the calculated and the experimental intensities was found. [24, 27, 28]

Figure 1 shows the chains of some isotactic polymers. We can immediately note an analogy with the structure found by Pauling and Corey for the crystalline proteins (Fig. 3). There is, however, a substantial difference, that is that in proteins, as in Price's polymers[25] (from asymmetrical propylene oxide), there is a succession of monomeric units which are already asymmetrical in the monomeric state, while in the poly-α-olefins the asymmetric carbon atoms contained in the chains are not such when they are in the monomer (Fig. 4).

Nature has followed a more direct way in the construction of crystalline polymers containing asymmetrical monomeric units. It starts with α-aminoacids all of them generally levo-rotatory, and in this case, since the relative orientation of the substituent groups is always the same, all the monomeric units must have the same orientation.

Each active centre of the stereospecific catalysts for the polymeriza-

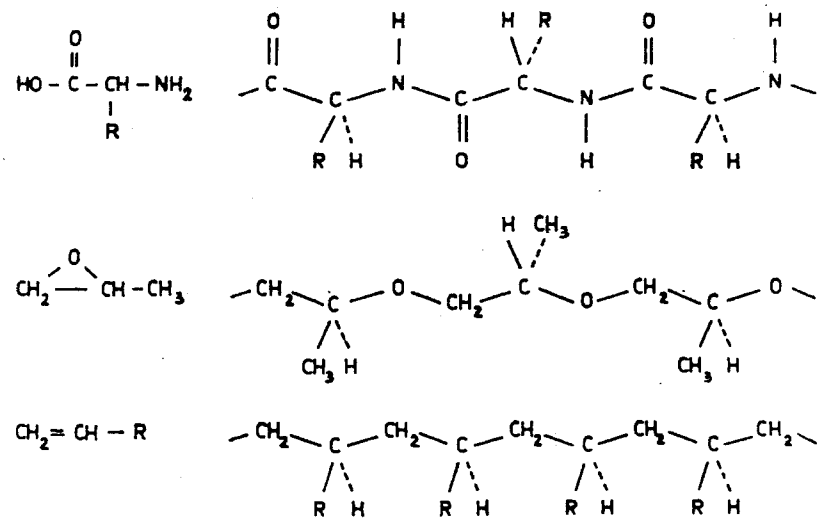


FIG. 4. Comparison of the isotactic chain of the poly-α-olefins, in which the tertiary carbon atoms are disposed between two equal adjacent groups (methylene groups) with the chains of crystallizable polypropylenoxides and poly-α-aminoacids, in which the tertiary carbon atoms are disposed between different adjacent groups.

tion of α-olefins must perform a more delicate function, that is, at the moment of polymerization it must create units having all the same steric configuration.

The active centres of Price's catalysts on the contrary must have a selective function, choosing from a racemic mixture of an epoxide the monomeric units which have the same steric configuration.

The high crystallinity (up to 80–85%) and the high crystallization rates of polypropylene are compatible only with the existence of crystals in which the two enantiomorphous forms can coexist.

The chains can be spiralized in the dextro- or levo-rotatory directions and in each chain the side groups can be all tilted toward the one or the other of the two terminal groups which are different one from the other.

The structures proposed by us for polypropylene, polybutene, etc., are characterized by the possibility of coexistence of two helices, dextro and levo-rotatory (Fig. 8 of paper 24) in the crystal, each of them having in its turn two possible different orientations.

In the case of polypropylene we have found that all the different chain types are present, grouped two by two, and that in each site the "down" and "up" chains can replace each other in an isomorphic way.

When the saturated side chain is branched on the carbon atom near the main chain, or when the side chain presents a considerable bulkiness, the helicoidal structure with ternary symmetry becomes unstable because of steric hindrances. A structure with a different symmetry

is then observed: the 3-methyl-1-butene chain takes for instance a helicoidal form with four monomer units per pitch (6·4Å), those of 4-methyl-1-pentene and of 4-methyl-1-hexene take the form of a helix containing 3·5 monomeric units per pitch, with an identity period of 14 Å, corresponding to two pitches per helix (Fig. 6 of paper 24).[26—27] It is interesting to note that the melting point decreases for the polymers of the first compounds of the normal α-olefin series, that is, from polypropylene to poly-1-butene and poly-1-pentene, while it increases the more the chain is branched and the nearer are the branches to the double bond.

Isotactic polymers present furthermore interesting polymorphism phenomena. Polybutene, for instance, presents at least two forms: one with quaternary and the other with ternary symmetry. The first, which may be obtained by crystallization from solutions, is easily transformed by standing or, more easily, by stretching into the second form.[28]

It has also been possible to stabilize the chain with quaternary symmetry by increasing the bulkiness of the side chains, e.g. by chlorination of polybutene. By varying the chlorine content it is possible to obtain a range of products in which the quaternary symmetry gradually becomes more stable.[29] The possibility of obtaining chains in which there is a balance among the different structures and in which the content of longer forms with a ternary symmetry increases by stretching, while the form with quaternary symmetry is more stable in the presence of solvents, has been considered.

Such chain polymorphisms present a remarkable analogy with those of muscle proteins, which also may present several forms of spiral-shaped chains with different pitches, the chains being more or less contracted depending on whether the muscle is in a state of rest or of strain.

NEW PLASTICS

The importance of stereospecific catalysis in the field of plastics is due to the fact that said catalysis makes it possible to investigate a vast new branch of macromolecular chemistry and to produce new classes of linear and highly crystalline polymers.

From the practical point of view of technological properties, the highly crystalline polymers are of real interest only when they have a very high average molecular weight, higher than 40,000–50,000, in the case of hydrocarbons (or more precisely a linear chain with a length

of at least some thousands of angstroms) so that each chain belongs to many crystalline regions (in general with a length not exceeding some hundreds of angstroms) and connects them by means of non-crystallized portions. The high mechanical characteristics depend on the crystalline portions while the chain portions which connect the crystals cause the disappearance of brittleness (which is a characteristic of the highly crystalline, low molecular weight substances) and make the product capable of absorbing mechanical energy in plastic deformations before break.

In Fig. 5 the stress–strain curves of very high molecular weight crystalline products are compared with those of low molecular weight polymers and of amorphous polymers.

The practical difference between the crystalline polymers with very high molecular weight and the non-crystalline polymers (conventional polystyrene, polyvinyl chloride, etc.) is that these last polymers are brittle below the second order transition temperature and are rubber-like above this temperature. The crystalline polymers maintain high mechanical characteristics over the whole range between the 1st order and the 2nd order transition temperatures and, when oriented, even below this last temperature.

Few natural thermoplastic and macromolecular products are highly crystalline. An example is supplied by gutta-percha.

The production of synthetic crystalline products as plastics in bulk

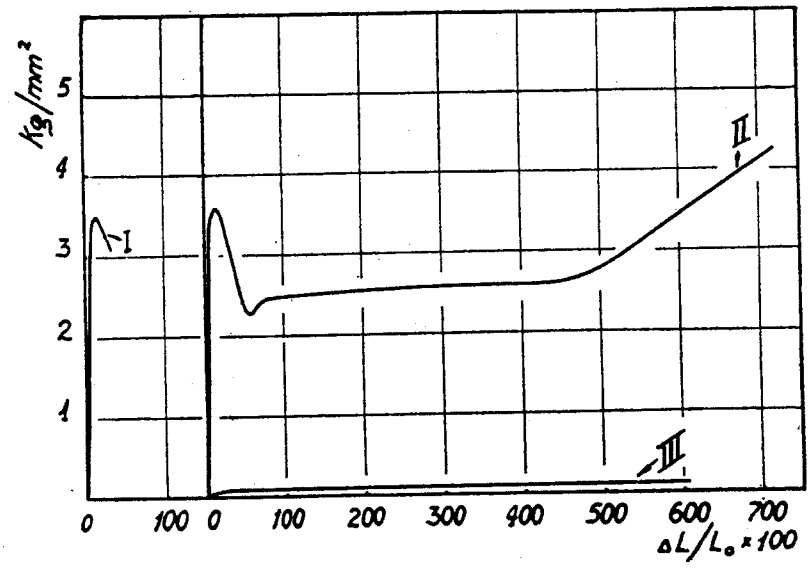


FIG. 5. Comparison of stress–strain diagrams of three polypropylenes: I, isotactic with low molecular weight ($[\eta] \simeq -1$); II, isotactic with high molecular weight ($[\eta > 2.5$); III, atactic ($[\eta] = 1 \div 2$).

is comparatively recent. The first synthetic, highly crystalline polyhydrocarbon, which has found very wide application, is polyethylene, obtained by the high pressure processes of I.C.I.; the characteristic roperties of the said polymer depend prevailingly on its crystallinity, which, in general, is not very high (30–60 per cent).

The discovery of the new polymerization processes has today made possible the production of linear, highly crystalline polymers, of completely linear polyethylenes with a melting point of 138°C, and of a complete series of isotactic polyolefins such as poly-3-methyl-1-butene and poly-3,3-dimethyl-1-butene, having melting points higher than 250°C,that is, than for isotactic polypropylene.[26-27]

From the practica point of view the most interesting polymers are highly crystalline polypropylene (m.p. 175°C), and poly-1-butene (m.p. 136–140°C), becau se of the low cost of the monomers, and their available supply from the petroleum cracking gases.

Certain linear isotactic and low crystalline stereoblock polymers having high molecular weight are of particular interest, due to their higher elasticity compared with that of the highly crystalline polymers.[30]

They consist of macromolecules containing isotactic chain sections interposed with atactic sections or with isotactic sections of opposite steric configuration (Fig. 19 of paper 24) whose properties can

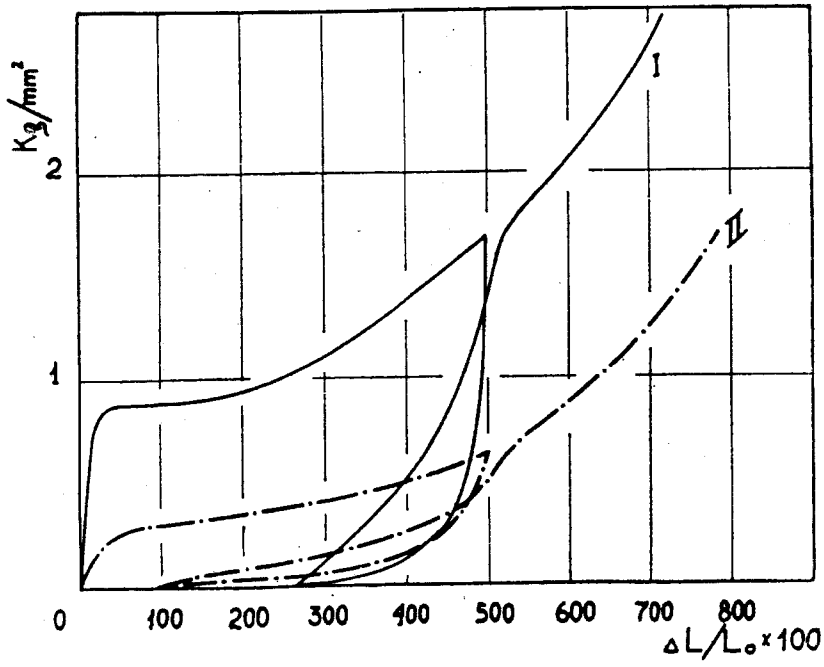


FIG. 6. Stress–strain diagrams of two different types of stereoblock propylene polymers having different crystallinity (I > II).

be varied gradually, in dependence of their stereoisomeric composition, from the properties of a hard, highly crystalline thermoplastic material, having a high tenacity, to a low crystalline material, having mechanical properties like leather, and so on to elastic rubber-like materials (Fig. 6).

Among the new isotactic vinyl polymers with a high melting point I shall mention those having aromatic substituents: isotactic polystyrenes, having a melting point between 230°C and 240°C, polystyrenes substituted in the ortho-position, and vinyl polymers of polycyclic rings, such as polyvinylnaphthalene, having melting points higher than 300°C.[31]

It has recently been found that polystyrenes obtained by the Morton process, if annealed for a long time in the presence of swelling solvents may partially crystallize.[32]

According to our experience the Morton process is certainly much less stereospecific, both for butadiene and styrene, than the processes described by us as highly stereospecific. In comparison with our polystyrenes, those obtained by the Morton process, examined by us as well as those described in recent papers, show a much lower crystallinity (lower than 20%) and a lower melting point, attributable to the presence of stereoblocks having a low number of long isotactic sections.

It is to be expected that, among the infinite number of isotactic polymers obtainable from various vinyl monomers, practical interest should concentrate particularly on those polymers whose monomers are already widely available (polypropylene, polybutene, polystyrene) and the synthesis will be possible at low cost.

In Italy the study of the possible applications of these polymers has been progressing for a considerable time, and has allowed the production, with conventional shaping methods (injection, extrusion, film forming) of articles presenting, in addition to high mechanical and technical characteristics, excellent surface features, in a wide variety of colours.

In particular, transparent crystalline products were obtained, both in the non-oriented and in the oriented state.

NEW FIBRES

The most important and tough fibres, both natural and synthetic, are more or less crystalline. Silk, cotton, wool, nylon, terylene and saran are crystalline. The lower tenacity of certain artificial

cellulosic fibres with respect to cotton and ramié is, in general, to be ascribed to the lower crystallinity of regenerated cellulose. There are few exceptions to this rule. Polyvinyl chloride and polyacrylonitrile, which have almost no crystallinity, are still capable of yielding good fibres because their molecules present the property of being well orientable by stretching (owing to the small volume of the side-groups) and because they show a high transition temperature and consequently a high resistance to viscous flow (due to the presence of polar groups). Their mechanical and thermal strength would certainly be very much higher if the said polymers could be obtained with a regular steric configuration which would make them crystalline.

The crystallinity is an absolutely necessary condition to obtain valuable fibres in the case of highly flexible macromolecules having a low 2nd order transition temperature. A clear example is given by polyethylene; the polymer obtained by free radical processes, having a density of 0·92, gives very bad fibres with a resistance of about 1–2 g/den, while the polymer obtained by ionic processes, having a density of 0·94–0·96 and a very high molecular weight can yield fibres with a strength up to 5 g/den.

It is evidently clear why the new processes of stereospecific polymerization, which can produce by polyaddition crystalline polymers even from asymmetrical monomeric units, with or without bulky side groups, greatly increase our possibilities of obtaining fibres. In the past the presence of hydrogen bonds or polar groups, which by association could contrast the viscous flow of the macromolecules, was believed to be a necessary condition for obtaining high strength fibres. The discovery of the highly crystalline isotactic polymers has shown that very high tenacity fibres can be obtained from macromolecules of pure hydrocarbons, free of hydrogen bonds and polar groups (Fig. 22 of paper 24).

The low value of the Van der Waals' forces between the methyl and methylene groups of neighbouring molecules is counter-balanced by the high length and regularity of the chains. In fact, while fibres having a good tenacity with a molecular weight of 10,000–20,000 (corresponding to a chain length of about 1000 Å) can be obtained from Nylon, in the case of poly-α-olefins, macromolecules having an average molecular weight of over 30,000 and chain lengths of over 2000 Å must be used.

In the case of isotactic hydrocarbon polymers having a helix-type chain structure of very weak van der Waals' forces, the possibility of ob-

taining fibres with a high melting point depends mainly on the capacity of packing of the macromolecules into crystals. The shape and size of the side groups which are bound to fixed positions of the main helix-type chain exert an important influence on the packing ability and consequently on the crystallization ability.

This explains the high melting point of polypropylene, of poly-3-methyl-1-butene (both materials very suitable for making fibres), the lower melting point of polybutene and polypentene, the non-crystallinity at room temperature of polyhexene, the polymorphism of polybutene, the ternary symmetry form of the helix of the poly-4-methylpentene and poly-4-methylhexene chains. The density of polypropylene in the solid crystalline state (0·935) is higher than that in the amorphous state (0·85) but the difference is lower than for polyethylene (0·99 for the crystalline and 0·85 for the amorphous). We believe that in the case of polypropylene the chains are largely helix shaped, with a low entropy, even in the liquid state. The high melting point can be ascribed to the low entropy variation accompanying the melting.

Some isotactic polymers of vinyl aromatic compounds could be employed for the production of fibres having a very high melting point, higher than that of isotactic polystyrene (230–240°C).

Poly-*p*-fluorostyrene melts at 280°C, poly-α-vinylnaphthalene and poly-ortho-methylstyrene melt at a temperature higher than 300°C in spite of the asymmetrical position of the side group in some of them, and some of them crystallize much better than polystyrene.

Although various isotactic polymers can be employed for the production of fibres, from the practical point of view the highest interest in the field of textile fibres is now concentrated on polypropylene. A considerable work has been carried out in Italy where the problem of dyeing polypropylene has been solved. Conditions have also been found for the economical production of monofilaments and staple fibres, by extrusion of the molten propylene polymer with machines operating at very high spinning rate.

The factors which will make possible the production on a commercial scale of textile fibres from polypropylene, whose production cost is likely to become lower than that of any other synthetic textile fibre, are: its low cost, which is probably lower than that of any other vinyl monomer; the high yield and ease of its low pressure polymerization; the direct obtainment, by polymerization, of a highly crystalline material which, without any fractionation, gives directly by melt extrusion

filaments with a low count and high strength. The great lightness of the polymer and the possibility of obtaining extremely soft staple fibres, with a high thermal insulating power and a much higher strength than wool, open up wide possibilities of use for this new and very interesting textile material.

NEW ELASTIC RUBBERS

The field of elastic rubbers represents one of the most fascinating branches of macromolecular chemistry and physics.

The requirements for obtaining a good elastic rubber, such as natural rubber, consist of: high molecular weight, linear structure of very flexible macromolecular chains, disorder, high entropy which makes rubber resemble a high viscosity liquid, orientation caused by an elastic strain induced by stress and partial crystallization occurring only when the molecules are compelled to dispose themselves in parallel segments. All these requirements have never been grouped together in synthetic products before the discovery of stereospecific polymerization processes.

However, the extraordinary properties of natural rubber, whose lattice structure in the crystalline state is reported in Fig. 7, according to our interpretation of Nyburg's structure,[23] are not so much due to the fact that it crystallizes, but rather that it crystallizes with difficulty.

I believe that up to now a fact of fundamental importance has not been stressed sufficiently, namely that the properties of natural rubber are due not only to the presence of *cis* double bonds, but also to the fact that natural rubber does not consist solely of monomeric units with *cis*-1,4-structure. The infrared spectra reveal 2–3 per cent of different units, mostly with 3,4-structure. I think that this small amount of different units, probably with a statistical distribution, has a very considerable influence on the properties of natural rubber.

The stereospecific processes have made it possible to solve the problem of the synthesis of highly elastic rubbers, and particularly the synthesis of polyisoprene with prevailingly *cis*-1,4-structure[9–10] like natural rubber, and of a polybutadiene with a *trans*-1,4-structure, like gutta-percha.[6]

They also have made possible the synthesis of new classes of linear macromolecules, which did not exist in nature.

All four crystalline stereoisomers of butadiene, which can be foreseen

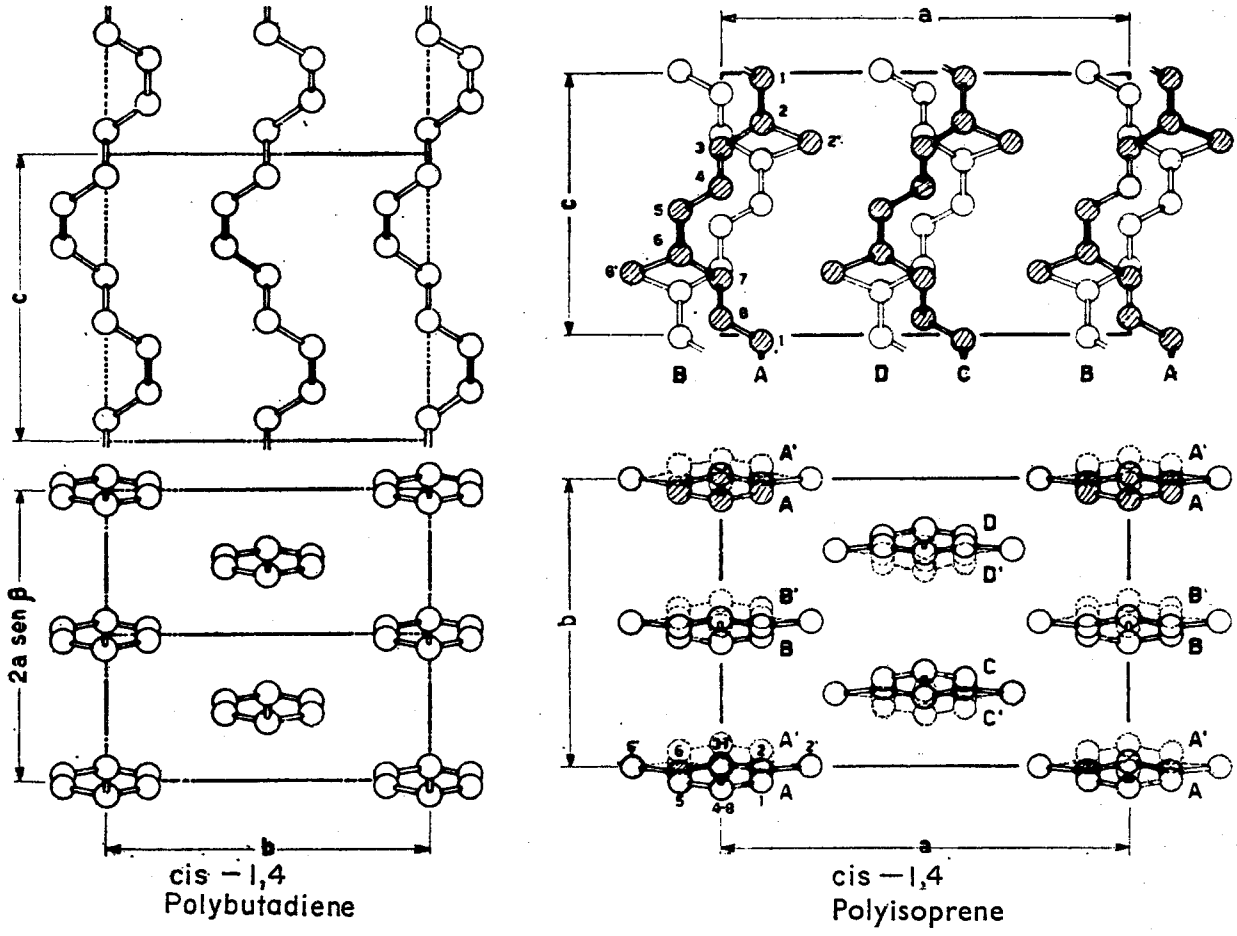


FIG. 7. Comparison of the structure of *cis*-1,4-polyisoprene with that of *cis*-1,4-polybutadiene.

theoretically, have been synthesized by us; we have also determined their properties and lattice structure.[7, 8, 12]

The chain configuration in the crystalline state of the different stereoisomers are shown in Fig. 8 and the lattice constants in Table 1. The broader base of experimental data, thus created, opens a new and vaster horizon to chemical thinking. The properties of numerous linear polyhydrocarbons, examined by us, make it possible to define the prerequisites for the structure of a chain in order to obtain a good rubber. These prerequisites are the following:

1. The linear chains must be very long to prevent viscous flow and they must be highly disjoined so that they can preserve certain properties of liquids. It was said in the past that a good rubber must have a "mobile and flexible" chain, but these adjectives do not indicate as accurately as the word "disjoined" the structure of the free molecules of a good rubber. In order to have a good rubber it is necessary for the macromolecules to be able to easily modify their conformation by overcoming very low potential energy barriers; they must, therefore, be flexible and also "disjoined". It is necessary for the bond of

TABLE I

X-RAY DATA OF THE CRYSTALLINE STEREOISOMERS OF POLYBUTADIENE

Polymer	*Space group*	*No of monomeric units per unit cell*	*Size of the unit cell Å*			*X-ray density*	*Melting temperature by X-rays*
			a	*b*	*chain axis c*		
trans-1,4	—	—	—	—	4·9	1·02 [a]	148°C
cis-1,4 (monoclinic)	C2c	4	4·60	9·50	8·60 ($\beta = 109°$)	1·01	[b]
syndiotactic-1,2 (rhombic)	Pacm	4	10·98	6·60	5·14	0·96	155°C
isotactic-1,2 (hexagonal)	$R\bar{3}c$	18	17·3	17·3	6·50	0·96	125°C

(a) Calculated starting from the distance 4·54 Å between the chain axes in a pseudo-hexagonal system.
(b) The melting temperature of the pure *cis*-1,4-polymer is unknown. The impure polymers have temperatures depending on their composition and stretching.

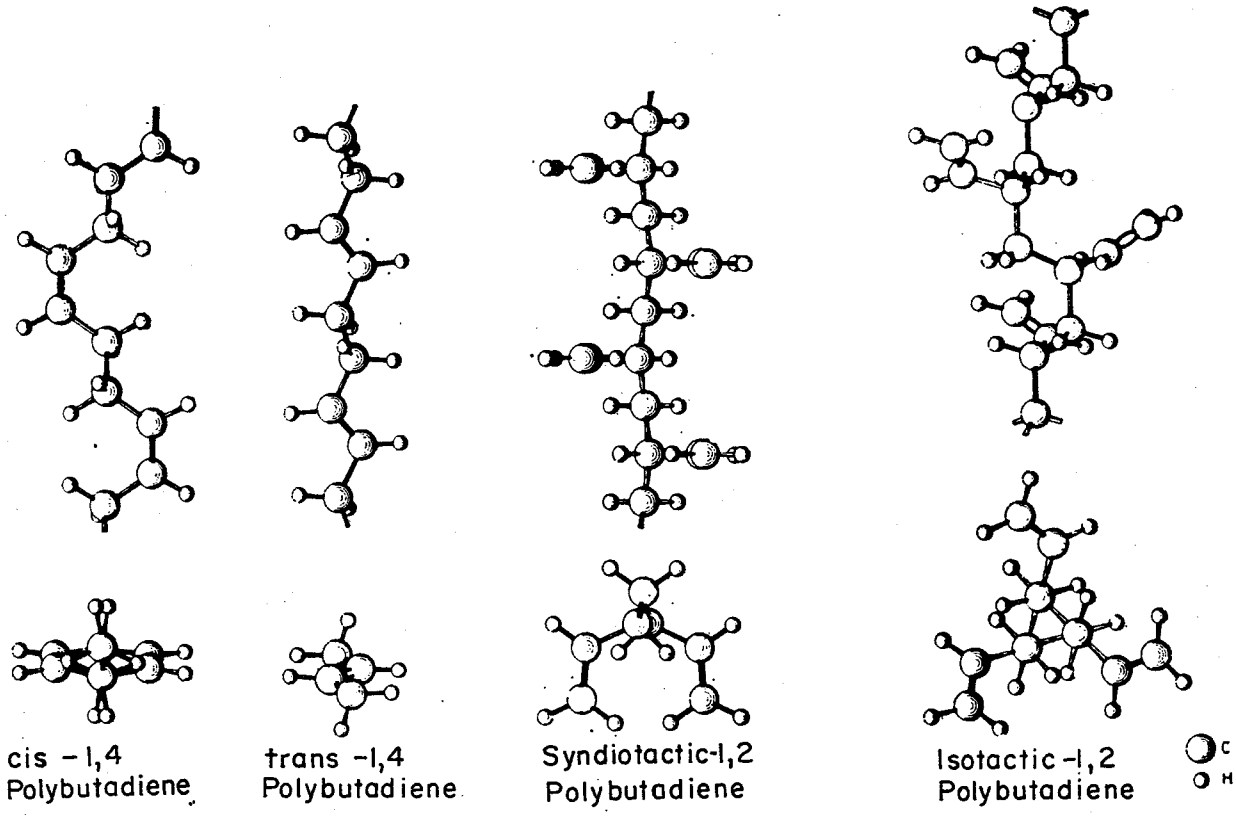
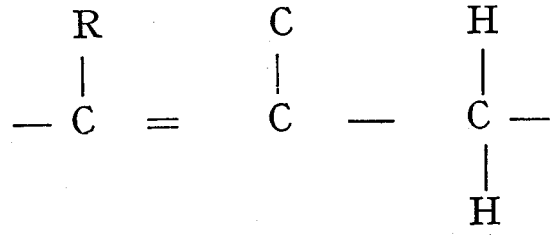


FIG. 8. Structures of the chains of different stereoisomers of polybutadiene in the crystalline state.

the chain atoms to oscillate with low deformation, at a very low level of energy included between not too high energy maxima.

In a saturated carbon atom chain the freedom of rotation around the valences is highly reduced when side substituents containing bulky portions are present near the chain.

The low resilience of butyl rubber derives from this fact. The simple bond in the following group:



presents instead a higher freedom of oscillation than that of the $-CH_2-CH_2-$ group (Fig. 9).

2. The elements of the chain and their successions should have some dissymmetries, such as to make crystallization difficult. The rubbers, even with a very high molecular weight (in the order of hundreds of thousands) should remain liquid in their state of rest. Poisson's coefficient should be 0·5 like normal liquids.

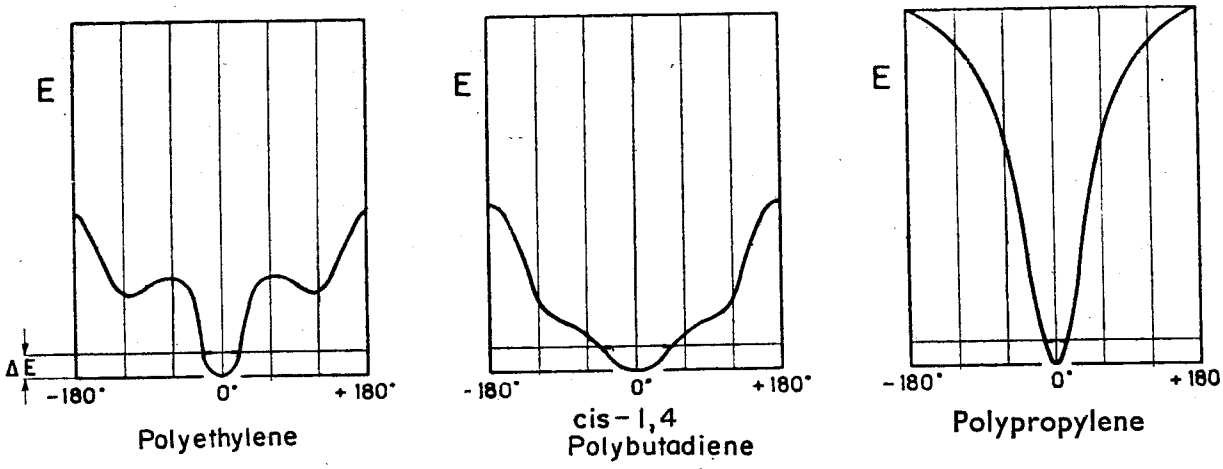


FIG. 9. Qualitative comparison among the forms of the curves giving the potential barriers that contrast the rotation around the simple bond in the free chains of polyethylene, *cis*-1,4-polybutadiene and polypropylene, and among the different rotation angles determined by a very small deformation stress ΔE.

3. No causes (for example, polar groups or hydrogen bonds) which promote associations between molecules or reduce their mobility should be present.

4. The chains should have, however, a sufficiently regular structure, so that, in spite of the asymmetries of monomeric units or irregularities in their succession and of the "disarticulations" of the bonds, they can be oriented by stretching and associated in crystalline aggregates, which melt if the stress is released. In fact, crystallization by stretching causes decrease of entropy and increase of the elastic modulus; thus a considerable aid is given to chemical vulcanization, by contrasting viscous flow and break. Unless reinforced, non-crystallizable rubbers do not resist high stresses.

Let us now consider how these concepts can be applied to the synthesis of new rubbers.[34]

We have seen that the linear chains, containing double bonds, are highly "disjoined". When the double bond is in a main chain and the mobility of the neighbouring single bonds is not greatly hindered by bulky side groups, we have rubbers with a high resilience. If on the contrary, the double bond is in the chains (1,2- or 3,4- structure) rubbers having a lower resilience are obtained. The macromolecules show a sterically disordered structure, while high melting crystalline materials are formed when the structure is sterically ordered (isotactic or syndiotactic structure).

In the case of butadiene 1,4-polymers, various stereoisomeric structures are possible, with macromolecules containing all *cis*-, all

TABLE 2.

RESILIENCE (*) OF DIFFERENT STEREOISOMERS OF POLYBUTADIENE (ESSENTIALY AMORPHOUS AFTER VULCANIZATION).

	Resilience [%] *at*	
	20°C	*90°C*
trans-1,4	75—80	90—93
rich in *cis*-1,4	88—90	92—95
1,2	45—55	90—92

(*) ASTM D 1054-49T.

trans- or mixed monomeric units. In all these cases the resilience is always high, provided the material is not too crystalline (Table 2).

With the complete *trans*-1,4 arrangement the chain takes a more linear form. Crystallization is easier and the pure crystalline product has a melting point which is too high for a rubber to be used at room temperature, unless one reduces its crystallinity.

The polymers with 1,4-structure, which can never crystallize because they contain both *cis*- and *trans*-configurations arranged disorderly in the same macromolecule, are good rubbers with a resilience better than that of GRS and Buna S. Their chains are more "disjoined" but, like GRS and Buna S, they do not crystallize under stress and, therefore, do not present the high tensile strength of natural rubber.

The synthetic *cis*-1,4 polymer of isoprene has the same properties as natural rubber with only small differences. *Cis*-1,4-polybutadiene is difficult to obtain with a very high degree of purity, but it resembles natural rubber, the more closely, the more similar its stereoisomeric composition is to that of natural rubber. Samples have already been obtained which crystallize a little even at room temperature and which show a higher crystallization by stretching and have interesting properties. Probably a very pure *cis*-1,4-polybutadiene would be too crystalline and its best properties would be those of a product containing a very low percentage of sterically different units.

We have thus generally outlined the path to obtain good synthetic rubbers from diolefins; it is only difficult to foresee if and when it will be attained economically.

Synthetic rubbers from isoprene appear to be expensive, at least

at the present time, and, like natural rubber, they have a poor chemical resistance.

The questions we have been asking ourselves for a long time are the following:

1. Is it possible to prepare hydrocarbon macromolecules which do not contain double bonds in the main chain, which are sufficiently mobile and "disjoined" to yield a good rubber and which crystallize only when stretched?

2. If it is not possible to obtain other types of chains as flexible and "disjoined" as natural rubber, is it possible to find a compromise solution namely to forego a certain percentage of resilience, if the other properties, such as the mechanical, thermal and wear strengths and the resistance to ageing, are good and the cost is low?

Among the saturated chains, that of polymethylene which does not contain large side groups should present the highest flexibility. Due to the contacts between the hydrogens which contrast the free rotation of the carbon–carbon linkage, the polymethylene chain cannot be as "disjoined" as that of *cis*-1,4-polybutadiene, but nevertheless, the energy necessary to induce an elastic deformation correspondent to a rotation of less than 20° is moderate (Fig. 9). These small deformations of 10–20° can occur elastically in all the bonds of the main chain with a minimum absorption of energy.

The free polymethylene molecule should theoretically behave as a good, if not a very good, rubber. We all know however that polymethylene is not a rubber, but can become one if it is sulpho-chlorinated; however, in this case it acquires elastic properties which are very poor with respect to hysteresis.

How can these facts be brought into agreement? Their reason lies in the high symmetry of the ethylene monomeric units, in their order and their excessive ease of crystallization, which requires considerable amount of chlorine to be sufficiently reduced.

If the regularity of the polyethylene chain could be reduced so as to prevent crystallization, without introducing any polar groups and without reducing the flexibility of the chain and the ability of rotation of the C—C linkages, then a chain should be obtained suitable as the basic material for a good rubber.

The problem has been solved with the ethylene-α-olefin copolymers (for example, ethylene-propylene); those having a content of α-olefin, such as to make them non-crystalline in the state of rest, have proved to be interesting rubbers.[35] The possibility of maintaining not

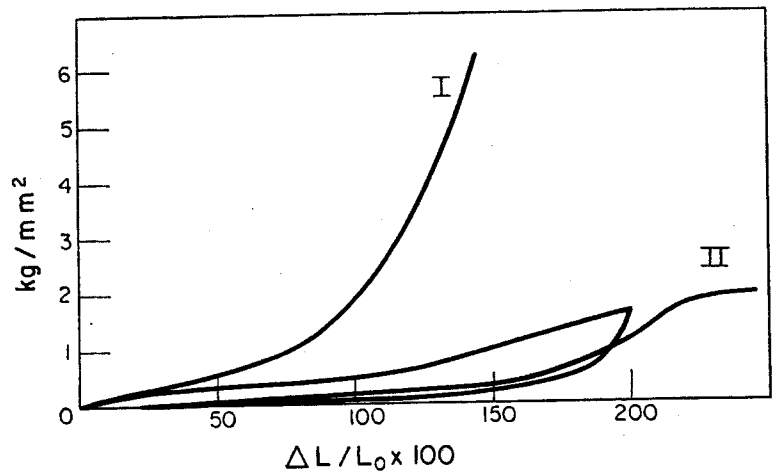


FIG. 10. Stress-strain diagrams of two non-vulcanized stereoblock propylene polymers, oriented by stretching: (I) with intrinsic viscosity = 1; II) with intrinsic viscosity = 1·7.

too short portions of ordered ethylenic units, capable of crystallizing when the molecules are oriented by stretching, is a favourable aspect of the problem and can make it possible to realize better mechanical behaviours, in particular high tensile strengths, and a stress–strain curve similar to that of natural rubber (Fig. 18 of paper 36).

These new rubbers are particularly interesting in view of the low cost of the raw materials, of their good elastic behaviour in the vulcanized state, which is better than that of the old reinforced synthetic diolefinic rubbers, of their low values of elastic hysteresis (which however are higher than those of natural rubber), and because of their high tensile strength and very good chemical resistance.

Less interesting with respect to the elastic hysteresis and tensile strength are instead the linear atactic polymers and copolymers of α-olefins which do not contain ethylene; they behave like elastic rubbers when they reach very high molecular weights (in the order of hundreds of thousands).

A particular and brand-new category of rubbers having high tensile strength, with elastic elongations of 100–200 per cent (Fig. 10), has been obtained from isotactic stereoblock polymers of α-olefins, having a crystallinity of 10–20 per cent in the non-stretched state.[30]

Such a crystallinity increases in the stretched products and it is the reason for their high tensile strength; it acts like a reversible vulcanization, which can substitute the chemical vulcanization in the oriented products.

Unlike the chemically vulcanized rubbers the vulcanization, in materials of this type, is thermolabile and disappears at a temperature

higher than the melting of the crystals. On the other hand this material is always thermoplastic and can be melted, moulded and oriented as many times as desired. This is impossible, without decomposition, in the common vulcanized rubbers.

POLYMERIZATION PROCESSES BY COORDINATED ANIONIC CATALYSIS AND STEREOSPECIFICITY

Coordinated Anionic Polymerization

The most selective processes of stereospecific polymerization act with a mechanism which is clearly different from those of the previously known polymerization processes and in particular from those which characterize the processes taking place by free radical mechanism.

The first catalysts which proved to be highly stereospecific in the polymerization of α-olefins, are those we obtained by employing low valence crystalline halides of highly electropositive transition metals (having a crystal lattice of layers of positive ions of small diameter between two compact planes of negative ions).[36]

Such catalysts are different from the typical catalysts prepared by Ziegler, which are based on transition metal compounds soluble in hydrocarbon solvents. Some of the Ziegler catalysts in fact polymerize ethylene very easily but do not polymerize α-olefins. Some others polymerize α-olefins poorly and with extremely low yields, and still others polymerize α-olefins, giving, however, complex mixtures of stereoisomers.[37]

Our research work has led to the preparation of certain catalytic systems (Table 3), which yield highly crystalline crude polymers (prevailingly isotactic), and of other systems which yield amorphous polymers (prevailingly atactic). We have succeeded in explaining certain aspects of the causes of stereospecificity.[38]

We note first of all that independently of their stereospecificity, the catalysts used by us represent a special type of catalysts since in many cases they make it possible to obtain polymers having a chemical constitution which is different from that of the previously known polymers, and this even in the case of the atactic polymers of α-olefins. The infrared examination has in fact made it possible to demonstrate that the new α-olefin polymers present a higher regularity of structure, in particular a more regular head-to-tail arrangement than the polymers obtained by other processes. They are characterized

TABLE 3. STEREOISOMERY IN THE POLYMERIZATION OF α-OLEFINS AT 70-80°C WITH CATALYTIC SYSTEMS OBTAINED FROM A METAL-ALKYL COMPOUND (LiR, ZnR_2, AlR_3, BeR_2) AND A TRANSITION METAL COMPOUND

Type of original compound of the transition metal	*Type of stereoisomery mainly contained in the polymers*
Crystalline compounds of a lower metal valency than its maximum, insoluble in hydrocarbons, with an ionic layer lattice: $TiCl_2$, $TiCl_3$, VCl_3, etc.	isotactic
Compounds with a higher valency, soluble in hydrocarbons: $TiCl_4$, VCl_4, etc.	atactic, isotactic, or both
Oxygenated compounds: $TiCl(OR)_3$, $Ti(OR)_4$ on the amorphous support	atactic

by the presence of terminal vinylidenic groups at one end of the chain and, at the other end, of terminal alkyl groups corresponding to the normal saturated alkyl, containing the same number of carbon atoms as the polymerized normal olefins. [39]

The low molecular weight poly-α-olefins, having a vinylidene terminal group, can hardly copolymerize with α-olefins. This is the main cause, together with others, relating to the anionic polymerization mechanism, of the regularity and of the absence of long branches in the chains.

Our research work on soluble catalysts and on crystalline catalysts, obtained for instance from dicyclopentadienyl titanium compounds and from alkyl or phenyl aluminium compounds, has shown that some of them consist of complexes containing two different metals.[40-41] The chemical constitution of such complexes has led us to believe that there are bridge-linkages between two different metals, similarly to what occurs for example between the atoms of the same metal in the dimeric molecule of trimethyl aluminium.

The results of these studies demonstrate that, in all the catalysts obtained from alkyl aluminium compounds, an alkyl-aluminium bond is involved in the polymerization. The alkyl-aluminium bond appears to be more reactive if the alkyl aluminium is complexed with a low valence compound of a highly electropositive transition metal.

In previously published papers [38-39] we had attributed an anionic mechanism to the new polymerization processes. Friedländer on the other hand has attributed a free radical type mechanism to them[42] similar under certain aspects to the one proposed by Morton to the "alfin" butadiene polymerization.[43] Overberger and Price [44] have given evidence to the existence of intermediate coordination complexes containing the catalyst and the monomer.

We are of the opinion that the difference between the more classic anionic mechanisms and the mechanism which we attribute to our processes is to be attributed to the particular coordination bonds contained in our catalysts.

The argument in favour of the hypothesis of a coordinated anionic catalysis are the following:

(*a*) The nature of the terminal groups contained in the macromolecules.[39]

(*b*) The most active catalysts contain different metals which are highly electropositive, both the transition metal and that combined as alkyl metal compound. Of the alkyl metal compounds the most active are those capable of forming complexes.

(*c*) The most active complexes are those containing metallic ions which generate locally more intense electrostatic fields and have a small ionic radius. Among the elements which yield alkyl metal compounds of very high catalytic activity we can mention beryllium (ionic radius 0·35 Å), aluminium (0·51 Å), and, among the monovalent, lithium (0·68 Å). The catalytic activity of the complex is higher, the more electropositive is the transition metal, and, in general, the lower the valence of the metal.

(*d*) The solutions of alkyl metal compounds (such as trialkyl aluminium) and of their catalytically active, soluble complexes with transition metals show an electric conductivity of ionic type, with migration of the groups richer in alkyls to the anode.

(*e*) The reactivity of the monomers in the catalysis follows a reverse order with respect to that of the cationic catalysis.

(*f*) The chain termination reaction leads to the formation of a vinylidene bond by the transfer of a hydrogen from the group –CHR–. This transfer is the easier, the more electron-donor is the R group, and it is to be assumed, therefore, that a hydride ion transfer is involved. This may explain the lower molecular weight of polypropylene, with respect to polyethylene or polystyrene.

(*g*) The use of certain substances, known for their ability to capture

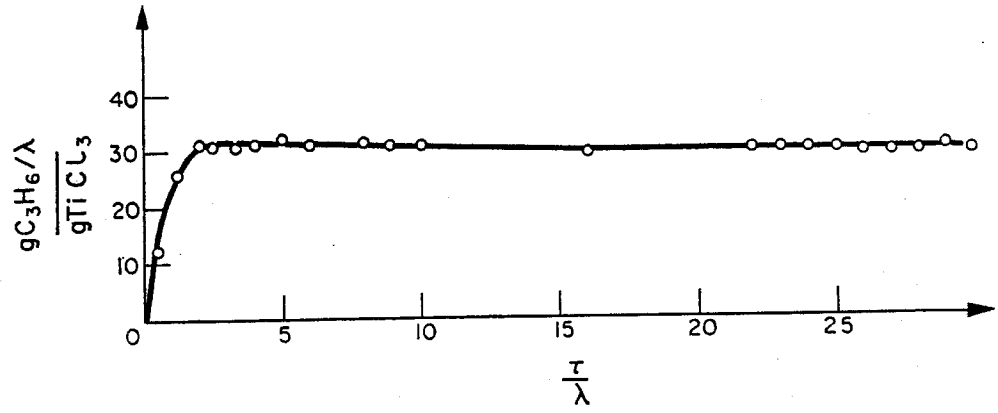


FIG. 11. Reaction rate as a function of time, in the catalytic polymerization of polypropylene using a catalyst with a high stereospecificity.

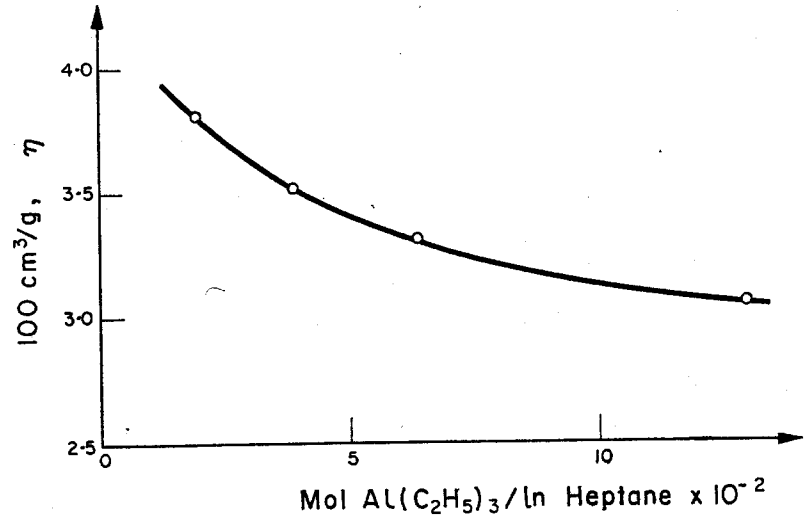


FIG. 12. Influence of concentration of metal alkyl compounds in solution on the intrinsic viscosity of polypropylene obtained in the presence of catalysts with high stereospecificity (crystalline $TiCl_3$ and $Al(C_2H_5)_3$).

free radicals (e.g. cumene, isoctane, etc.) as solvents does not lower the molecular weight of the polymer, unlike what happens in free radical processes.

The addition of a monomer molecule to the organometal compound may be considered an ionic reaction with heterolytic rupture of the metal–carbon bond, comparable with the addition of halogens to an olefin. This addition requires a polar environment, which in the absence of polar solvents, is made possible by a polar surface.

An increase of catalytic activity, attributable to a polar environment, has been observed by addition of crystals having an ion layer lattice, or of atoms having a different polarity.

The results of the kinetic study of propylene polymerization are in agreement with this hypothesis of coordinated ionic catalysis:

(*a*) When using stabilized catalysts the polymerization reactions show a rate which is practically constant with time (Fig. 11).[45] The catalyst is not consumed, unlike to what occurs with all the free radical initiators.

(*b*) The molecular weight decreases with an increase of the alkyl aluminium concentration (Fig. 12). This can be explained by a transfer of an ionic nature. The use of an alkyl aluminium containing ^{14}C or of a phenyl aluminium compound allows to identify the chains initiated by the alkyl bound to the Al, those derived from chain transfer with the monomer and those due to the transfer from the alkyl aluminium in solution. Furthermore it allows to count the active centres which are present on a stabilized catalyst.

This is one of the few cases in heterogeneous catalysis where it has been possible to determine directly the number of the active centres present and, consequently, the average life of the growing macromolecules.

Characteristics of Coordinated Anionic Catalysis

One of the most important features of anionic catalysis is the high instability of the carbanion which can be noted even when it is coordinated in complexes with highly electropositive transition elements.

The carbanions are in fact stable only in the absence of protons and in the absence of nucleophilic groups, capable of forming more stable anions than the carbanion, or to coordinate permanently a highly electropositive metal in the organometal compounds. While the cationic catalysis is favoured by the presence of polar solvents, this does not appear to occur with the anionic coordinated catalysis. This different behaviour seems to be attributable to the fact that in the anionic catalysis, it is impossible to operate in the presence of well-known polar solvents since they would decompose the organometal compound and poison the catalyst. On the other hand the fact that in coordinated anionic catalysis the soluble catalysts are much less active than the heterogeneous ones, leads us to believe that in the case of heterogeneous catalysis, the polar environment required for a heterolytic addition of a monomer, is supplied by the polar surface. This effect is particularly evident in the case of crystal lattices with layers of different polarity such as the ones observed for compounds of the AB_2 and AB_3 types,(*) when the diameter of cation A is small. In this case the

* Having a structure like that shown in Fig. 13.

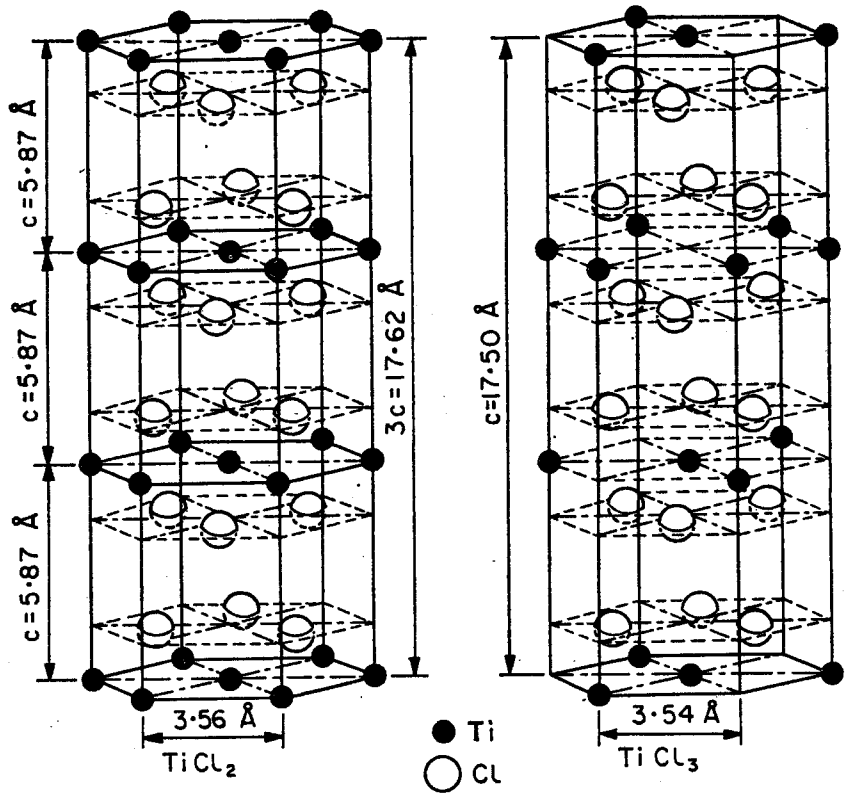


FIG. 13. Crystalline lattices of $TiCl_2$ (violet modification) and $TiCl_3$.

strong electrostatic actions due to the high charge and to the small diameter of the cation cause a "close" coordination of the negative ions with the coordinating cation (thus explaining the easy cleavage of the layer lattices).

The most active catalysts in the anionic and cationic catalysis are characterized by the fact that the carbon ion (either cation or anion) is stabilized by the presence of coordination complexes.

In the case of coordinated cationic catalysis it is not the carbon ion but the ion with which the latter is combined which coordinates itself into a complex; while in the case of coordinated anionic catalysis it is the carbanion itself which is coordinated. This difference allows to explain from the point of view of the stereospecificity, the different behaviour of certain anionic catalysts.

In a cationic catalyst, such as that formed, e.g. from Al_2Cl_6 in the presence of an alkyl chloride, complexes of the type $(AlCl_4)^-R^+$ are present:

$$\tfrac{1}{2}\,Al_2Cl_6 + ClC_2H_5 = \left[\begin{matrix} Cl & & Cl \\ & Al & \\ Cl & & Cl \end{matrix}\right]^- \overset{+}{C}H_2\ CH_3$$

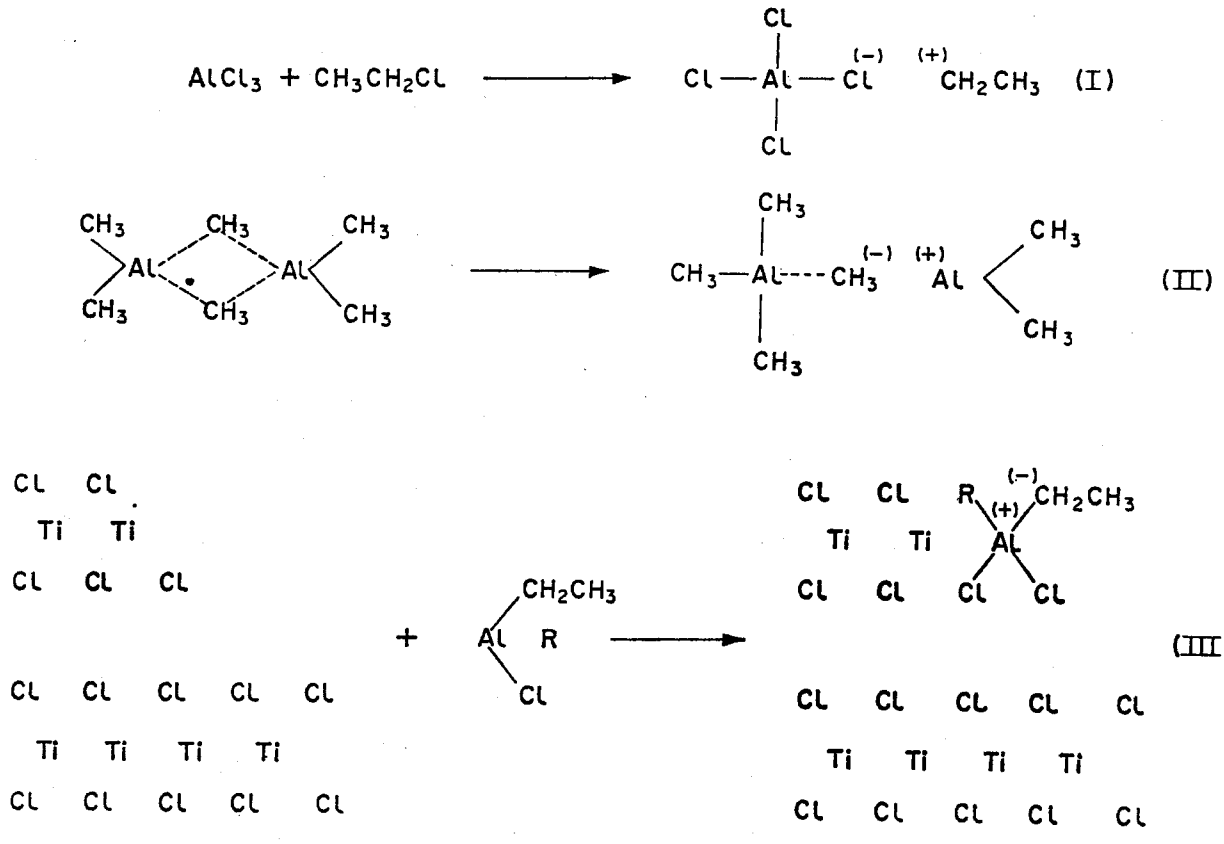


FIG. 14. Comparison among different catalytic complexes in the ionic polymerizations: I, cationic, not stereospecific; II, ionic, not stereospecific; III, anionic stereospecific (complex formed on the edge of a layer lattice).

The chlorine of the alkyl aluminium, which takes part in the formation of the complex, enters into a symmetric $(AlCl_4)^-$ anion, and therefore the cationic character of the carbon increases.

The chlorine which was bound to the alkyl chloride loses its identity and we can suppose that a large diameter ion $(AlCl_4)^-$ replaces the carbanion. This is the cause of the lack of stereospecificity in cationic catalysis.

On the contrary in the case of anionic coordinated catalysis, e.g. with Ti-Al complexes, the carbanion initially partaking with the alkyl-metal compound coordinates itself in a complex in which the electropositive character of the transition metal stabilizes the carbanion (Figs. 14 and 15).

The formation of bridge bonds between two metals, the preferential coordination of ions of a given type in the bridge linkage and the asymmetries of the bimetallic complex, when the two metals are different, can determine a definite position of the carbanion in certain complexes. This can be the reason for the higher stereospecificity of the anionic

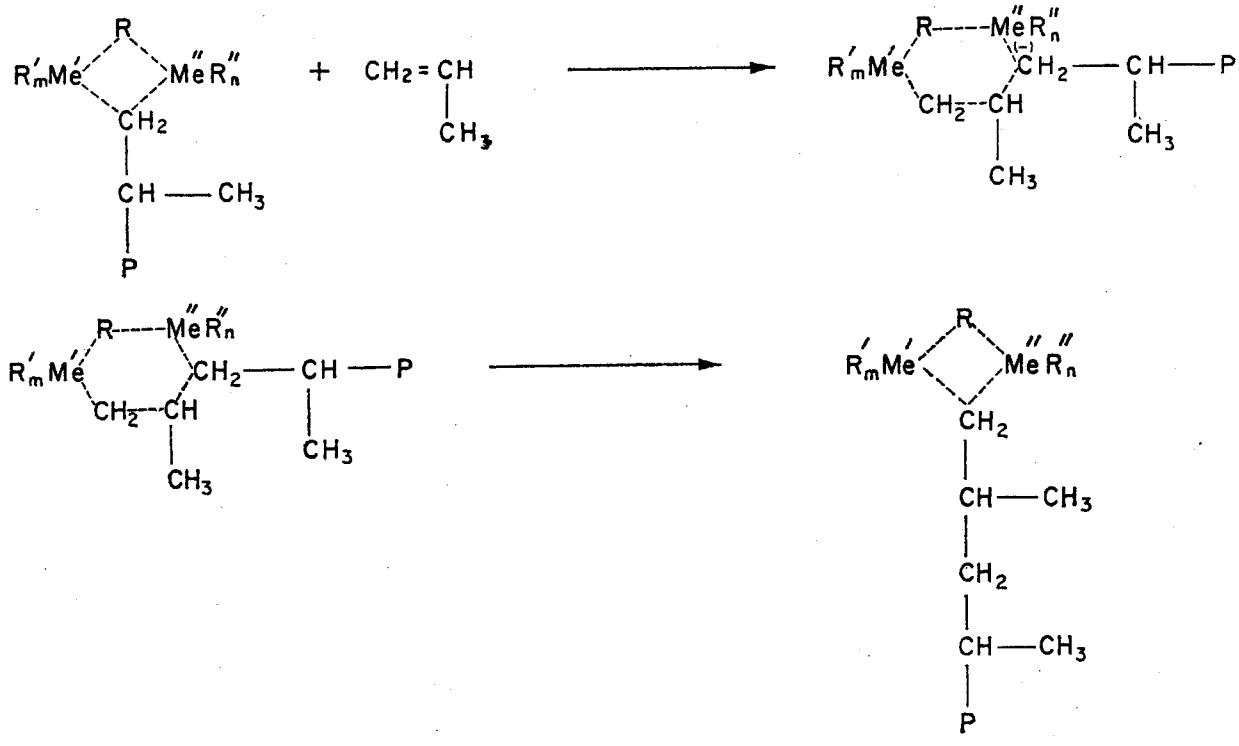


FIG. 15. Hypothesis about the mode of addition of a monomer molecule on the bond between the catalytic complex and the growing chain in the anionic coordinated polymerization.

TABLE 4. DEPENDENCE OF THE STEREOSPECIFICITY OF THE CATALYSTS PREPARED FROM $TiCl_3$ ON THE NATURE OF THE METAL CONTAINED IN THE ORGANOMETALLIC COMPLEX

Metal (of the matel alkyl)	*Ionic radius of metal alkyl*	*Stereospecificity (% of non-extractable polypropylene in boiling n-heptane)*
Be	0·35 Å	94÷96%
Al	0·51 Å	80÷92%
Mg	0·66 Å	78÷85%
Zn	0·74 Å	30÷40%

coordinated catalysis and for the fact that, in the α-olefin polymerization, the most active catalysts are given only by asymmetric bimetallic complexes, containing two different metals and not by complexes containing atoms of only one metal.

It should be kept in mind that the most stereospecific catalysts are those in which the carbanion is coordinated to a metal cation having a very small diameter (e.g. Al, Be, Li).

The highest stereospecificity is observed with alkyl-beryllium compounds (Table 4).

A parallelism may be made with cationic catalysis which, as we have observed, is generally not stereospecific. The only known case of cationic catalysis which presents a certain stereospecificity and this only at low temperature, is that described by Schildknecht [46-47] for the polymerization of vinyl ethers. Thus it represents the first known case of stereospecific polymerization of a vinyl monomer. It is a significant fact that such a catalyst, which probably contains the BF_3O^-R complex, has not only a coordinating boron atom with a small ionic radius (0·3 Å), but contains also fluorine and oxygen atoms which, among negative ions, have the smallest radius.

Ion	*Ionic radius*
B^{+++}	0·30
O^{--}	1·31
F^{--}	1·33
Cl^{--}	1·81

In the etherate and hydrate of boron fluoride one can assume that the oxygen ion, to which the alkyl chain of the etherate is bound, is in a geometrically stabilized position, thus explaining its catalytic stereospecificity, which does not appear in the presence of symmetrical complex anions, such as, for example $(AlCl_4)^-$.

Stereospecificity in the Polymerization of Diolefins

The problem of stereospecific catalysis in the polymerization of diolefins can have various aspects, because of the different types of possible stereoisomery, i.e. geometrical and optical, and because of the higher reactivity of diolefins themselves.

It is interesting to note that in the case of the stereospecific polymerization of isoprene to *cis*-1,4-polymer, it is not necessary to have as a catalyst a complex containing two different metals. It is sufficient that the organometal bond corresponds to a cation of very small diameter, such as lithium, which creates a strong electric field and can exert a coordinating action.

The small Li-C distance favours the *cis*-1,4-arrangement, particularly in the case of isoprene, in which the CH_3 group exerts an inductimetric effect differentiating the two terminal methylenes, while it inhibits the 1,2-addition by steric action. The polymerization of diolefins to high polymers is also possible in a homogenous phase, not only by *cis*-1,4-addition but also by 1,2-(or 3,4-) addition.

TABLE 5. STEREOISOMERY IN THE POLYMERIZATION OF DIOLEFINS AT 0°C WITH CATALYTIC SYSTEM OBTAINED BY THE REACTION OF TRANSITION METAL COMPOUNDS WITH ALUMINIUM ALKYLS IN HYDROCARBON SOLVENTS

Starting compound of the transition metal	*Al/Me ratio*	*Type of stereoisomer*
soluble $TiCl_4$	1∼	prevailingly *cis*-1,4
soluble $TiCl_4$	2∼	prevailingly *trans*-1,4
violet $TiCl_3$, crystalline and insoluble VCl_3 (layer lattice)	any	*trans*-1,4 (up to 98%)
coordinated complexes of chromium containing O or N or CO, etc.	<6	syndiotactic-1,2
coordinated complexes of chromium containing O or N or CO, etc.	>6	isotactic-1,2

The *trans*-1,4 stereoisomery seems to be favoured by the presence of lattices with layers of ions having different charge. It is probable that both the double bonds of the diolefins are chemically adsorbed. It is very probable that in *trans*-1,4 addition the reaction takes place among 3 species, which may be considered distinct from a kinetic point of view; one given by the diolefin, the other two by the cation and by the anion, respectively. A simultaneous collision leading to a single transition state is very improbable and, therefore, the process will probably take place in more stages, at least two.

The use of oxygen-containing transition metal complexes, e.g. containing alcoholates or carbonyls, or of polydentated complexes (acetyl acetonates) on the contrary favours the 3,4 arrangement. This is due to the fact that the oxygenated groups are more strongly coordinated with the transition metal.

These hydrocarbon soluble catalysts do not in general polymerize α-olefins. In the case of diolefins they can yield atactic, isotactic or syndiotactic polymers. The causes of stereospecificity in the case of the 1,2-polymerization are not yet clear.

We have observed that the scarcely reduced complexes, containing more oxygen atoms coordinated with the transition metal, yield syndiotactic polymers.

In the case of highly reduced complexes, in which probably the number of oxygen atoms coordinated with the transition metal is low, isotactic polymers of polydiolefins are obtained. In the case of stereospecific 1,2-polymerization of diolefins the presence of a solid lattice does not seem necessary for the stereospecificity; but it is sufficient

to have a complex of considerable size, such as that obtained by reacting acetylacetonates or carbonyl compounds of highly electropositive transition metals with AlR_3 (Table 5).

The ability of AlR_3 to coordinate with the electron pair of the oxygen atom makes the reaction between acetylacetonates and alkyl aluminium able to absorb a considerable number of alkyl aluminium molecules, with the formation of a large size complex ion.

KINETICS OF THE STEREOSPECIFIC POLYMERIZATION OF α-OLEFINS

We have seen that the polymerization processes under consideration are initiated by organometallic catalysts or by hydrides or by metals capable of forming organometallic compounds under the reaction conditions. The more active catalysts contain compounds of at least two different metals one of them being in general a transition metal.

In heterogeneous catalysis the molecule grows on the surface of a solid, the negative carbon ion being bound to an insoluble complex. The growth of the macromolecule can resemble (as Mark suggests) that of a hair, comparing the hair bulb with the active centre on the catalyst surface.

In this catalysis the polymer growth stops if the monomer is withdrawn, but it starts again immediately and at the same rate once the monomer concentration is brought back to its initial value.[45]

This behaviour is very frequent in anionic polymerization such as in the polymerization of ethylene oxide.

The low temperature polymerization of ethylene with triethyl aluminium[20] occurs, at least at its start and under certain aspects, in a way similar to that observed later on by Szwarc in the polymerization of styrene with anionic catalysts.[48-49]

The polymerization of ethylene, however, stops when the long tentacles of the growing chains, which originate from the central Al atom once they have reached a length of a few hundred angstroms tend to crystallize.

On the contrary, in the polymerization of ethylene and styrene on heterogeneous catalysts, consisting of certain insoluble bimetallic complexes, the growth, which may be limited to a single alkyl of the complex, is very fast and the polymers obtained show high molecular weights, which can easily reach values of some millions.

In our stereospecific catalysis the average life of each molecule is very short, unless lethargy is induced by cooling or lack of feed; while

the macromolecule generating capacity of the active catalytic complex remains unchanged.

The polymer molecule lives as long as it is bound to a metal which can enter into and partake of the active complex. The separation of the growing chain from the ionic bond with the complex causes its death but it does not destroy the activity of the complex which can generate other macromolecules.

Borrowing an expression frequently used for other polymerization processes, in which the polymer molecules can grow for long periods of time, like in the case of polymerization of styrene according to Szwarc,[48-49] one can call "living" the macromolecules generating complex in our heterogeneous catalytic polymerization. This complex produces the successive macromolecules and it survives after their death by generating other macromolecules.

The macromolecules grow quickly and, like plants having a thin and extraordinary long stem, are exposed to many dangers of accidental death. The highly exothermic growing reaction can lead to local increases of temperature and, therefore, to the thermal activation of the hydrogen atom of the tertiary carbon near the anionic carbon, with transfer of the hydride ion into the complex and the resulting formation of a vinylidene double bond, present in the end of the chain.

It is a spontaneous death whose probability is not very high, if one operates at sufficiently low temperatures. In such a case the molecules die and separate from the complex to which, before dying, a hydride ion has been given. The latter, which is bound to the complex, can join a molecule of the monomer, thus forming a carbanion which can generate a new macromolecule.

The different phases of polymerization can be schematically shown as follows:

1. The growth of the macromolecular chain:

$$(Cat)^{(+)(-)}\,CH_2—CHR—P + CH_2=CHR \rightarrow (Cat)^{(+)(-)}CH_2—CHR—CH_2—CHR—R$$

2. Spontaneous death of a macromolecule by transfer of a hydride ion to the complex:

$$(Cat)^{(+)(-)}\,CH_2—CHR—P \rightarrow (Cat)^{(+)}H^{(-)} + CH_2=CR—P$$

and subsequent formation of a new macromolecule:

$$(Cat)^{(+)}\,H^{(-)} + CH_2=CHR \rightarrow (Cat)^{(+)(-)}\,CH_2—CH_2R$$

3. Death of a macromolecule, and simultaneous formation of a new macromolecule by transfer of a hydride ion to the monomer:

$$(Cat)^{(+)(-)}\,CH_2—CHR—P + CH_2=CHR \rightarrow (Cat)^{(+)(-)}\,CH_2—CH_2R + CH_2=CR—P$$

4. Termination of the growth of a macromolecule by transfer of a polymeric ion on an inactive compound and formation of a new macromolecule:

$$(Cat)^{(+)(-)}\,CH_2—CHR—P + MeR'_n \rightarrow MeR'_{n-1}—CH_2—CHR—P + (Cat)^{(+)(-)}\,R'$$

5. Shortening of the life of the molecule without death of the starting complex:

$$(Cat)^{(+)(-)}CH_2—CHR—P + H^{(+)}H^{(-)} \rightarrow CH_3—CHR—P + (Cat)^{(+)}H^{(-)}$$

At low temperature, since the molecular weight is slightly influenced by pressure (Fig. 16), the most frequent cause of the death of the molecule is related to the probability that the same monomeric units differentiate from other units and refuse to become one of the many by the long polymeric chain; due to a different activation they would then expel the old chain by the removal of a hydride ion from it. The latter, leaving the monomeric unit, leads to the formation of a new living molecule which in its turn will be fed through the same complex.

When the molecule becomes too long it behaves like a tall tree in a forest exposed to a storm. Even a simple mechanical agitation can tear the tree from its roots. The catalytic complex embedded in the soil is represented here by the crystal lattice of the support.

When the monomer feed is stopped, the system does not die but remains in lethargy and its growth stops; it starts again at the same rate when further monomer is supplied to the generated complex.

The poisons, which are generally anions more stable than the carbanion, cause the death of the macromolecules and also of the complex generating them. When anions which are not much more stable than the carbanion are present, the generating complex does not die but their competitive action causes some transfers which reduce the life and therefore the molecular weight of the polymer.

It may be interesting to examine the life and the growth of the macromolecules from the point of view of stereospecificity.

If we start with a triethylaluminium solution and titanium trichlo-

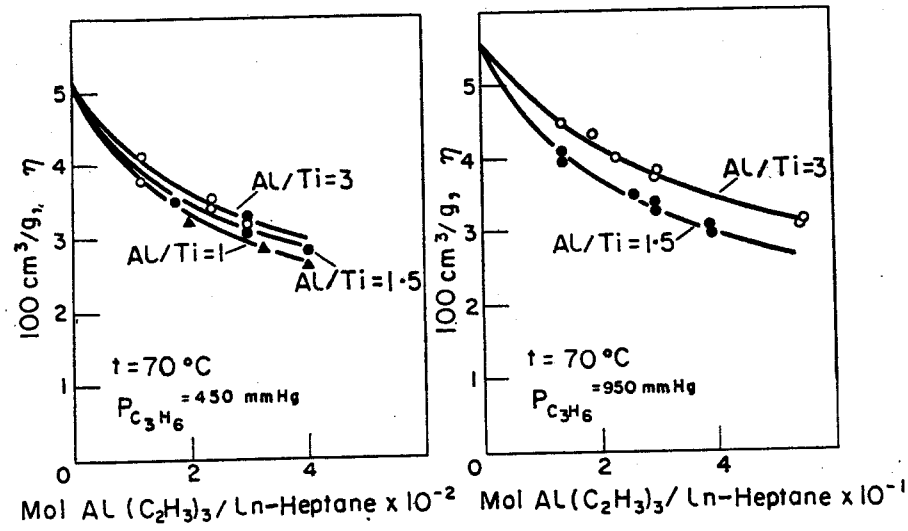


FIG. 16. Demonstration of chain terminating by transfer with the monomer, in addition to that by transfer with the alkyl, in the polymerization of propylene with the aid of very stereospecific catalysts (crystalline $TiCl_3$ and $Al(C_2H_5)_3$), in comparison with the intrinsic viscosity of the polymers obtained at two different pressures.

ride in the formation of the catalyst, the steric structure of the macromolecules generated by the complex containing the aluminium–titanium couple depends on the physical state and on the morphological structure of the titanium compound. If we start with a solid and compact stock (well-developed $TiCl_3$ crystals such as those prepared at high temperature), we observe that a certain time is necessary for the catalytic activity to reach a maximum value, which remains then constant.

This induction period (or better arrangement period) is due to the time needed for the completion during the polymerization of the chemisorption of the AlR_3 on $TiCl_3$ on the fresh crystal surfaces generated by the cleavage caused by the pressure of the growing macromolecules.[45] The macromolecules obtained with these catalysts are sterically very pure, and almost all isotactic.[36]

When, on the contrary, a poorly crystallized titanium chloride, such as that one obtained by the reaction of $TiCl_4$ with metallo-alkyl compound is used, the initial reactivity is higher but the products of the reaction with AlR_2 are less sterically pure.

The high initial catalytic activity decreases rapidly with time, and the generated macromolecules are often more delicate and have a shorter growth; they are sterically impure and many of them are stereoblock molecules, with lower melting point, or even atactic, amorphous molecules.[35] The sterically purer species, obtained with

crystalline $TiCl_3$, is stronger, its life is longer and the molecular weights are higher.

In the case of heterogeneous catalysts, the stereospecificity does not depend exclusively on the chemical nature of the catalytic complex, but also on morphological factors. Each titanium of each Al–Ti couple has a particular character, which determines the stereospecificity.

This character derives from geometrical reasons, and precisely from the way this couple is oriented with respect to the crystal surface and the alkyl aluminium.

In general in all the known processes of organic synthesis, which are not derived from optically active substances, statistical factors determine the distribution of the steric configurations of the molecules produced. In our case one has to admit that each active centre does not work at random, but produces isotactic molecules of a determined type.

It is interesting to note that, according to the way of distribution of the different species (the two possible steric configurations of the successive monomeric units), due to a competition between statistical and fixed events by the structure of the active complex, an infinite number of possible types of generated molecules can be obtained. The properties of the polymer depend on the way in which these species combine rather than on its molecular weight.

Before concluding I wish to stress that with the words "life of the macromolecules generating complex" I only wanted to indicate in a more expressive form some kinetic facts, which result from very accurate chemical–physical determinations. The word "life" is intended to mean merely "growth in time", referred to a chemical process, just as the words "life of a crystal" can be used to represent a growth process which in this case is purely physical.

Imagination, which sometimes likes to take long flights, can be tempted to look for analogies, however simplified in nature, with the genesis of the macromolecules produced in biological processes. Many natural macromolecules also consist of asymmetrical monomeric units and they too can assume various properties and different structures, depending on how they are generated by the enzymatic complex, and the repetition of a given model.

Let us be lenient towards these flights of fancy. When conveniently controlled they do no harm to the research worker: it can sometimes be useful, in order to explore new horizons, to extrapolate with the

imagination the method illustrated by Pauling[50] beyond strict logical limits.

The whole history of organic chemistry, whose development in the past might appear to have been largely empirical, comprises innumerable results which often sprang from the seed of a few brilliant intuitions.

A slow progress due to a tremendous amount of experimental work by many research scientists gradually creates solid bases from which our thoughts can soar towards the highest goals.

Many new discoveries at their inception were based on a very few experimental tests. Intuition, following uncontrollable and unforeseen paths, sometimes suddenly illuminates the road to be followed. Such a combination of dreams and reality can make the hard, daily task of the research chemist attractive and even poetically fascinating.

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THE POLYMERIZATION OF PROPYLENE WITH CATALYSTS OBTAINED FROM TITANIUM TETRACHLORIDE. NOTE I: THE INFLUENCE OF THE TYPE OF ALKYLALUMINIUM ON THE POLYMERIZATION OF PROPYLENE

by G. MAZZANTI and P. LONGI

(3 Sept. 1957)
[*Rend. Ist. Lomb. Sci. e Lettere* **91**, 743 (1957)]

ABSTRACT

A polymerization study of propylene is reported, carried out with the aid of catalysts obtained from titanium tetrachloride and aluminium trialkyls.

As it was pointed out in another paper from this institute [*Gazz. Chim. It.* **88**, 219 (1958)], if one varies the number of carbon atoms of the alkyl groups, present in the aluminium trialkyl, the activity, the stereospecificity and other properties of the catalyst are markedly varied. These variations exert an influence on the amount, on the crystallinity and on the molecular weight of the polypropylenes obtained.

Thus, it has been observed that, an increase in the number of carbon atoms of the alkyl groups, in the aluminium trialkyl, produces a polymer whose highly isotactic fraction (which is non-extractable in boiling n-heptane) is markedly decreased; for example, at a molar ratio of AlR_3 to $TiCl_4 = 1{\cdot}5$, the highly isotactic polymer fraction gradually decreases from a value of 23–24 per cent when aluminium trimethyl is used to a value of 17–18 per cent with aluminium trioctyl.

The influence of the length of the alkyl groups on the catalytic activity is even more pronounced. First of all we have established that, for all the tri-n-aluminium alkyls, comprised between the trimethyl and tri-n-octyl, the highest catalytic activity in the described experimental conditions, is obtained when a ratio of about 2 exists between the moles of the tri-n-alkyl aluminium and of titanium tetrachloride.

By relating the highest catalytic activity, with the amount of obtainable polymer, at comparable conditions, and at a molar ratio of AlR_3 to $TiCl_4=2$, one can observe that the most active catalysts are those obtained from trimethyl and tri-n-octyl aluminium, whereas those catalysts obtained from triethyl-, tri-n-propyl-, tri-n-butyl- and tri-n-hexyl aluminium possess an almost identical catalytic activity.

The greatest difference in the catalytic activity is observed among catalysts prepared from trimethyl and tri-n-propyl aluminium: the ratio between the two activities, (trimethyl aluminium/tri-n-propyl aluminium) is of about 2.

These different activities might be attributed to the changing behaviour of the curves of the rate of polymerization of propylene, of which some examples are given for the various trialkyl aluminiums.

It has been finally observed that the molecular weight of polypropylenes undergoes a variation which is opposite to that observed for the catalytic activity. In other words, the lowest molecular weights can be observed in polypropylenes (highly isotactic fractions) obtained with the use of trimethyl and tri-n-octyl aluminium.

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THE POLYMERIZATION OF PROPYLENE WITH CATALYSTS OBTAINED FROM TITANIUM TETRACHLORIDE. NOTE II: CATALYSTS FROM ORGANOMETALLIC COMPOUNDS OF METALS OF THE I, II AND III GROUPS OF THE PERIODIC TABLE

by G. MAZZANTI and P. LONGI

(3 Sept. 1957)

[*Rend. Ist. Lomb. Sci. e Lettere* **91**, 755 (1957)]

ABSTRACT

We have studied the polymerization of propylene carried out with the aid of catalysts obtained from titanium tetrachloride and organometallic compounds of metals of the I, II and III groups of the periodic table.

In analogy with what has already been observed with catalysts prepared from aluminium trialkyls and titanium tetrachloride, we have here observed that the mole ratio of the organometallic compound to $TiCl_4$ used in the preparation of the catalyst, exerts a remarkable influence on the activity and on the stereospecificity of the catalyst.

It is believed that this influence may be of two different types depending on the "alkylating power" of the organometallic compound used.

Thus, a first class of catalysts is that with organometallic compounds of high "alkylating power" (e.g. diethyl beryllium and n-butyl lithium), which achieve a maximum catalytic activity under conditions very similar to those obtained with aluminium trialkyls.

In particular, the highest catalytic activity is observed with diethyl

beryllium, at molar ratio $Be(C_2H_5)_2$ to $TiCl_4$ of about 1 and with n-butyl lithium at molar ratio Li n-C_4H_9 to $TiCl_4$ of about 2.

However, it was observed that the stereospecificity of these catalysts does not show a behaviour comparable with that of the catalysts obtained from aluminium trialkyls. Polypropylenes having a gradual increase in the contents of highly isotactic fraction are produced up to values of the molar ratio Me $R_n/TiCl_4$ which are at least 1·5 times higher than the values corresponding to the highest catalytic activities (i.e. up to 1·5 and 3 for beryllium diethyl and for n-butyl lithium, respectively).

Quite similar trends are also observed in the molecular weight of the same polymers.

The catalysts prepared from diethyl zinc and aluminium diethyl monochloride belong to the second class of catalysts. These organometallic compounds show an "alkylating power" which is much lower than that of the n-butyl lithium, of the diethyl beryllium or the trialkylaluminium.

In this case it can be observed that the catalytic activity increases very slowly with the increase of the molar ratio of the organometallic compound to $TiCl_4$, and it reaches a maximum at high values (between 15 and 20 in the case of $Al(C_2H_5)_2Cl$ and between 5 and 8 in the case of Zn $(C_2H_5)_2$).

In every case the amount of polymer obtained was so negligible that a definite characterization of the product was not possible.

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THE POLYMERIZATION OF PROPYLENE WITH CATALYSTS OBTAINED FROM TITANIUM TETRACHLORIDE. NOTE III: THE INFLUENCE OF TEMPERATURE ON THE STEREOSPECIFICITY OF THE POLYMERIZATION

by G. MAZZANTI, P. LONGI and R. MATTEUCCI

(3 Sept. 1957)

[*Rend. Ist. Lomb. Sci. e Lettere*, **91**, 768 (1957)]

ABSTRACT

A study of the influence exerted by the temperature of polymerization and of the preparation of the catalyst on the anionic polymerization of propylene is reported here.

When using catalysts prepared from $Al(C_2H_5)_3$ and $TiCl_4$, the stereospecificity decreases linearly with the increase of the temperature of polymerization up to values ranging from 40 to 170°C, whereas, it increases linearly with the increase of the temperature of the catalyst preparation.

46

STRUCTURE OF AMORPHOUS, HIGH POLYMERS OF α-OLEFINS, WITH SPECIAL EMPHASIS ON POLYETHYLENE

by P. CORRADINI

(13 Sept. 1957)

[*Rend. Ist. Lomb. Sci. e Lettere*, **91**, 889 (1957)]

ABSTRACT

The causes for the incomplete crystallinity observed in the linear high polymers are discussed here. The non-crystallizable polymer fraction is fairly-ordered even in the amorphous state, as it has been proved by X-ray investigations.

A detailed calculation of the diffraction of a polyethylene model, in which the chains constantly keep a certain parallelism among themselves, has been found to be in agreement with the experimental results.

47

CRYSTALLIZABLE COMPLEXES OF TITANIUM AND ALUMINIUM WHICH ARE CATALYTICALLY ACTIVE IN THE POLYMERIZATION OF ETHYLENE

by G. NATTA, P. PINO, G. MAZZANTI and U. GIANNINI

(21 Sept. 1957)

[*La Ricerca Sci.* Suppl. **28**, (1958)]

ABSTRACT

Some of the most active catalysts for the low-pressure polymerization of ethylene and of α-olefins are obtained by the reaction of transition-metal compounds with organometallic compounds of very electropositive metals.

The activity of those polymerization catalysts obtained by the reaction of titanium halides with alkyl aluminium compounds can be attributed to the presence of organometallic complexes containing titanium, aluminium and organometallic bonds.

Our study on the nature of these polymerization catalysts, allowed us to isolate a series of crystallizable complexes containing titanium and aluminium which are catalytically active in the polymerization of ethylene. These complexes have the following formulas:

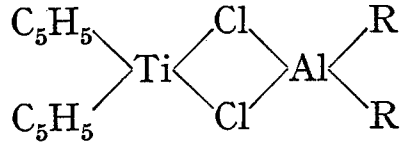
$(C_5H_5)_2$	$TiCl_2$	$Al(C_2H_5)_2$
$(C_5H_5)_2$	$TiCl_2$	$AlCl(C_2H_5)$
$(C_5H_5)_2$	$TiCl_2$	$AlCl_2$

They were prepared by reacting titanium bis-(cyclopentadienyl) dichloride with triethyl aluminium, aluminium diethyl monochloride, aluminium monoethyldichloride, respectively, in a heptane solution at 60°C.

The complexes could be recrystallized from n-heptane.

The chemical analysis and the paramagnetic value of these complexes indicate that the titanium atom has an oxidation number of 3.

On the basis of their chemical behaviour and of their physical properties, a formula of the type shown below has been proposed:



in which the titanium and the aluminium atoms are bridge-bonded by two chlorine atoms.

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STEREOSPECIFIC POLYMERIZATION BY MEANS OF COORDINATED ANIONIC CATALYSIS *

by GIULIO NATTA

(21 Sept. 1957)

[*La Ricerca Sci.*, Suppl. **28**, (1958)]

SUMMARY

The stereoisomerism phenomena in the linear polymers of olefins and diolefins and the nature of the stereospecific polymerization processes are shortly discussed. They allowed the first synthesis of isotactic and syndiotactic polymers and of the four pure stereoisomers of polybutadiene, that is: the polymers having isotactic-1,2, syndiotactic-1,2, *cis*-1,4 and *trans*-1,4 arrangement.

The structure of catalytic complexes, that promote the stereospecific polymerization in the ionic coordinated catalysis, is pointed out. They are electron deficient complexes containing bridge-bonds between very electropositive transition metals, with valence less than the maximum, and very electropositive metals with very small ion diameter, to which electronegative carbon atoms are coordinated.

Some soluble complexes, based on titanium and aluminium, are described, that act as catalysts in homogeneous solution.

The best stereospecific catalysts for the synthesis of isotactic polymers are heterogeneous and their stereospecificity is connected with the presence of a crystalline substrate, formed by a layer lattice on which the active centers contain chemisorbed or epitactically bound metallorganic complexes (that may exist in enantiomorphous forms).

INTRODUCTION

I have accepted the invitation of my friend Prof. Caglioti to deliver this lecture because it is my opinion that chemists who work on complexes might be interested to know how a new field, fertile of im-

* Introductory Lecture presented at the International Symposium on the chemistry of the Coordination Compounds, Rome, Sept. 1957.

portant applications, has recently been opened to catalysis and to chemistry of coordination compounds.

It is not my intention to speak here in general about the use of complexes as catalysts: this is a very wide subject matter, with a large number of examples, many of which have been known for a very long time. It will be sufficient to mention the wide field of Friedel-Crafts catalysts, most of which in fact are formed by complexes. They have had various important practical applications also in the industrial field, for inst. in alkylation processes, in the polymerization of olefins to low polymers and in cationic, non-stereospecific processes, whereby unsaturated ethylenic monomers containing electron releasing substituents (such as isobutene and isobutyl vinyl ether) are polymerized to high molecular weight polymers.

I am going to deal here only with the new field of coordinated anionic catalysis, which has been introduced to practice only recently and which has led to the discovery of truly stereospecific polymerization processes yielding polymers of olefins and diolefins having a sterically regular structure.

The synthesis of these new polymers is of scientific interest, but also of the greatest practical significance because of their applications in the production of new plastics, new textile fibres, and new rubbers.[1]

Stereoisomerism in the Linear Polymers of Olefins and Diolefins

I will consider briefly stereoisomeric phenomena in high, linear polymers because they are related with the nature of the catalytic complexes which give rise to them.

The stereospecific catalysts have made it possible to obtain, by polyaddition of vinyl monomers, long linear head-to-tail chains consisting of sequences of monomeric units having the same steric structure. These polymers, which we called "isotactic" polymers,[2] can crystallize, while those in which the monomeric units of different steric structure are arranged at random ("atactic" polymers) generally cannot crystallize. With certain monomers and special stereospecific catalysts we obtained also another type of crystalline polymers containing long regular head-to-tail sequences of monomeric units with alternatively opposite steric configuration, which we called "syndiotactic" polymers. The chains of these types of stereoisomeric vinyl polymers, supposed stretched in a plane, are represented in Fig. 1 of paper 19.

In Fig. 1 of paper 42 the conformations which the chains of isotactic polypropylene and polystyrene assume in crystals are shown.[3]

In the case of diolefins the new stereospecific polymerization processes have made it possible to obtain not only crystalline polymers corresponding respectively to the two types of geometrical stereoisomery[4] which are present in nature in hevea-rubber and in gutta-percha, but also other stereoisomers which do not exist in nature, such as the isotactic and syndiotactic polymers, obtained by 1,2 or 3,4 arrangement of monomeric units deriving from conjugated diolefins.[5]

In Fig. 5 of paper 19 the structures of the stereoisomeric polymers which we prepared from butadiene are shown, while in Fig. 8 of paper 42 we represent the conformation which the same chains assume in crystals, whose structures were determined by us.[6]

Catalytic Complexes in Coordinated Anionic Catalysis

In some of my previous papers I have discussed the kinetics of the polymerization and indicated the composition of some catalysts which promote the stereospecific polymerization of α-olefins.

TABLE I.

Metal	*Electro-negativity(1)*	*Atom radius* Å	*Ion radius* Å *(2)*
Li	*1.0*	*1.33*	*0.68*
Na	0.9	1.57	0.97
K	0.8	2.03	1.33
Rb	0.8	2.16	1.47
Cs	0.7	2.35	1.67
Be	*1.5*	*0.90*	*0.35*
Mg	*1.2*	*1.36*	*0.66*
Zn	*1.5*	*1.31*	*0.74*
Ca	1.0	1.74	0.99
Ba	0.9	1.98	1.34
B	2	0.88	0.23
Al	*1.5*	*1.26*	*0.51*
Si	1.8	1.17	0.42

(1) Electronegativity, according to L. Pauling.
(2) L. H. Ahrens: *Geochim. et Cosmochim. Acta* **2**, 155-169 (1952).

Those papers show that most of these catalysts have in common that they are formed by metallorganic complexes of strongly electropositive metals of small ionic diameter, in which carbon atoms, derived from an anionic form, are coordinated (Table 1).[7]

The underlined metals, that are highly electropositive and have small ion radius, give the more interesting metal alkyls for coordinated anionic catalysis.

While the practical applications of coordinated anionic catalysis have already reached a remarkable development, the study of the true nature of the catalysts is just at its very beginning and might represent a fascinating research in the field of the chemistry and structure of metallorganic complexes. It presents, however, difficulties and complications, because the composition of the best heterogeneous catalysts now in use is mostly not well defined.

It frequently occurs in heterogeneous catalysis that the catalytic activity is connected with the existence of surface irregularities, of reticular gaps or of solid phases whose composition is not well defined. No wonder, therefore, if the same thing happens also in the case of heterogeneous anionic catalysis, in which the catalytic action is related to the existence of active centers on the surface of the catalyst and of chemisorption compounds whose composition differs from the overall composition of the catalyst itself.

It cannot any longer be doubted, however, that the activity of the best stereospecific catalysts in the α-olefin polymerization is connected with a coordinating action of strongly electropositive transition metal atoms, situated on the surface of a solid, microcrystalline phase (for instance of low-valence halides) which promotes the chemisorption of metallorganic compounds.

It is of significance to recall here that many halides of polyvalent metals (some of which corresponding to the highest valence of the same transition metals which in their lower valence state are employed now in anionic catalysis) may act as Friedel-Crafts catalysts, that is as catalysts of cationic type.

The electropositivity of a transition metal atom increases as its valence decreases. Only low valence compounds of transition metals can operate in a coordinated catalysis of the anionic type, but not those of poorly electropositive metals (e.g. platinum, palladium, etc.) which are inactive, even if in a low valence state. The compounds formed by platinum (II) or palladium (II) halides with olefins, which were in the past the best known and are stable compounds of well-defined composi-

tion of metal halides with olefins, do not act as catalysts. This is due to the fact that in the olefin molecule bound in these complexes there is no considerable change in the nature of the olefinic double bond, while catalysis either cationic or anionic requires the presence of bonds of the ionic type, in which carbon ions take part.

Crystallizable complexes of transition metals, having a definite composition and having by themselves catalytic action in anionic polymerization of ethylene even in homogeneous phase, such as $(C_5H_5)_2$ $TiCl_2$ $Al(C_2H_5)_2$ have been obtained by us only in a few particular cases, but their catalytic action is always rather poor. Their X-ray examination in our laboratory demonstrates the existence of Al-Cl-Ti bridges, with a Ti–Cl distance of about 2·5 Å and a Ti–Cl–Al angle of about 90°. These compounds polymerize ethylene,[8] but not α-olefins at all, and therefore no stereospecific action can be ascribed to them.

The most interesting catalysts which are stereospecific in the polymerization of α-olefins, act only in a heterogeneous phase.[6]

In spite of the difficulties encountered in establishing the true chemical nature of the active centres which catalyse the stereospecific polymerization of α-olefins a great number of experimental data are now available. These allow one to establish that such a catalytic action is always connected with the existence of metallorganic complexes, mostly electron deficient molecules, in which the carbon atom, in order to be coordinated with the central strongly electropositive metals, must be rich in electrons; and it must therefore derive from an anionic form, which may be originated by the polarization of the olefinic double bond.

Homogeneous Catalysts for the Polymerization of Ethylene and Diolefins

Some simple metallorganic compounds act even in homogeneous phase in the anionic polymerization of ethylene. However, not all the metallorganic compounds containing a carbon–metal bond and having a certain percentage of ionic nature show a catalytic action in ethylene polymerization.

The simple, most typically ionic metal alkyls, such as those from sodium to caesium, for which the ionic character of the carbon–metal bond has been evaluated comprising between 47 per cent (Na) and 57 per cent (Cs),[10] are not, by themselves, catalysts in the polymerization of α-olefins and polymerize only diolefins, however, in a non-stereospecific way.

Even the metallorganic compounds of the alkaline-earth metals, from calcium to barium, do not polymerize ethylene. These metals, in fact, have no tendency to form stable complexes and form labile complexes only in particular cases, in which they make use of the inner *d* orbitals. This type of coordination is stabilized by the presence of several complexable groups belonging to the same molecule (polydentate complexes). The coordination of water in the hydrates of the ions of these metals is not an exception to these rules because it may be explained by the fact that water is associated in polymeric molecules, so that these hydrates present an analogy with the polydentate complexes.

Aluminium-alkyls (ionic character of the bond = 22 per cent) and lithium-alkyls (43 per cent) polymerize ethylene to low polymers while with α-olefins they only yield dimers.[11]

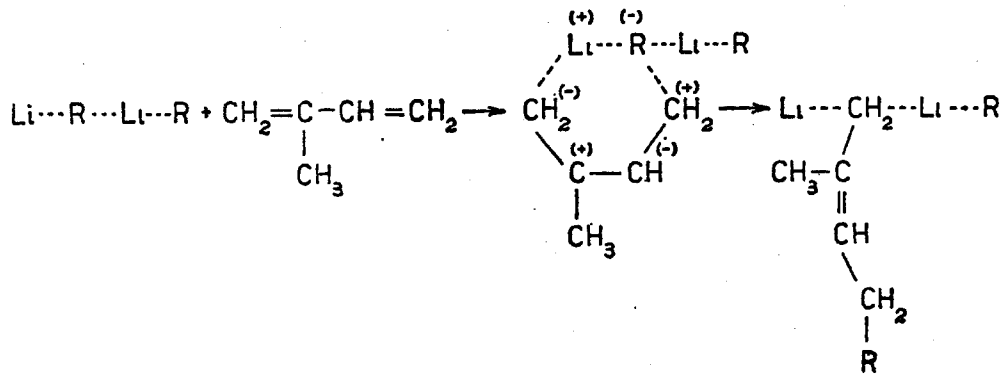
Already from a comparison of the behaviour of several simple metal-alkyls, one can observe that in ethylene polymerization the strongest catalytic action is shown by the alkyls of metals having the smallest ionic diameters (Be, Al). These metals are, as it is known from mineral chemistry, the ones among the metals of the first subgroup of the first three groups in the periodic table, which most easily originate complexes.

Boron which also has a very small ionic diameter, and of which a large series of metallorganic compounds is known, gives by itself only metallorganic compounds which do not show any marked catalytic action in the polymerization of α-olefins and this is due to the low electropositivity of the metal (2·0 in the Pauling's electronegativity scale).

In the case of lithium, it is known that its alkyls are mostly associated in a dimeric form Li_2R_2.[12] Its catalytic action may be connected with the resonance between the two forms: $Li^+(R_2Li)^- \rightleftharpoons (LiR_2)^-Li^+$ related to the ionic nature of the Li – C bond.

A lithium alkyl in a hydrocarbon solvent is a stereospecific catalyst for the polymerization of isoprene,[13] with formation of the polymer having a *cis*-1,4 arrangement, while in ether solution it loses its stereospecificity, yielding a polymer containing atactic monomeric unit with 1,2 arrangement. The small Li^+ $(CH_2)^-$ distance and the ability of lithium to give complexes is most probably the reason of the stereospecific *cis*-1,4 polymerization.

The sodium alkyls, like the alkyls of other strongly electropositive metals having a greater diameter and a smaller tendency to give com-



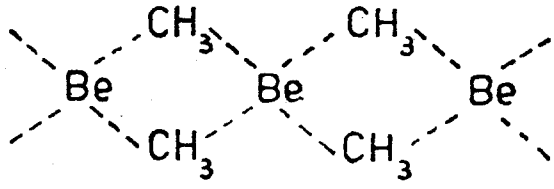
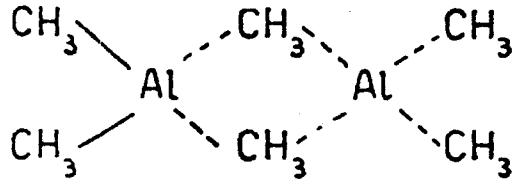
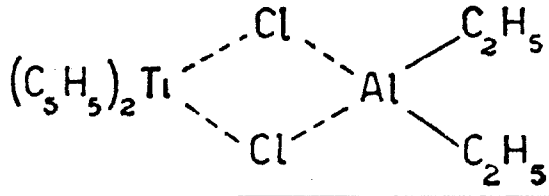
plexes, do not polymerize ethylene and are not stereospecific catalysts in the polymerization of diolefins.

Metallorganic complexes containing transition metals in a low valency state, for instance the complexes obtained by reaction between transition metal compounds and alkyl compounds of metals (like aluminium, lithium, etc.) having small ionic radius, may, according to the type and composition of the complex itself, respectively yield prevailingly stereounitary polymers of *trans*-1,4, *cis*-1,4, isotactic-1,2 or syndiotactic-1,2 arrangement or polymers with random distribution of the different isomeric units.[4—5]

I will mention, as an example, certain complexes obtained by reaction between aluminium alkyls and chromium acetyl-acetonate. By low ratios (lower than 6) between AlR_3 and Cr acetyl-acetonate used in the preparation of the catalyst, in the polymerization of butadiene a polymer with syndiotactic-1,2 arrangement is obtained. By higher ratios a polymer with the same arrangement, but having an isotactic structure is obtained.

A similar behaviour is shown by other complexes containing oxygen or nitrogen, as for inst. those obtained from alcoholates, carbonyls, carbylamines of transition metals by the action of aluminium alkyls. Their stereospecificity and their activities depend from the ratios between the reactants. These complexes do not act as catalysts in the polymerization of α-olefins, but some of them polymerize ethylene. In this last case, where there is no possibility of stereoisomerism in the polymerization products, the ratio between the titanium compounds (for instance Ti alcoholates) and aluminium alkyls influences only the activity of the catalysts and the molecular weight of the polymers. By low ratios, ethylene dimerization to butene-1 occurs,[14] while by higher ratios a polymerization to unbranched high polymers takes place.[15]

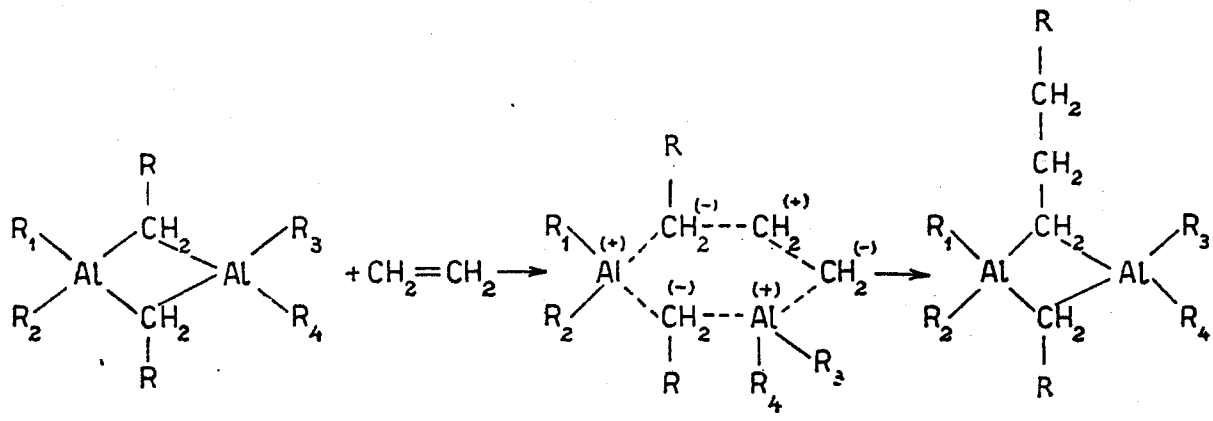
TABLE 2/

	Angle Me-C-Me	*Distance C-M Å*	
		bridge	*terminal*
	66°	1·93	—
	70°	2·24	1·99
	90°	~2·5 (Ti — Cl)	—

Aluminium or beryllium alkyls have a tendency to form complexes and this is demonstrated by the fact that some of them are usually in an associated form (dimers). The X-rays and electron-rays analysis of the aluminium-trimethyl dimer has made it possible to calculate the distance C–Al for the two carbon atoms forming a bridge between the two Al atoms. This distance is 2·24 Å and, being much greater than the distance existing in the four terminal C–Al bonds (1·99 Å), is the cause for the easier dissociability of that bond.

The Al–C–Al angle of the bridge is very small (70°) because of the particular type of bond in the bridge between the two metallic atoms and the alkyl group. (The so called "3-centre" bonds whose molecular orbitals appear to be composed by the hybrid orbitals of two Al atoms and one C atom.)[16]

In this case the catalytic action in the polymerization of ethylene to linear polymers may be interpreted as a penetration of a carbon anion (rich in electrons) deriving from a polarized ethylene molecule $CH_2 = CH_2 \rightarrow {}^{-}CH\text{–}CH_2{}^{+}$, in the coordinating field of the electron deficient complex, with simultaneous dissociation of a metal alkyl bridge bond, and as a competitive action of the carbon anion of the polarized olefin with the carbon atom, which is also negatively



polarized, which was before a part of the bridge between the two metallic atoms.

The greater distance of the carbon of the metallic atom bridge can justify a greater dissociability of that bond in comparison with the dissociability of the terminal C–Al bonds.

The fact that the solubility of ethylene in heptane and its dissolution heat (contrary to what happens with methylether) are not increased in the presence of aluminium alkyl demonstrates that no process takes place with a low activation heat which joins the ethylene molecule, by means of its π electrons, to the electron deficient molecule of the aluminium alkyl.

A different interpretation of the ethylene addition mechanism can be considered taking into account the electric conductivity of the aluminium alkyl solutions in hydrocarbons. This conductivity is attributed by Bonitz[18] to an ionic dissociation. Also in this case the insertion of an ethylene polarized molecule between the two ions of opposite charge is considered.

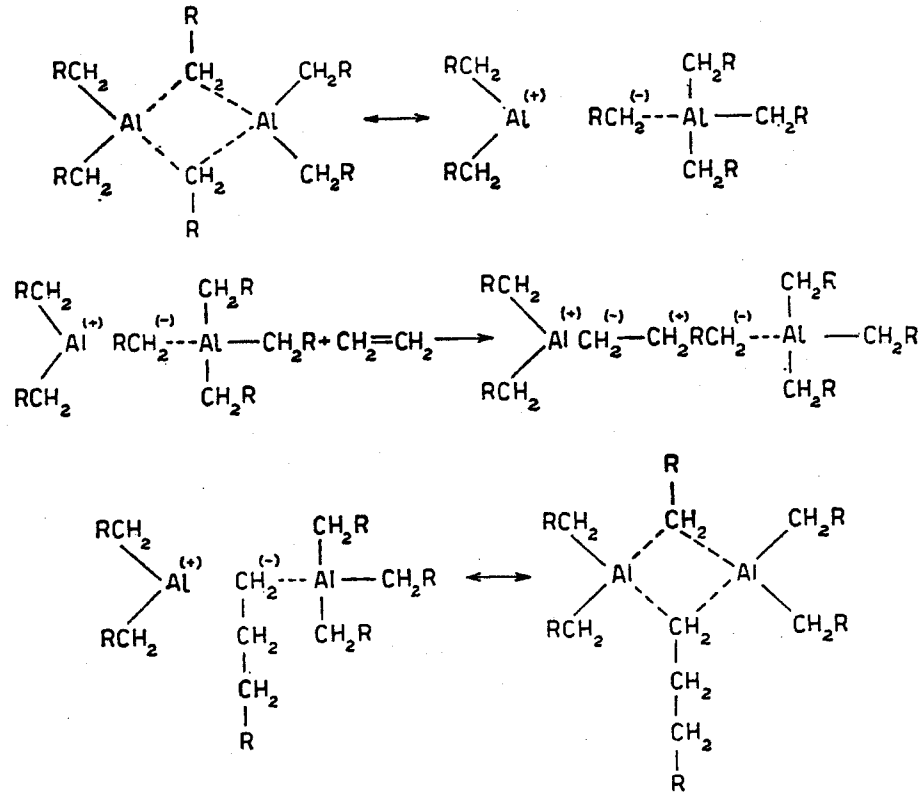
Soluble, well-defined compounds which act as catalysts in the polymerization of ethylene are, for example:

Metal alkyls, mostly existing in polymeric forms (for instance dimers) polymerizing ethylene to low polymers, such as:

$$Li_2(C_2H_5)_2 \; ; \; Be_2(C_2H_5)_4 \; ; \; Al_2(C_2H_5)_6$$

Soluble crystallizable metallorganic complexes polymerizing ethylene both to low and high polymers:

$(C_5H_5)_2TiCl_2Al(C_2H_5)_2$	melting point 126–130°C
$(C_5H_5)_2TiCl_2AlClC_2H_5$	melting point 88–92°C



Other soluble catalysts are not crystallizable (for inst. the reaction products between Ti alcoholates and Al alkyls), but the most active catalysts in the polymerization of ethylene are those insoluble in hydrocarbons, described in the next paragraph.

Heterogeneous catalysts

The simple metal alkyls considered in the preceding chapter, and even the most active of them (aluminium, berillyum, lithium alkyls), polymerize ethylene in a rather slow way through a stepwise addition process. When used alone, they allowe to obtain only rather low ethylene polymers, of average molecular weight below 10,000, which are of scarce practical interest.

The reason of this is probably the fact that in the polymerization at high temperatures the chain termination step is very fast, while it is very slow at low temperatures. Then, the linear polymeric chain becomes very long, the polymer has a tendency to crystallize, thus hindering the small diameter metals strongly linked to the chain end.

The Ziegler's polymerization process[17] for the low pressure polymerization of ethylene to very high molecular weight polymers, uses catalysts obtained by reaction of a metal alkyl with some transition

metal compounds. The first catalysts described by Ziegler and most widely studied both in Europe and in U.S.A. are those obtained by reacting $TiCl_4$ with aluminium trialkyls. The reaction, which is a very complex one, takes place in several stages. The first step of titanium alkylation is followed by a successive stage of homolytic decomposition of the titanium mono-alkyl compound. During this stage free radicals are formed and at the same time a reduction of titanium from valency 4 to 3 or less takes place. If Al-triethyl is used the free ethyl radicals disproportionate, for the most part, to ethane and ethylene, and the latter partially polymerizes to polyethylene.

The reaction between $TiCl_4$ and AlR_3 can be considered as taking place in several steps:

(I) Alkylation of $TiCl_4$ and homolytic decomposition of organo-titanium compounds:

$$TiCl_4 + Al(C_2H_5)_3 \rightarrow Al(C_2H_5)_2Cl + TiCl_3C_2H_5$$

$$TiCl_3C_2H_5 \rightarrow TiCl_3 + \cdot C_2H_5$$

$$TiCl_4 + 2Al(C_2H_5)_3 \rightarrow TiCl_2(C_2H_5)_2 + 2Al(C_2H_5)_2Cl$$

$$TiCl_2(C_2H_5)_2 \rightarrow TiCl_2C_2H_5 + \cdot C_2H_5$$

$$TiCl_2C_2H_5 \rightarrow TiCl_2 + \cdot C_2H_5$$

$$2 \cdot C_2H_5 \rightarrow C_2H_4 + C_2H_6$$

(II) Formation of insoluble complexes of the type:

$$TiX_2Y + R''AlR''_2 \longrightarrow X_2TiYR'AlR''_2$$

An example of this type of complexes is given in the soluble crystallizable compound $(C_5H_5)_2$ $TiCl_2Al(C_2H_5)_2$, which can be formed by addition of one mol. of $(C_5H_5)_2$ TiCl to one mol. of $AlCl(C_2H_5)_2$.

Only when the alkylation of $TiCl_4$ is carried out with Al-dimethyl-monochloride the greater stability of the CH_3^- ion in comparison with the CH_2^- ion allows the separation and even the purification by distillation of the $TiCl_3 \cdot CH_3$ compound.[19] The latter decomposes, however, very fast by mild heating yielding the brown modification of $TiCl_3$ which crystallizes in needles. According to our X-rays measurements this modification is isomorphous with the TiJ_3 in the modification described by Klemm.[20]

In general, when higher alkyl aluminium compounds are reacted with a titanium tetrahalide, a precipitate is obtained whose composition

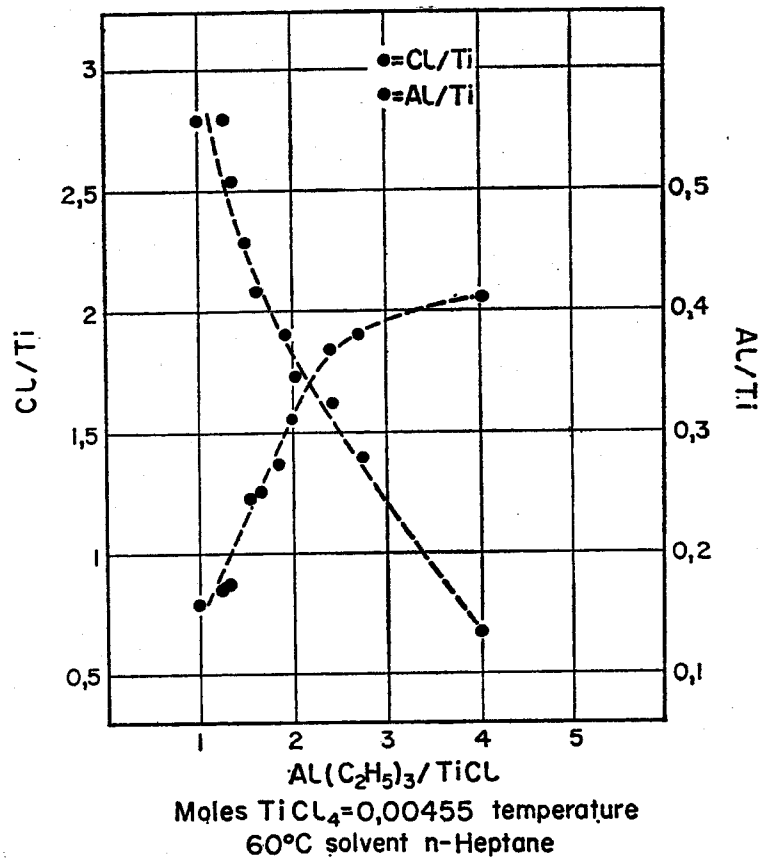


FIG. 1. Composition of the catalysts obtained in the reaction between Al $(C_2H_5)_3$ solution (0.729 mol/l) and $TiCl_4$ solution in n-heptane (0.0455 mol/l) at 60° C, in function of the Al/Ti ratio.

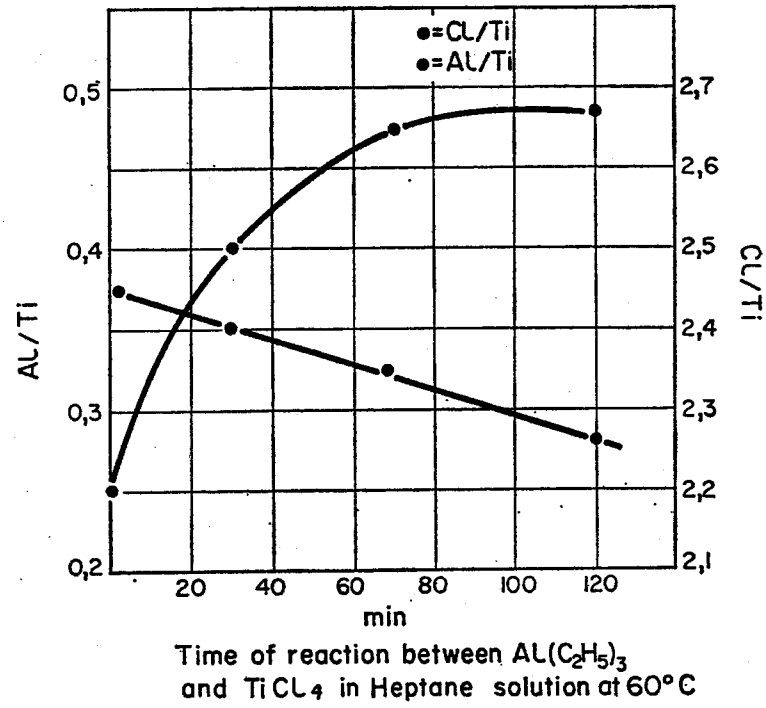


FIG. 2. Composition of the catalysts obtained by reacting Al $(C_2H_5)_3$ and $TiCl_4$ (Al/Ti = 1.5) in heptane solution, at 60° C, at different reaction times.

varies according to the Al/Ti ratio (Fig. 1), the temperature, the time (Fig. 2), and the kind of alkyl group used.

As a consequence, this precipitate exhibits a catalytic action which varies with its composition and with the time, but which is in some cases very high, particularly by Al/Ti ratios of about 2. Such a precipitate contains, besides titanium and chlorine, also aluminium and alkyl groups. Doubtless it contains those elements combined with other in complexes whose formation is partly due to character of a Lewis' acid of the Al-trialkyl. In fact it is not possible even by accurate washing with inert solvents to separate completely the aluminium alkyl compounds from the di- and trivalent titanium halides.

It must be assumed that in such complexes the compound $AlClR_2$ or AlR_3 is combined with a tri- or divalent titanium compound, according to the conditions in which the catalyst is prepared.

The fact that the primary process in the reaction of $TiCl_4$ with AlR_3 is an alkylation, leading to the formation of an alkylated titanium compound (which decomposes yielding free radicals) induced many chemists to think that the $TiCl_4$–AlR_3 system could act as the initiator of a free radical type polymerization and that monomeric units, absorbed in ordered succession on the surface of a solid phase, could add to each other thus forming sterically ordered structures.[21]

The formation of free radicals, which is observed during the formation of the catalyst, can in fact start the polymerization of certain monomers (e.g. styrene, diolefins) but not that of aliphatic α-olefins to high polymers, when the process is carried out at low temperature and low pressure, in the presence of solvents.

At first the study of the Ziegler's catalysts presented some difficulties and their kinetics of polymerization appeared very intriguing because they are quite unstable, and their activity varies during the time. They polymerize ethylene and some of them, if prepared in particular conditions, and with particular ratios between metalkyls and transition metal compounds, may polymerize α-olefins, but their stereospecificity is generally poor.

In studying the α-olefin polymerization we succeeded in obtaining certain highly stereospecific catalysts, yielding substantially only isotactic polymers, and others yielding only atactic polymers.[22]

The most interesting results, from both theoretical and practical standpoints in producing isotactic polymers were achieved by us by means of catalysts which show a high stability in the time. We obtained them by contacting insoluble crystalline halides (with layer lattices)

of di- or trivalent transition metals with organometallic compounds. Such catalysts may, if suitable metallorganic compounds are used (Al-triethyl, Be-diethyl, etc.), be highly stereospecific and yield isotactic, highly crystalline polymers.

On the contrary, by means of the same organometallic compounds absorbed on amorphous carriers containing transition metal compounds, amorphous atactic polymers are obtained.

Features of the Coordinated Anionic Catalysis

Before giving an interpretation of some aspects of stereospecificity and trying to explain its causes, the exposition of some characters of coordinated anionic catalysis may be useful.

Independently of their stereospecificity, the catalysts used by us represent a special type of catalyst, since in many cases they make it possible to obtain polymers having a chemical constitution which is different from that of the previously known polymers. It was possible to demonstrate in fact, through infrared examination, that the new α olefin polymers have a greater regularity of structure, and particularly a head-to-tail arrangement which is more regular than that of polymers obtained by other processes.

In our opinion the difference between the conventional anionic mechanism and the mechanism which we attribute to our processes is to be ascribed to the particular coordination bonds contained in the catalysts used by us.

The arguments in favour of the hypothesis of a coordinated anionic catalysis are the following:

1. The linear, regular head-to-tail structure of the macromolecules, obtained by polymerization of $CH_2 = CHR$ monomers, in which R is an alkyl group, according to the greater tendency of the CH_2 group (in comparison with the CHR group) to give a carbanion capable of being coordinated in a metallorganic complex.

2. The nature of the terminal groups contained in the macromolecules of poly-α-olefins, characterized by the presence of terminal vinylidenic groups at one end of the chain and generally, at the other end, of terminal alkyl groups corresponding to the normal saturated alkyl containing the same number of carbon atoms as the normal chain of the polymerized olefins.[23]

3. The presence, in the most active catalysts, of at least two different metals which are highly electropositive and capable of forming complexes.

4. The stronger catalytic activity of the complexes containing metallic ions, which have a small atomic radius and generate locally more intense electric fields: beryllium (ionic radius 0·35 Å), aluminium (0·51 Å) and, among the monovalent ions, lithium (0.68 Å).

5. The electric conductivity of ionic type, with migration of the groups richer in alkyls toward the anode, shown by the solutions of the alkyl metal compounds (such as an aluminium trialkyl) and of their catalytically active soluble complexes.

6. The different reactivity of the monomers in the catalysis which follows a reverse order in respect of that of the cationic catalysis (with exclusion of those monomers containing substituents which can poison the catalysts). The reactivity of propylene and butene is lower in comparison with ethylene according to the presence in their molecule of the electron releasing — CH_3 group.

7. The nature of the chain propagation:

$$\text{I (Complex)—}CH_2\text{—CHR—P} + CH_2 = CHR \rightarrow$$
$$\rightarrow \text{(Complex)—}CH_2\text{=CHRCH}_2\text{—CHR—P}$$

and of the chain termination which leads to the formation of a vinylidene bond through transfer of a hydride ion from the—CHR group of the last monomeric unit to the catalytic complex, which can then initiate a new polymeric chain:

$$\text{II (Complex)—}CH_2\text{—CHR—P} \rightarrow \text{(Complex)—H} + CH_2 = CRP$$
$$\text{III (Complex)—H} + CH_2\text{=CHR} \rightarrow \text{(Complex)—}CH_2\text{—CH}_2R$$

The easier this transfer, the more electron-donor is the R group, and therefore it is to be assumed that a hydride ion transfer is involved. This may explain the lower molecular weight of poly-α-olefins, with respect to polyethylene or polystyrene.

8. The fact that the molecular weight is not lowered, contrary to what happens in radicalic polymerization, when the polymerization is carried out in the presence of certain solvents (e.g. cumene, isoctane, etc.) known for their ability to capture free radicals.

9. The constant rate of polymerization during the time, observed when using stabilized catalysts. The solid catalyst is not consumed, unlike to what occurs with all the radicalic initiators.

10. The decrease of molecular weight with increasing of alkyl aluminium concentration (Fig. 12 of paper 42) which can be explained by a transfer of ionic nature, or as a dissociation of the catalytic complex,

followed by its reconstitution with a different aluminium alkyl compound.

The addition of a monomer molecule to the organometallic compound may be considered an ionic reaction with heterolytic opening of the metal–carbon bond comparable to the ionic type addition of a halogen to an olefin. This addition requires a polar environment which, in the absence of polar solvents, is made possible by a polar surface.

An increase of catalytic activity, attributable to a polar environment, has been observed by addition of crystals having a layer lattice consisting of atoms having a different polarity.

One of the most important features of the anionic catalysis is the high instability of the carbanion, which occurs also when it is coordinated in complexes with a highly electropositive transition metal.

The carbanions are in fact stable only in the absence of protons which would transform the carbanion into a more stable alkyl group, and in the absence of nucleophilic groups, capable of forming anions more stable than the carbanion and to coordinate themselves in a more stable way to the highly electropositive metal of the metallorganic compound.

In the case of coordinated cationic catalysis the ion combined with the carbon ion is coordinated in a complex: on the contrary, in the case of coordinated anionic catalysis it is the carbanion itself which is coordinated. As we will see, this difference allows one to explain from the point of view of stereospecificity, the different behaviour of certain anionic catalysts.

In a cationic catalyst, such as the one formed from Al_2Cl_6 in the presence of an alkyl chloride, complexes of the type $(AlCl_4)^-R^+$ are present. The chlorine of the alkyl chloride which takes part in the formation of the complex enters into a symmetric $(AlCl_4)^-$ anion.

The chlorine which was bound to the alkyl chloride loses its identity and we can admit that a large diameter ion $(AlCl_4)^-$ corresponds to the carbon cation. This is the cause of the lack of stereospecificity in cationic catalysis with catalysts based on aluminium chloride.

On the contrary in the case of coordinated anionic catalysis, e.g. with Ti–Al complexes, the same carbanion initially partaking of an alkyl metal compound coordinates itself in a complex in which the electropositive character of the transition metal favours the coordination of a negatively polarized carbon atom.

The formation of bridge bonds between two metals (for instance observed in the aluminium alkyls and in the crystallizable metallorganic

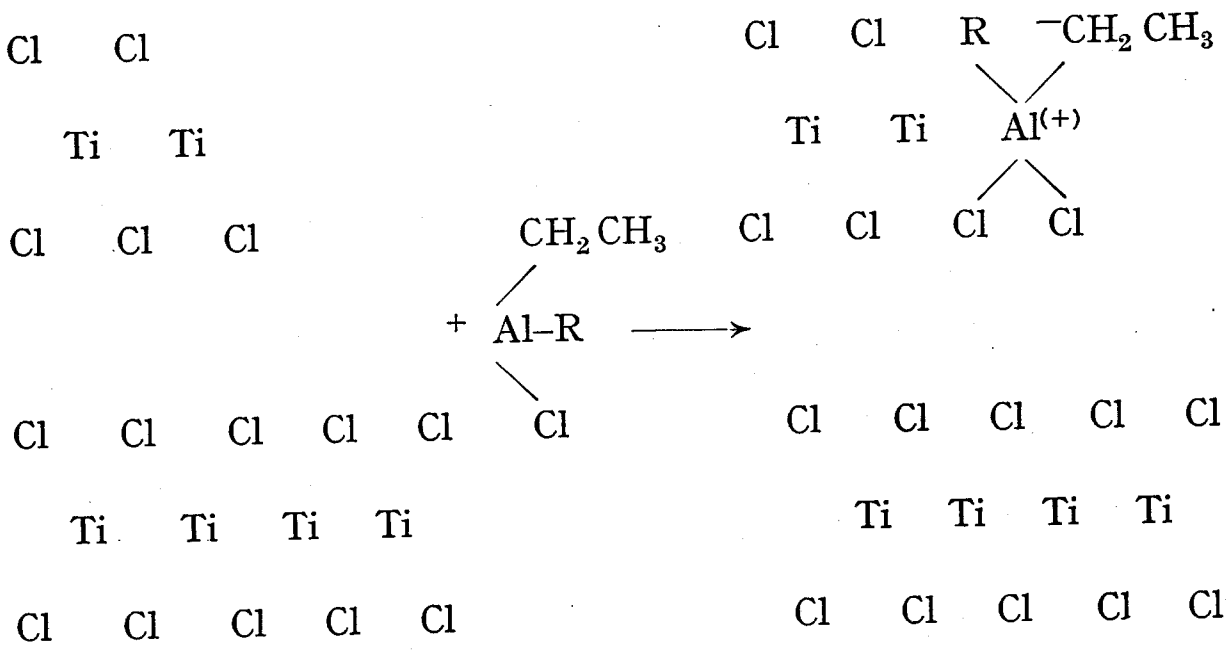


FIG. 3.

Ti–Al complexes previously decribed), the preferential coordination of ions of a given type in the bridge linkage and the asymmetries of the dimetallic complex, can determine a defined position of the carbon anion in certain complexes. This clearly appears when the complex is formed by chemisorption on a crystalline surface, as it is schematically represented in Fig. 3 in the case of the layer lattice of the violet $TiCl_3$ crystals.

This can be the reason for the higher stereospecificity of the coordinated anionic catalysis and for the fact that, in the α-olefin polymerization, the most active catalysts are given only by asymmetric bimetallic complexes, containing as central atoms two different metals (or atoms of different valency of the same metal) and not by complexes containing equivalent atoms of one single metal.

It should be kept in mind that the most stereospecific catalysts are those in which the carbanion is coordinated to a metal cation having a

TABLE 3

Metal of the metal-organic compound	*Ionic radii of the metals*	*% of polypropylene non extractable in boiling n-heptane*
Be	0·35 Å	94 — 96 %
Al	0·51 Å	80 — 92 %
Mg	0·66 Å	78 — 85 %
Zn	0·74 Å	30 — 40 %

very small diameter (e.g. Al, Be, Li) and in fact the highest stereospecificity is observed with alkyl beryllium compounds (Table 3).

The catalyst obtained with violet $TiCl_3$ and $Be(C_2H_5)_2$ yields an higher fraction of polypropylene insoluble in boiling n-heptane. The percentage of this highly crystalline fraction can be assumed as an index of the stereospecificity of the catalyst.

Transition Metal Complexes and Stereospecificity

It has already been briefly discussed that only transition metals of a high electropositive character, in a low valency state, can lead to the formation of catalysts suitable for the anionic polymerization of α-olefins to high polymers.

Simple organometallic compounds of transition metals, in which an alkyl group is bound to the metal by a strongly polarized bond, are still unknown. In most of the transition metal organometallic compounds, which in general have poor stability, the bonds are merely of the covalent type (which decompose with a homolytic mechanism) or of the covalent "delocalized" type (in which a metal atom is bound jointly to an electron rich system of several carbon atoms).

In the complexes of some not very electropositive metals (platinum, palladium, etc.) with olefins, of the type $Pt_2Cl_4(C_2H_4)_2$, the olefinic double bond remains mostly unmodified in the complex and the whole olefin molecule acts with two of its π electrons as a donor to the vacant orbitals dsp^2 of the metal. Such olefinic compounds do not behave as catalysts in the polymerization of olefins which requires a polarization of the reacting monomer molecules.

In some compounds of the covalent "delocalized" type (for instance bis-cyclo-pentadienyl compounds of transition metals) the central atom can yield metallorganic compounds in which also a σ type bond is stabilized (e. g. diphenyl-bis-cyclo-pentadienyl-titanium).

The nature of the organometallic bond and particularly its ionic character are modified when a metallic atom becomes part of a complex, as it appears from the change in conductivity of its solutions in hydrocarbons.

The processes of heterogeneous anionic catalysis throw now a new light on a particular field of the chemistry of complexes, i.e. of the complexes formed by chemisorption on solid crystalline surfaces.

In particular cases, with crystalline supports, chemisorption may

occur connected with epitaxy phenomena, which can impart to the chemisorbed molecule coordination numbers different from the normal ones. In general to a different coordination number corresponds a different hybridation of the molecular orbitals.

It is known for inst. that aluminum exhibits in general in its liquid or gaseous non ionic compounds a coordination number 4, and to them a tetrahedral structure (sp^3) should be attributed.

If we consider however many solid crystalline compounds of aluminium, e.g. Al_2O_3 in which the strong field due to the small ionic diameter and to the Al charge strongly attracts the oxygen ions, we observe a coordination number 6 (sp^3d^2), as in the crystal lattice of Al_2O_3 (corundum). When the anion bound to the aluminium has a very small diameter, e.g. in fluorine, the coordination number 6 of the metal becomes more stable especially in the crystal lattices.

It appears therefore possible that the aluminium present in the planar molecule of a monomeric AlR_3, which loses its planarity when aluminium assumes the coordination number 4 of the dimer, might assume a higher coordination degree in the case that it is chemically adsorbed in an epitactic way onto a lattice, the metal atoms of which present the coordination number 6.

It is already known that if the fields existing in the crystals are applied to atoms with different states of excitation, they can induce state changes which depend on the field direction and on its symmetry. For instance in the case of certain iron complexes, these fields can lead them to overcome the transition from the paramagnetic to the diamagnetic state.

We must therefore foresee that the field connected with the crystal lattice may act in modifying the coordination number and also the ionic character of a metal–carbon bond.

Asymmetry phenomena can occur with greater frequency in the surface chemisorbed compounds than in free molecules, as for instance in solution. They may be caused by difference in the chemical composition among the coordinated groups, which are usually considered in the stereochemistry of complexes, and also by d fferences produced by the bond type or also by the topological differences between atoms having the same chemical nature, when these atoms instead of being inside, are on the surface plane or on the edges or on the corners of a crystalline lattice. Topological differences may cause also chemical differences; for inst. an atom which lies inside the lattice appears to be non polarized or symmetrically polarized, while an atom which lies on the

surface and particularly in an irregular part of the surface can present a particularly oriented polarization.

A molecule of the type $AlR'R''R'''$ or $AlClR'_2$ chemisorbed on the $TiCl_3$ crystalline surface, should show more easily optical stereoisomerism if it is adsorbed on irregular site of the lattice surface, which presents locally asymmetric characters.

The higher stereospecificity of violet, well crystallized $TiCl_3$ and the induction phenomena (settling period with an increase of the catalytic activity during the time) observed in violet $TiCl_3$, can be attributed to the fact that in this type of $TiCl_3$ the (001) faces are well formed; and therefore the alkyl aluminium compound is adsorbed more tenaciously by epitaxy on the border of these faces or on irregular sites. In this way stable complexes are formed with a particular asymmetrical steric configuration acting as catalysts in the polymerization. In Fig. 11 of paper 42 and 6 of paper 29 the kinetic curves relating to the propylene polymerization by means of $TiCl_3$ crystals are reported (Fig. 11 of paper 42 : unground; Fig. 6 of paper 29 : finely ground).

The induction phenomenon observed in unground $TiCl_3$ can be attributed to an increase of the active centres, due to the formation of fresh surfaces caused by cleavage along the base planes of the crystals which occurs by a mechanical action due to the formation of bulky polymer on the edges of the crystalline laminae. With finely ground $TiCl_3$ such a phenomenon is observed in a lesser degree because it is masked by a recrystallization which acts in the opposite sense.

The determination of aluminium alkyls by means of C^{14} labelled alkyls shows that only a portion of the aluminium alkyl adsorbed at low temperature on $TiCl_3$ (viz. the more tenaciously adsorbed) can initiate the polymerization of α-olefins.

If the adsorbed aluminium alkyl assumes, by epitaxy, the coordination number 6 of $TiCl_3$, asymmetry cases are foreseeable even when the groups of different type, bound to the aluminium atom, are only three or even two (Fig. 4). For instance a complex group of the type Cl_nAlR_2, epitactically partaking of a locally asymmetrical zone of the $TiCl_3$ lattice, should easily exhibit an optical type asymmetry.

If one of the R groups, coordinated with the asymmetrical complex of Al and with the $TiCl_3$ crystal lattice, can exhibit in the activated state an ionic nature, it can become the initiator of a chain of asymmetrical addition reactions. The synthesis of isotactic polymers can thus take place, since each macromolecule, synthesized from a single

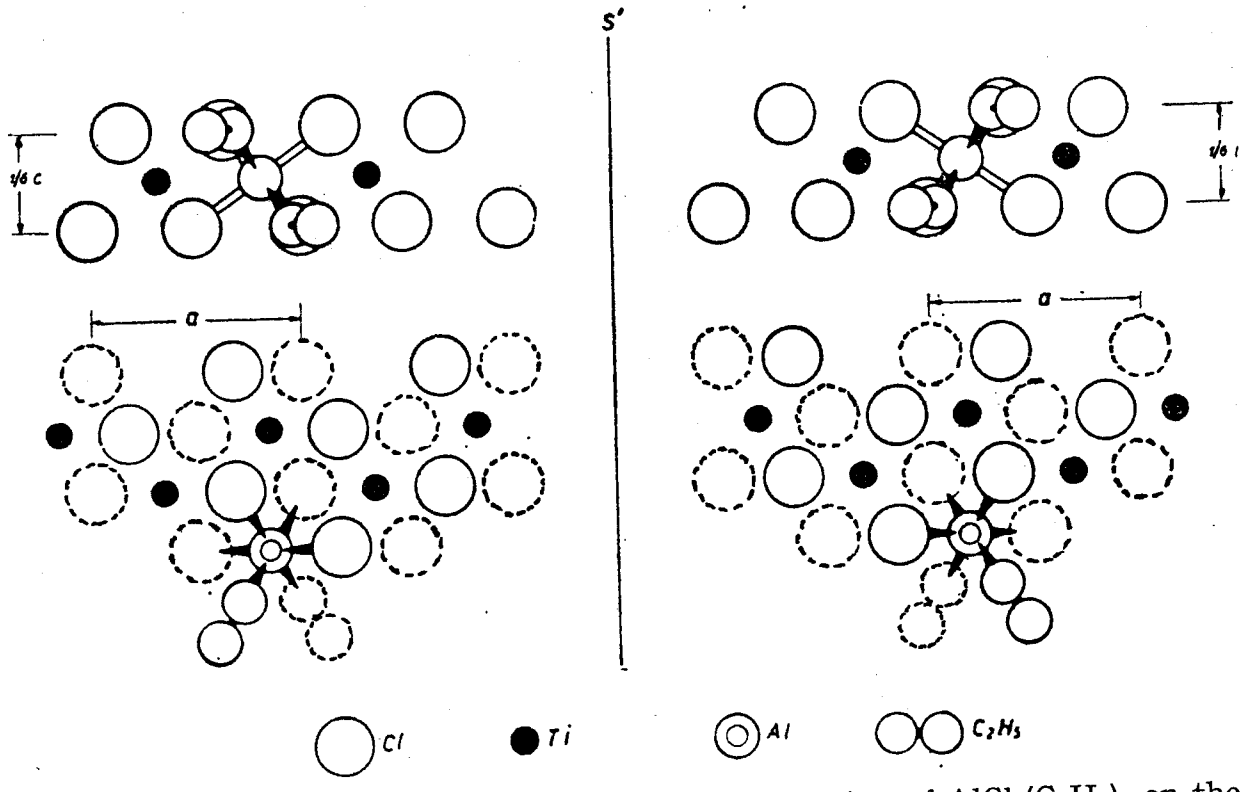


FIG. 4. Schematic model of how an epitactic adsorption of $AlCl(C_2H_5)_2$ on the border of the base plane of a crystal of $TiCl_3$ ($a = 6.12$ Å, $c = 17.50$ Å) may give rise to enantiomorphous active centres.

active centre, consists of monomeric units having the same steric configuration.

Since there is the same probability of having active centres of both enantiomorphous forms, the crude polymer will consist of a mixture of enantiomorphous macromolecules, each formed by a large number of sterically equal units.

A further research field, i.e. the isolation of asymmetric active centres corresponding to only one of the two enantiomorphous isomeric forms, can be of remarkable interest, from the scientific point of view since it could solve the problem of asymmetric organic synthesis in the field of macromolecules.

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KINETICS OF PROPYLENE POLYMERIZATION WITH HIGHLY STEREOSPECIFIC HETEROGENEOUS CATALYSTS. NOTE I: OVERALL KINETICS OF THE POLYMERIZATION PROCESS

by G. NATTA, I. PASQUON and E. GIACHETTI

(Sept. 1957)

[*Chimica e Industria* **39**, 993 (1957)]

ABSTRACT

The kinetics of the polymerization of α-olefins to isotactic polymers has been investigated, in order to enhance our knowledge of the stereospecific polymerization processes and of their mechanisms. This series of papers represents the results obtained in the polymerization of propylene with highly stereospecific catalysts consisting of crystalline titanium trichloride (violet modification), and aluminium alkyls.

The process of polymerization is a true catalytic one, with respect to $TiCl_3$. The reaction rate appears to be of the first order with respect to the partial pressure of the olefin and to the amount of $TiCl_3$, whereas, it is practically independent of the concentration of the $Al(C_2H_5)_3$ and of the ratio $Al(C_2H_5)_3$ to $TiCl_3$.

The activity of the catalytic systems used is constant for very long times, even if the systems were previously kept for many hours in the absence of olefin.

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KINETICS OF PROPYLENE POLYMERIZATION WITH HIGHLY STEREOSPECIFIC HETEROGENEOUS CATALYSTS. NOTE II: NATURE OF THE SETTLING PERIOD

by G. NATTA, I. PASQUON and E. GIACHETTI

(Sept. 1957)

[*Chimica e Industria*, **39**, 1002 (1957)]

ABSTRACT

Following our research study on the kinetics of stereospecific polymerizations, we now report the results of the polymerization of propylene to isotactic polymers at different temperatures (30–70°C), in the presence of crystalline titanium trichloride (violet modification), and of triethylaluminium.

The apparent activation energy of the overall kinetic process (referred to the olefin in solution) is 14,000 cal/mol; in the presence of ground $TiCl_3$ the activation energy apparently decreases to 11,000–12,000 cal/mol.

The nature of the period of increasing polymerization rate (defined as "settling period"), which is noticed at the start of the reaction when operating with $TiCl_3$ crystals of the order of some microns, is discussed here.

This increase of the rate is attributed to the splitting of the $TiCl_3$ crystals, during the polymerization, caused by the mechanical action of the polymeric growing chains.

A reduction in the size of $TiCl_3$ crystals, by grinding, does not alter

noticeably the value of the rate of polymerization in conditions of advance reaction, but it substantially alters the catalytic activity in the initial "settling period".

The length of the period of increasing polymerization rate is sharply reduced, and the catalytic activity rapidly reaches a maximum more or less sharp, in order to reach a value which is kept practically constant with time.

51

COPOLYMERIZATION OF ETHYLENE WITH ALIPHATIC α-OLEFINS. NOTE III: ETHYLENE–PROPYLENE COPOLYMERIZATION WITH CATALYSTS OBTAINED FROM VANADIUM TETRACHLORIDE

by G. MAZZANTI, A. VALVASSORI and G. PAJARO

(Sept. 1957)

[*Chimica e Industria*, **39**, 825 (1957)]

ABSTRACT

Ethylene–propylene copolymers of high molecular weight and free from homopolymers have been produced with the aid of catalysts prepared from vanadium tetrachloride and tri-n-hexyl aluminium. The copolymers so obtained have a solubility which is different from that of the homopolymers, have a characteristic I.R. spectrum, and within a wide range of compositions, are amorphous, as revealed by X-ray diffraction methods.

For a determined feed the copolymer composition is independent of the ageing time of the catalyst, of its concentration, of the aluminium to vanadium ratio and of the reaction time.

The influence exerted on the composition of the copolymer by the composition of the monomer mixture was also studied.

The reactivity ratios, referred to the molar fractions of the two monomers, in the liquid phase, are:

$$r_{C_2H_4} = 7{\cdot}08 \qquad \text{and} \qquad r_{C_3H_6} = 0{\cdot}088$$

52

THE MECHANISM AND KINETICS OF THE POLYMERIZATION OF α-OLEFINS*

by G. NATTA, F. DANUSSO and I. PASQUON

(Sept. 1957)

[*Collection Czechosl. Chem. Commun.* **22**, 191 (1957)]

KINETICS ASPECTS OF THE POLYMERIZATION OF α-OLEFINS

During our investigations at the Polytechnic Institute of Milan on some catalytic systems (which differ from one another either in the transition metal, or in the metal-alkyl compound used, or even in their physical state, or in the promoting agents or different supports present) we have obtained catalysts which vary in their catalytic activity and in their degree of stereospecificity.

These catalysts can be grouped under a same type of kinetic mechanism, which is typical of those polymerizations called by us "anionic coordinated".

Here we shall describe only the results obtained with two types of catalysts, which were of particular interest to us. They differ considerably from each other in their stability and stereospecificity, even though they are both formed by the same elements, such as those obtained by treating with alkyl aluminium liquid titanium tetrachloride and crystalline $TiCl_3$ (violet modification). The main properties of these two classes of catalysts are summarized in Table 1.

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* Lecture held at the International Symposium on Macromolecular Chemistry (I.U.P.A.C.), Prague, Sept. 1957. (The three first sections Introduction, Co-ordinated Anionic Polymerization, and Activity and Stereospecificity of the Co-ordinated Anionic Catalysis are omitted. The corresponding topics have been substantially dealt with as in paper 42.)

TABLE 1

	Catalytic Systems	
	of the 1st type	*of the 2nd type*
Composition:	Systems prepared from a high-valency compound of a very electropositive transition metal	Systems prepared from a crystalline compound of a low-valency transition metal.
Examples:	$TiCl_4$, VCl_4, $VOCl_3$ (liquid), TiJ_4 (solid) and an alkyl metal compound	$TiCl_3$, $TiCl_2$, VCl_3 (crystalline) and an alkyl metal compound.
Effect of the metal alkyl:	Alkylation followed by reduction and formation of a dispersed heterogeneous phase	No apparent reduction and superficial adsorption.
Stereospecificity:	Partial; depending also on the nature and on the dispersivity of the precipitate	High
Catalytic activity:	Depending on the molar ratio of the two catalytic reagents and on the time.	Independent of these two factors: stable catalysts.

A comparison of these two catalysts, considered as two typical cases, seems to be worth while. The former corresponds to a particular type first used by Ziegler for the polymerization of ethylene; with certain ratios of Al to Ti, the catalyst can polymerize α-olefins in a partially stereospecific way. The latter corresponds to one of the most stereospecific catalysts we have used in the polymerization of α-olefins. Most catalysts of the former type show an activity, which can be high, but varies with time. This effect, due to the presence of unstable substances in the catalyst, often occurs in the heterogeneous catalysis.

The kinetic results, which we are going to describe, will be divided into two groups, corresponding to these two types of catalytic systems.

The monomer used by us in typical runs was propylene or styrene. They both gave comparable results, with regard to our kinetic study.[1-5]

In the case of propylene (gaseous monomer), the kinetic measurements were done mainly using the apparatus shown in Fig. 1. This figure shows the schematic drawing of an autoclave rocking at constant frequency, the vessel containing the monomer and other devices necessary to regulate or to measure both temperature and pressure. In the

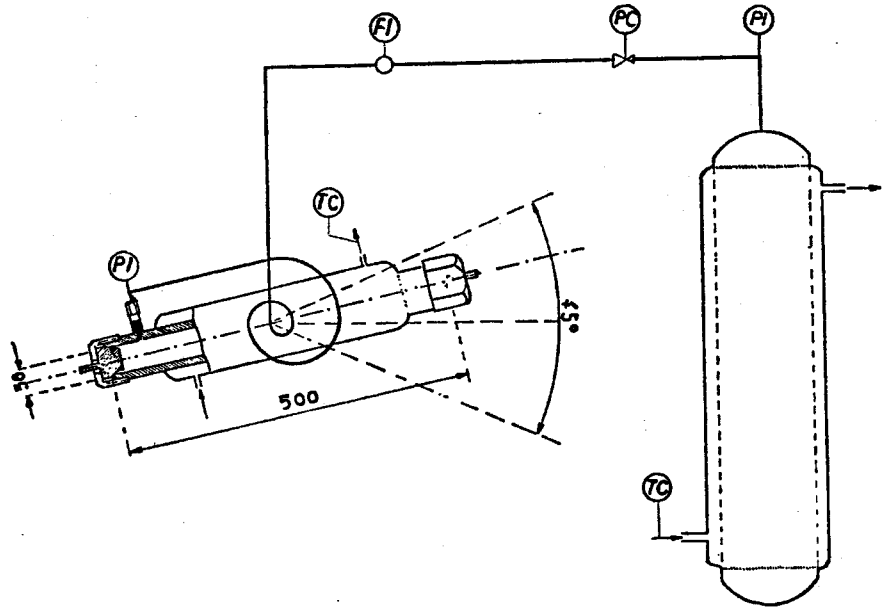


FIG. 1. Schematic drawing of the apparatus used for the kinetic measurements of the polymerization of propylene at constant pressure and temperature.

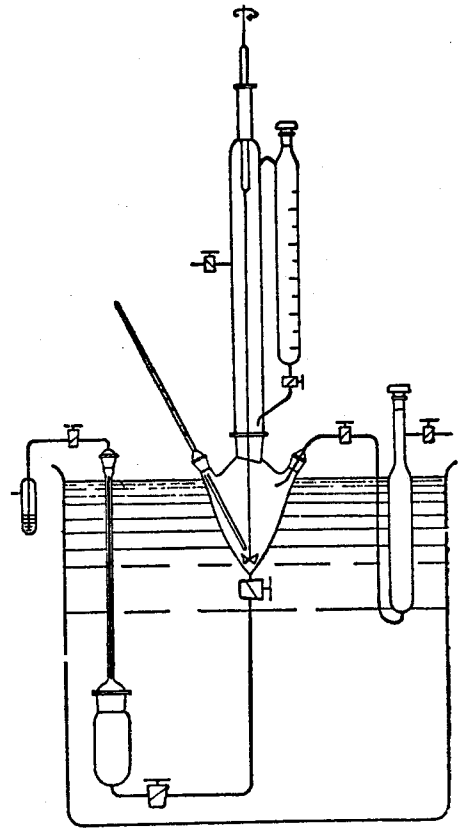


FIG. 2. Schematic drawing of the dilatometric apparatus used for the polymerization of styrene.

case of styrene (liquid monomer) we could often use the dilatometric technique, with a particular apparatus, whose scheme is drawn in Fig. 2: the reaction mixture, prepared in a flask, was introduced, at

a constant temperature, into a capillary dilatometer, by which it was possible to follow the course of the polymerization.

Other details on the technique of these experiments can be found in the original papers.[1-5]

(*a*) *Catalytic Systems of the First Type*

A number of investigations on the polymerization of ethylene have been effected both in Europe and in the United States with catalytic systems of the first type.

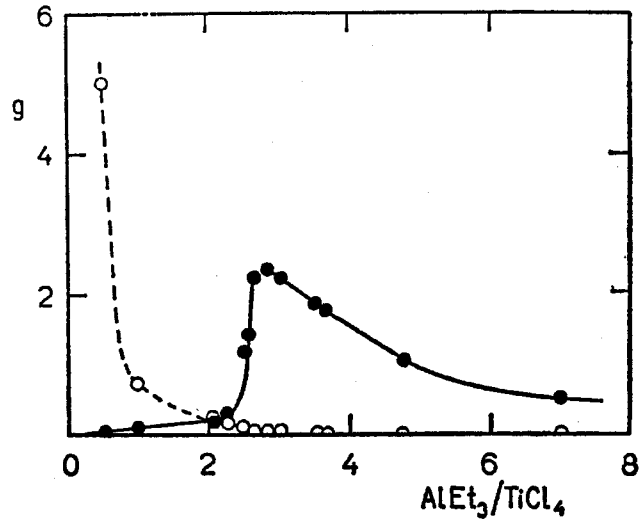


FIG. 3. Polystyrene (g) obtained with different molar ratios $AlEt_3/TiCl_4$ in benzene at 40° C. 3.5 mmoles $TiCl_4$; 20 ml styrene; 50 ml benzene; 7 hr. - - - - - - - - - Amorphous polymer. ———————— Isotactic polymer.

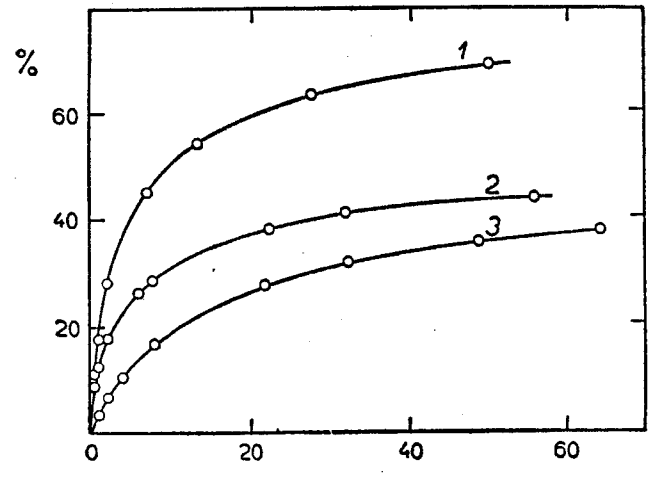


FIG. 4. Examples of the gravimetric conversion curves (%) with the system styrene-benzene-$AlEt_3$-$TiCl_4$. (1) Al/Ti = 2·7, 70° C; (2) Al/Ti = 4, 70° C; (3) Al/Ti = 4, 40° C; time: *t* in hours.

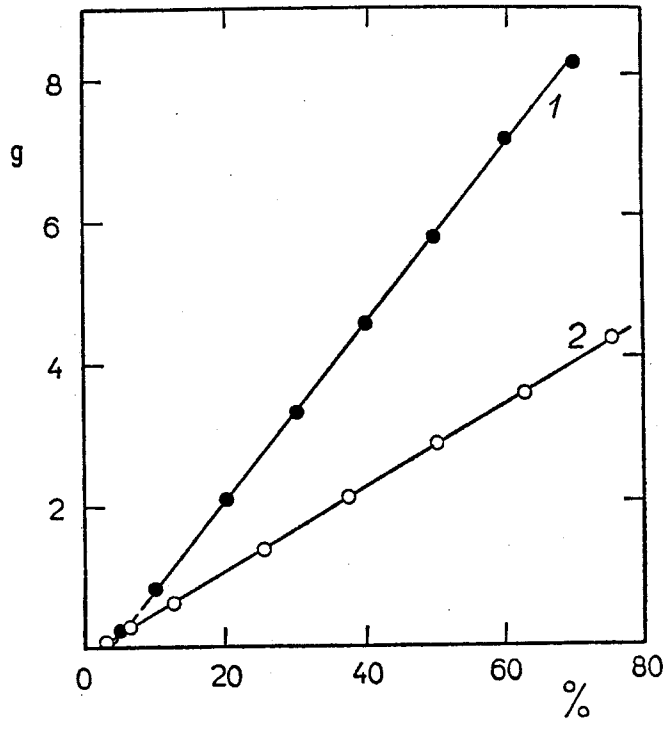


FIG. 5. Amount of polystyrene (g) produced at different initial concentrations of monomer, (% vol.), in benzene. (1) 70° C, 4 hr, 18 mmol/l. $TiCl_4$, $AlEt_3/TiCl_4$ = = 2 · 7; (2) 40° C, 6 hr, 25 mmol/l. $TiCl_4$, $AlEt_3/TiCl_4$ = 4.

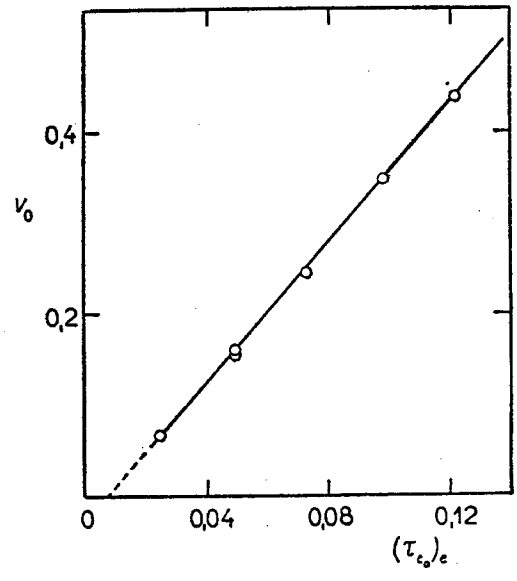


FIG. 6. Relationship between the initial rate (mol l^{-1} hr^{-1}) of the polymerization of styrene and of the concentration of $TiCl_4$ in mol/l.; $AlEt_3/TiCl_4$ = 3; 40° C; monomer concentration = 2 · 12 mol/l. in benzene.

Figure 3, for instance, shows the typical behaviour of styrene polymerized in benzene, with catalysts prepared from $AlEt_3$–$TiCl_4$ vs. the molar ratio of the two catalytic reagents (keeping $TiCl_4$ constant). The overall activity of the catalyst increases in an almost critical way

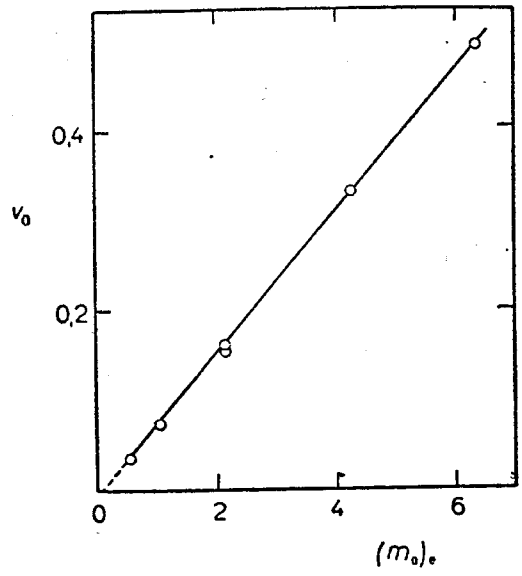


FIG. 7. Relationship between the initial rate of polymerization of styrene (mol l^{-1} hr^{-1}) and monomer concentration in mol/l.; $AlEt_3/TiCl_4 = 3$; 48 mmol/l. of $TiCl_4$ in benzene; 40° C.

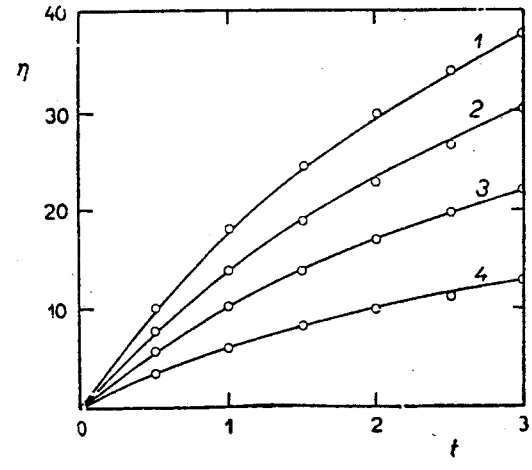


FIG. 8. Comparison between the calculated conversion curves and the experimental data obtained for the polymerization of styrene with different amounts of catalyst based on $TiCl_4$, in benzene; 40° C; time in hours.

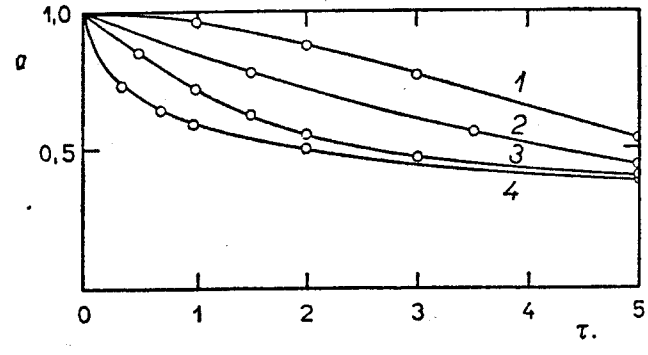


FIG. 9. Kinetic activity of the catalytic systems based on $TiCl_4$ (a) vs. the time (hr) elapsed from the preparation of the catalyst before the addition of styrene.

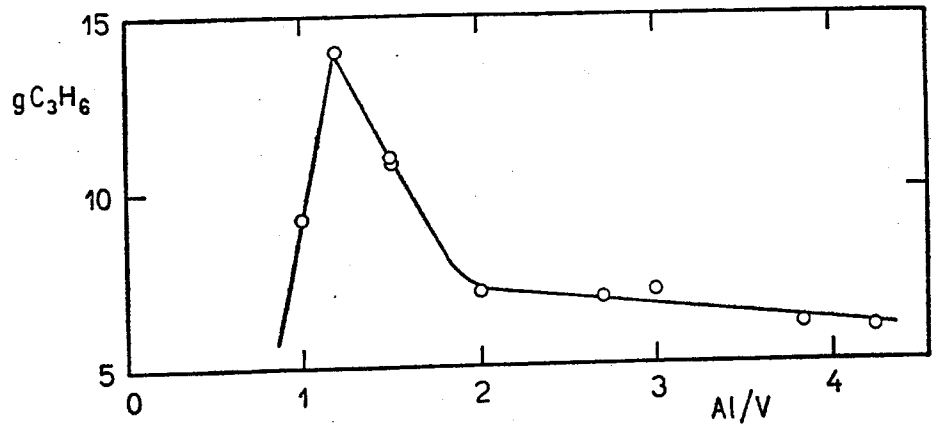


FIG. 10. Amount of propylene polymerized in the presence of $VOCl_3$ and Al $(iC_4H_9)_3$ in n-heptane, vs. the molar ratio Al/V. 15° C; $P_{C_3H_6}$ 1460 mm Hg; time 2 $^3/_4$ hr; $VOCl_3$ 0·92 g; n-heptane 150 cm³.

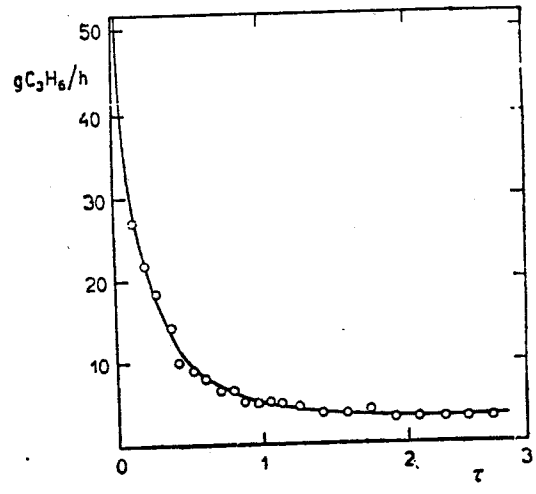


FIG. 11. Reaction rate vs. time (hr), obtained during the polymerization of propylene in the presence of $VOCl_3$ and Al $(iC_4H_9)_3$ in n-heptane. 70° C; $P_{C_3H_6}$ 747 mm Hg; Al $(iC_4H_9)_3$ 0·184 mol/l.; $VOCl_3$ 366 g; n-heptane 180 cm³.

for ratio values ranging from 2 to 2·5, and decreases with the increase of such a ratio.

The conversion curves (Fig. 4), obtained with the same catalytic system, can be interpreted only by an expression of high order. However, the amount of polymer produced in the same time of reaction is simply a linear function of the monomer concentration (Fig. 5), even if such a relationship is not of simple proportionality as it should be for a regular reaction of the first order.

In this case the study of the initial rates, by the dilatometric method, has shown the existence of a main polymerization process of the first order, with respect to both the concentration of the catalytic reagent (Fig. 6) and the monomer concentration (Fig. 7).

This main process is accompanied by an ageing process of the cata-

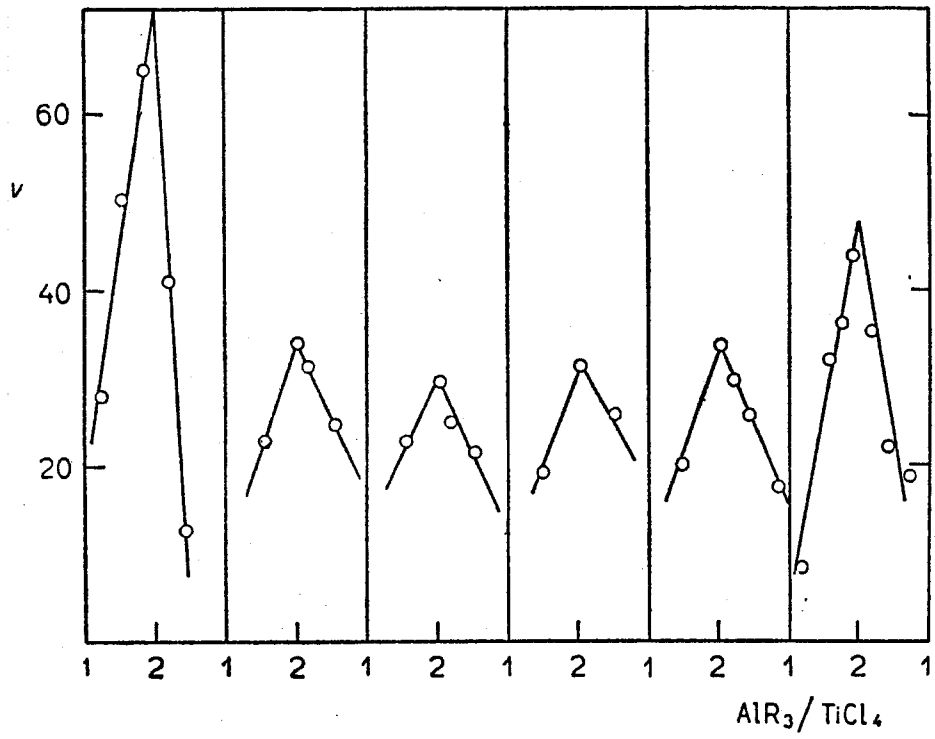


FIG. 12. Amount of propylene polymerized in a 30-min reaction in the presence of various catalysts obtained from trialkyl aluminium.

lyst during the polymerization. This ageing, in some particular cases, can be simply of a first order with respect to the concentration of the catalytic reagent, and of a zero order with respect to the concentration of the monomer. But in general it is complicated by other secondary processes which modify the kinetic activity.

Only by taking into account all these irregularities, one can make satisfactory calculation of the conversion curves obtained experimentally (Fig. 8).

A spontaneous ageing of the catalyst can be seen when one prepares the same type of catalyst under different conditions, and one introduces styrene at different times (Fig. 9): it is thus possible to observe that the kinetic activity decreases rapidly as a function of the time elapsed from the preparation of the catalyst.

Irregularities of this type can be observed also when one polymerizes propylene with other catalytic systems of the same class, such as $Al(iC_4H_9)_3$–$VOCl_3$. Figure 10 shows that the amount of polymer produced depends on the molar ratio of the two catalytic reagents while Fig. 11 shows that the polymerization rate decreases during the reaction.

We also report some data obtained by the polymerization of propylene with different alkyl compounds (Fig. 12); it resulted that the highest activity was obtained when the value of the Al/Ti ratio was

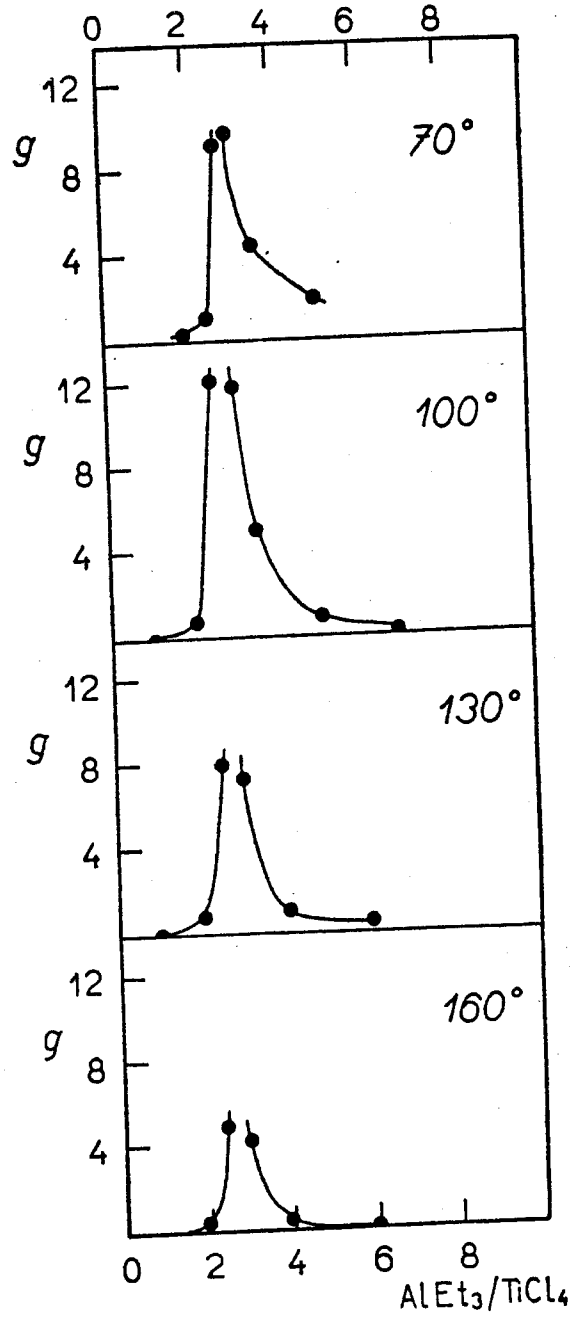


FIG. 13. Amount of isotactic polystyrene (g) vs. the ratio of $AlEt_3/TiCl_4$ in tetralin, at different polymerization temperatures. (3.5 mmol $TiCl_3$; 18 g styrene; 50 ml tetralin; 7 hr).

2 regardless of the aluminium alkyls examined (methyl, ethyl, propyl, butyl, hexyl, octyl).[6]

The optimum ratio is practically constant within a rather wide range of temperatures, as it can be observed in the case of the system styrene $-AlEt_3-TiCl_4-$tetralin (Fig. 13).

For this type of catalyst one can conclude that the preparation of active catalysts, by means of the reduction of transition metal compounds having a high valence, gives rise first of all to the formation

of several products with different catalytic activity and stereospecificity. Besides, the catalytic agents, prepared within a reasonable time, obviously have a physical structure or a chemical composition which is unstable, but considerably modified after the preparation of the catalytic system.

(*b*) *Catalytic Systems of the Second Type*

On the contrary, by using catalytic systems of the second type, one can expect considerable catalytic stability, and consequently, very regular polymerization runs.

It was surprising for us, especially at the beginning, to be able to carry out a series of regular reproducible experiments in the field of ionic polymerization, which is well known for its difficulties in a systematic study.

This fact is probably due, on one hand, to the heterogeneous nature of this type of catalysis, and on the other hand to the fairly high stability of the organometallic complexes acting as active centres in some heterogeneous systems.

It must be noticed, however, that the conditions under which the catalyst is prepared will always exert a certain influence on its activity and stability.

Figure 14, for instance, shows the different behaviour of the catalytic

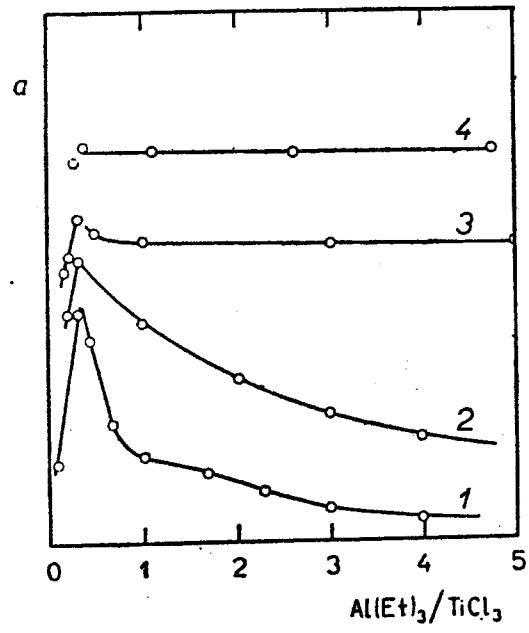


FIG. 14. Activity of the catalyst $AlEt_3$-$TiCl_3$ (a) vs. the ratio of Al/Ti (constant amount of $TiCl_3$; monomer: styrene). A comparison between the types of curves obtained with differently ground (2–4) and non ground (1) $TiCl_3$ (the ordinates of each curve have different origins).

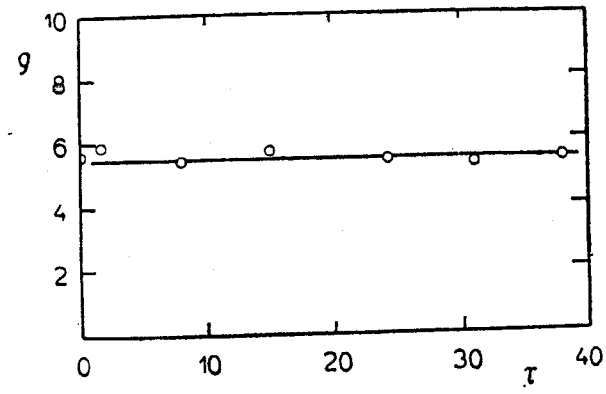


FIG. 15. Activity of a catalyst based on suitably ground $TiCl_3$ vs. the time (hr) elapsed from the preparation of the catalyst, before the addition of styrene.

activity of the system $AlEt_3$–$TiCl_3$ with styrene against the molar ratio of the two catalytic reagents and the catalysts prepared starting from $TiCl_3$ not ground or with different degrees of grinding.

The activity, which can vary when $TiCl_3$ is not ground, can become constant at suitable grinding conditions.

This constancy in activity can be achieved (Fig. 15) when one prepares the catalyst itself and starts the polymerization of styrene at different times.

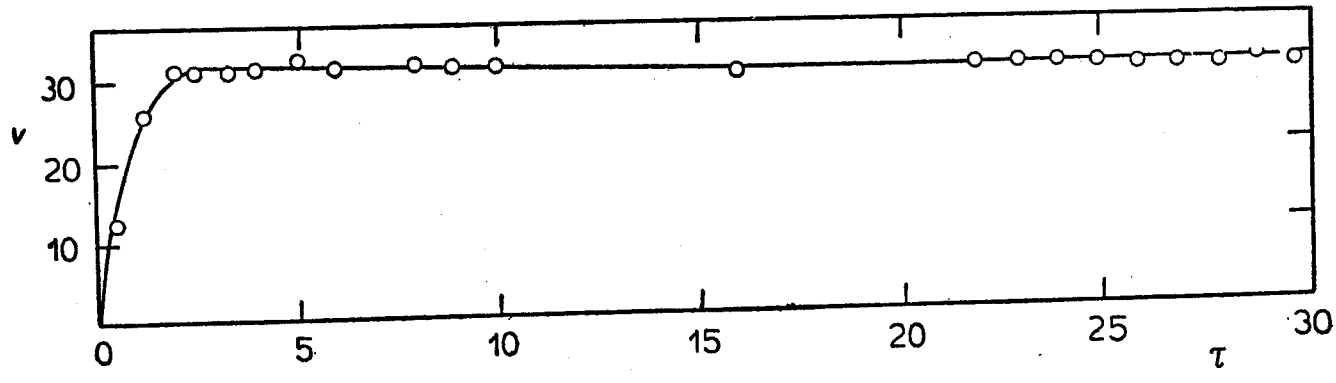


FIG. 16. Reaction rate (C_3H_6 g/hr g $TiCl_3$) vs. time (hr), obtained in the polymerization of propylene in the presence of $TiCl_3$ and Al $(Et)_3$ in n-heptane. 70°C; Pc_3H_6: 1450 mm Hg; $TiCl_3$: 0·80 g/l; $AlEt_3$: $4{\cdot}45 \times 10^{-2}$ mol/l.; n-heptane 250 cm³.

The polymerizations of propylene in n-heptane have allowed us to demonstrate very clearly that the catalytic activity of the system $AlEt_3$–$TiCl_3$ is constant during the reaction (Fig. 16). In fact in this case the absorption rate of the olefin, at a constant pressure can be easily measured in the polymerization, which is practically at a constant monomer concentration during the entire reaction. It can be observed

that the rate is practically kept constant during the reaction, except for the initial period, in which it increases.

We have studied in detail this initial anomaly, and we concluded that in the absence of impurities this is due to a progressive increase, up to a limiting value, of the number of active centres of solid catalyst entering in the reaction.

We have attributed this increase to the breaking of crystalline aggregates and to the cleavage of $TiCl_3$ crystals, which probably follows the 001 planes of its layer lattice. This hypothesis is confirmed by the fact that grinding remarkably influences this initial increase in activity, which can become practically negligible when the size of the new cleaved surfaces of the crystals is sufficiently high.

Too much grinding, however, can yield very small or very deformed crystals, susceptible again to crystallization at the operating temperature. In this case a lower catalytic stability may correspond to a very high initial catalytic activity, which can be maintained for a long time by the lowering of the temperature of polymerization. Figure 17 shows that the catalytic activity of the same system $AlEt_3$–$TiCl_3$, using styrene, with $TiCl_3$ ground to medium size, achieves a better independency of the Ti/Al ratio at the lowest temperature.

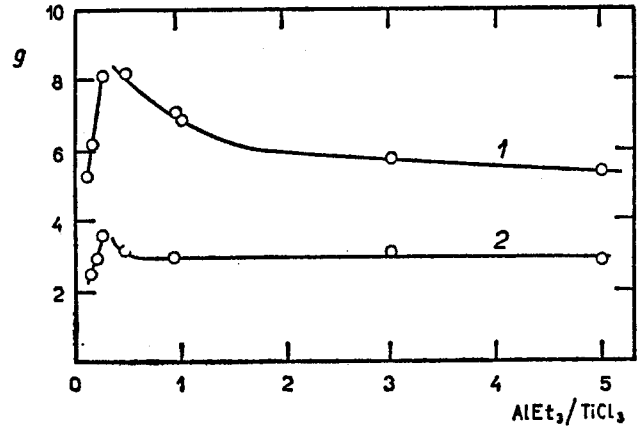


FIG. 17. Activity of a catalyst based on $TiCl_3$ ground to a medium size vs. the ratio $AlEt_3/TiCl_3$ at two temperatures, 70° C and 40° C (monomer= styrene).

Finally it is of interest to point out that a very stable catalyst can maintain its constant activity not only for days or months, but even if it is used under very different operating and resting conditions and then brought back to its original conditions.

All these experiments on the stability of these catalytic systems

demonstrate clearly that the heterogeneous sytems, used in our study, are to be considered catalysts and not initiators.

With regard to the overall reaction order, relative to the various reagents introduced, we have shown that with stable catalytic systems the order is zero with respect to the organometallic compound. On the other hand, the rate depends on the amount of the transition metal compound, with respect to which it is exactly of the first order. This is shown in Fig. 18, with styrene catalyzed by $AlEt_3$–$TiCl_3$, and in Fig. 19 with propylene.

Moreover, the overall reaction rate is also of the first order with respect to the monomer concentration. This is shown in Fig. 20 with

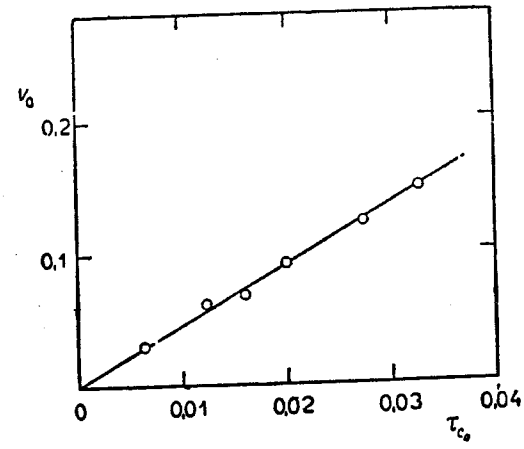


FIG. 18. Relationship between the initial rate (mol l^{-1} hr^{-1}) of the polymerization of styrene and the amount of $TiCl_3$ in mol/l. ($AlEt_3/TiCl_3$ = 1; 40° C; concentration of the monomer = 2 mol/l.; in benzene).

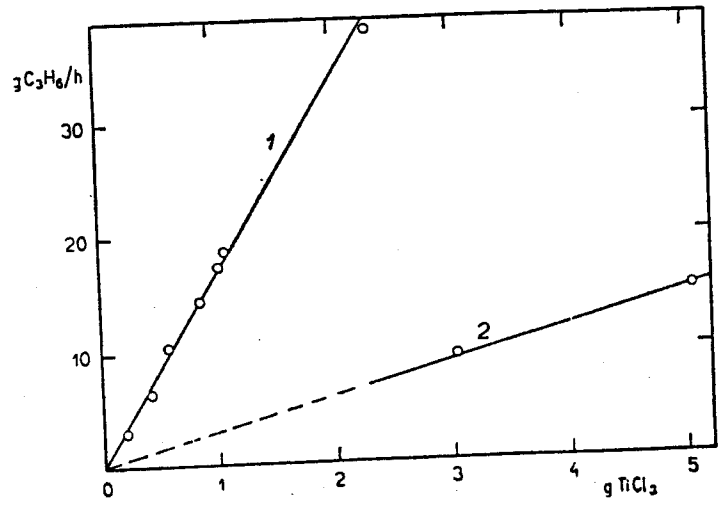


FIG. 19. Reaction rate vs. the amount of $TiCl_3$, during the polymerization of propylene in the presence of $TiCl_3$ and $AlEt_3$ in n-heptane. (1) t = 70°C; $P_{C_3H_6}$ = 1450 mm Hg; (2) t = 32°C; $P_{C_3H_6}$=1680 mm Hg.

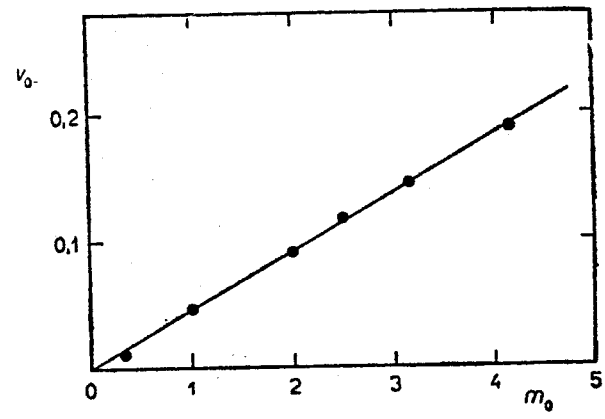


FIG. 20. Relationship between the initial rate of polymerization of styrene (mol l^{-1} hr^{-1}) and the concentration of the monomer in mol/l. $AlEt_3/TiCl_3 = 1$; 40° C; 20 mmol/l. $TiCl_3$; in benzene.

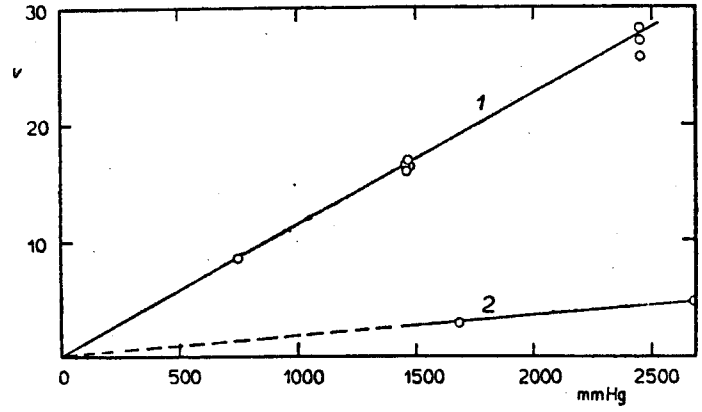


FIG. 21. Steady reaction rate (C_3H_6g/hr) (g $TiCl_3$) vs. the partial pressure of the olefin, during the polymerization of propylene in the presence of $TiCl_3$ and $AlEt_3$ in n-heptane, in relation to 1 g of $TiCl_3$. (1) 70° C, (2) 32° C.

styrene and in Fig. 21 with propylene using the same catalyst $AlEt_3$–$TiCl_3$ at two different temperatures.

The overall rate, therefore, can be expressed by the following formula:

$$v = kr_c m$$

where r_c is the amount of the coordinating metal compound, and m is the concentration of the monomer. The value of k is of the order of some unities (l/mol hr) for the system $AlEt_3$–$TiCl_3$–styrene–benzene, with an activation energy of about 10,000 cal/mol.

It is very interesting to point out that, in the case of propylene, the value of k, relative to the reaction rate, was observed to be the same whether the $TiCl_3$ used was ground or not. This means that the active surface (or the total number of active centres), is always proportional to the amount of $TiCl_3$.

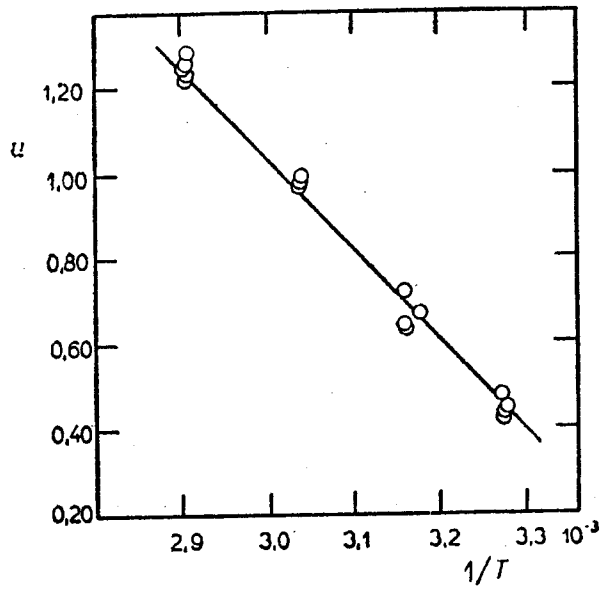


FIG. 22. Logarithm of the steady reaction rate, vs. the inverse of the absolute temperature (°K), in the polymerization of propylene in the presence of $TiCl_3$ and $AlEt_3$ in n-heptane. The rates are relative to 1 g of $TiCl_3$ and to 1500 mmHg of partial pressure of propylene; $u = \log$ [g C_3H_6hr/g $TiCl_3$].

With experiments carried out with propylene the relationship between the polymerization rate and the temperature can be seen in Fig. 22. The value of the activation energy of the overall reaction was calculated to be of the order of 14,000 cal/mol. This value, as well as the value given above, is fairly high with regard to the ionic polymerization, but, in any case, it is low if compared with the normal values corresponding to free-radical polymerizations.

Results of particular interest were obtained by the study of the intrinsic viscosities of polypropylenes obtained under different polymerization conditions, for the sytem $AlEt_3$–$TiCl_3$ in n-heptane.

First of all the molecular weight remains practically constant during the same polymerization run (Table 2); thus suggesting that the kinetic chain generated by these catalysts has a rather short length.

Since we have observed that the overall rate is also maintained constant, one could think that all the termination or chain transfer processes should occur in the same way and that the number of active centres present in the reaction at any moment, should also remain the same.

The intrinsic viscosity of polypropylene depends very little on the temperature, when low temperatures are considered (<70°C) (Fig. 23), but it decreases rapidly, when the polymerization temperature exceeds 100°C.

This variation is due to a termination reaction based on a ther-

TABLE 2

Monomer	*g polymer / g catalyst*	$[\eta]$ *100 cm³/g*
Styrene	1·2	4·6
	2·1	4·6
	3·3	4·2
	5·5	4·8
	6.3	4.9
	7.2	4.6
	9.2	4.9
Styrene	3.9	5.7
	6.4	6.1
	9.0	5.6
	11.1	5.7
	13.0	5.7
Propylene	7	3.7
	15	3.8
	22	3.6
	27	4.0
	48	3.9

mal dissociation, which does not have any practical influence at low temperatures.

The intrinsic viscosity depends also on the concentration (or the amount) of the components introduced in the system. We have suggested that the inverse of the degree of the polymerization of propylene can be represented by the following expression:

$$\frac{1}{DP} = \frac{k_1 + k_2 m + k_3 \sqrt{c_{Al}} + k_4 m \sqrt{G_{Ti}}}{k_p m}$$

where m is the monomer concentration, c_{Al} is the concentration of triethyl aluminium, G_{Ti} is the amount of $TiCl_3$ per litre of n-heptane, k_i are factors depending only on the temperature.

Actually, the intrinsic viscosity decreases in a sufficiently sharp way with an increase of the concentration of the organometallic compound present in the system (Fig. 24).

The reaction rate is constant with respect to the concentration of $AlEt_3$; it seems clear that an excess of organometallic compound does not modify the number and the activity of the active centres, but it

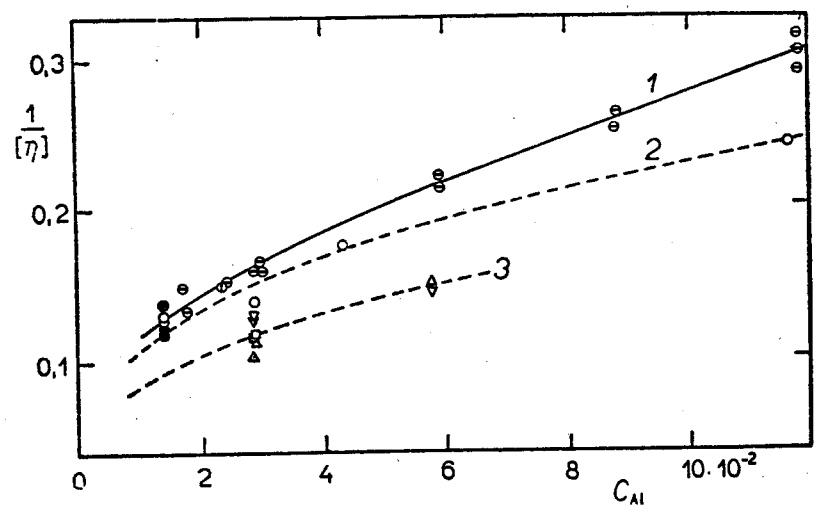


FIG. 23. Inverse of the intrinsic viscosity (100 cm/³ g) of polypropylene, obtained at different temperatures in the presence of $TiCl_3$ and $AlEt_3$ in n-heptane, vs. the concentration of $AlEt_3$. (1) $t = 70°C$, (2) $t = 51°C$, (3) $t = 31°C$. Other conditions in the following Table:

Al/Ti mol	*t °C*	$p_{C_3H_6}$ *mmHg*	$[C_3H_6]$ *mol/l.*	*Al/Ti mol/mol.*	*t °C*	$p_{C_3H_6}$ *mmHg*	$[C_3H_6]$ *mol/l.*
▽ 3	31	700	0·57	⊙ 3	41	1110	0·63
□ 1·5	31	1450	1·18	⊕ 6	51	1110	0·63
△ 3	31	1450	1·18	● 7·5	51	1110	0·63
+ 2	51	1110	0·63	⊖ 3	70	1450	0·62

can cause either a substitution on the organometallic molecules associated in the active centres or a chain transfer process, probably by means of ions originated by the organometallic compound itself or by soluble complexes formed from it.

It is of interest to point out that the inverse of the intrinsic viscosity is a function which can be considered almost linear with respect to the square root of the concentration of $AlEt_3$ (Fig. 25). This is probably caused by the dimeric nature of the triethyl aluminium or by some chemical equilibria giving rise to a real chain transfer agent.

The intrinsic viscosity varies also with the amount of $TiCl_3$ (Fig. 24). It has been possible to demonstrate that this is a transfer process and, with the aid of radioactive $AlEt_3$, the rate of this process is given by the factor $k_4 m \sqrt{G_{Ti}}$

The monomer concentration has only a weak influence on the molecular weight (Fig. 26): this means that the chain-termination process is

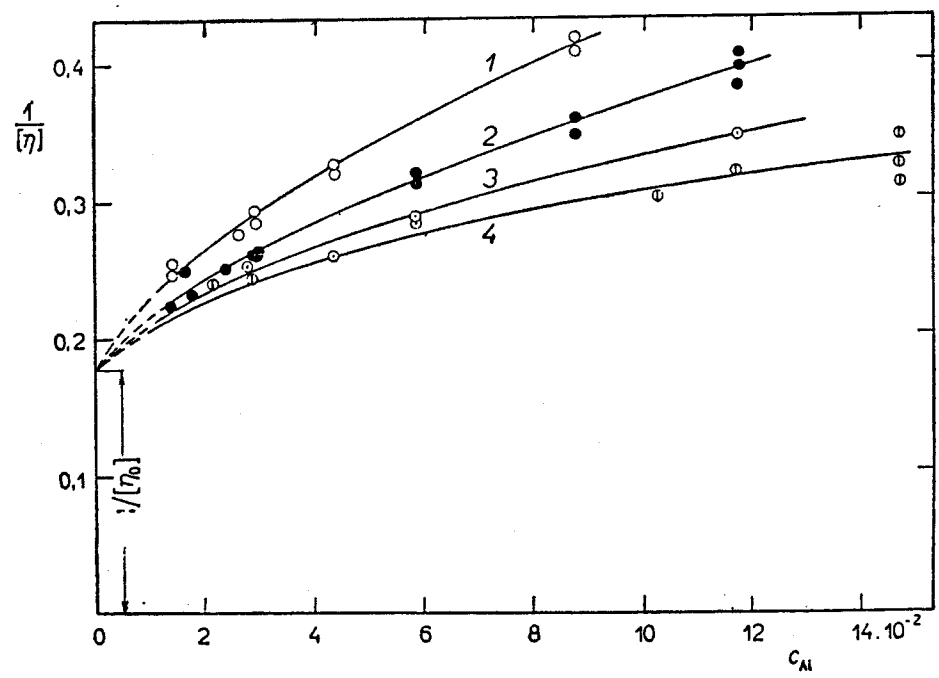


FIG. 24. Inverse of the intrinsic viscosity [(100 $cm^3/g)^{-1}$] of polypropylene obtained at 70°C and at a partial pressure of propylene of 950 mmHg in the presence of $TiCl_3$ and $AlEt_3$ in n-heptane, vs. the concentration of $AlEt_3$(mol Al $(C_2H_5)_3$/l n-heptane).

curve	1	2	3	4
Al/Ti	1·5	3	5	10

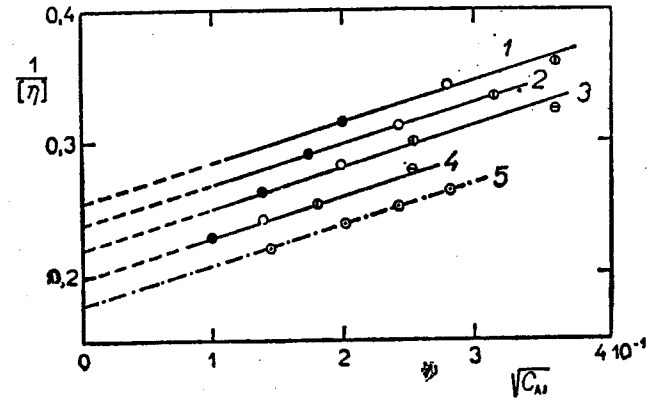


FIG. 25. Inverse of the intrinsic viscosity [(100 $cm^3/g)^{-1}$] of polypropylene obtained at 70°C and at a partial pressure of propylene of 950 mmHg in the presence of fixed amounts of $TiCl_3$, vs. the square root (mol$AlEt_3$/l n-heptane) $^1/_2$

	⊙	●		⊖		
Al/Ti, mol	1·5	3		5	10	
G_{Ti}, g $TiCl_3$/l. n-heptane		4	3	2	1	0
curve		1	2	3	4	5

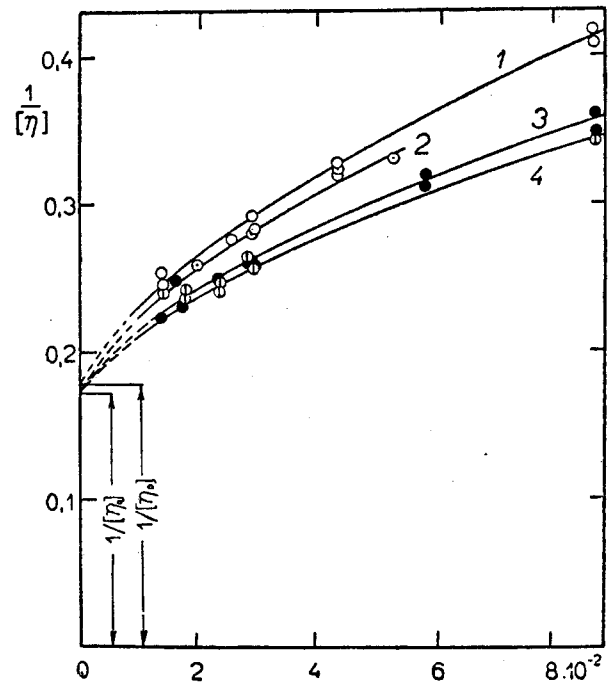


FIG. 26. Inverse of the intrinsic viscosity [(100 cm^3/g)$^{-1}$] of polypropylene obtained at 70°C, at two different pressures, in the presence of $TiCl_3$ and $AlEt_3$ in n-heptane vs. the concentration of $AlEt_3$

Curve	1	2	3	4
Al/Ti	1·5	1·5	3	3
$P_{C_3H_6}$, mmHg	950	1450	950	1450

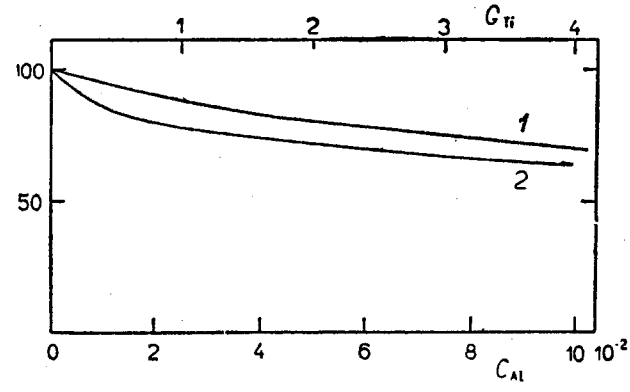


FIG. 27. Percentage of polypropylene macromolecules interrupted during the reaction (carried out at 70°C and at 950 mmHg $P_{C_3H_6}$ in n-heptane) by a termination process of the first order with respect to the monomer concentration vs. the amounts of $TiCl_3$ (g $TiCl_3$/l n-heptane) and of $AlEt_3$ (mol Al $(Et)_3$/l n-heptane) introduced in the system. (1) $C_{Al} = 0$ ($f(G_{Ti})$), (2) $G_{Ti} = 0$ ($f(C_{Al})$).

above all a process of the first order with respect to the concentration of the monomer. As we are going to see hereinafter, this is probably due to a series of consecutive chain processes, which produce a chain transfer with the monomer.

Actually, in Fig. 27 we have calculated, in the case of propylene, the percentage of the growing chains terminating by transfer with the monomer as a function of $AlEt_3$ or $TiCl_3$ concentration, assuming each time a limiting zero concentration for each of the last two reagents. The importance of the transfer with the monomer, in the sense described above, immediately appears.

To conclude this short description of our kinetic results, we suggest that in this polymerization there exist several elementary processes, summarized in the following scheme:

$$(Cat)^{(+)(-)}R_c + CH_2{=}CH \rightarrow (Cat)^{(+)(-)}CH_2{-}\underset{\displaystyle R}{\underset{|}{CH}}{-}R \qquad (1)$$

$$(Cat)^{(+)(-)}P + CH_2{=}CH \rightarrow (Cat)^{(+)(-)}CH_2{-}\underset{\displaystyle R}{\underset{|}{CH}}{-}P \qquad (2)$$

$$(Cat)^{(+)(-)}CH_2{-}\underset{\displaystyle R}{\underset{|}{CH}}{-}P \rightarrow (Cat)^{(+)(-)}H + CH_2{=}\underset{\displaystyle R}{\underset{|}{C}}{-}P \qquad (3)$$

$$(Cat)^{(+)(-)}H + CH_2{=}CH \rightarrow (Cat)^{(+)(-)}CH_2{-}\underset{\displaystyle R}{\underset{|}{CH}}{-}CH_2 \qquad (4)$$

$$(Cat)^{(+)(-)}P + CH_2{=}CH \rightarrow (Cat)^{(+)(-)}CH_2{-}\underset{\displaystyle R}{\underset{|}{CH}}{-}CH_2 + P \qquad (5)$$

$$(Cat)^{(+)(-)}P + CH_2{=}CH \rightarrow (Cat)^{(+)(-)}H + CH_2{=}\underset{\displaystyle R}{\underset{|}{C}}{-}P \qquad (6)$$

$$(Cat)^{(+)(-)}P + (Compl)^{(+)(-)}R_c \rightarrow (Cat)^{(+)(-)}R_c + (Compl)^{(+)(-)}P \qquad (7)$$

$$TiX_nAlY_2P + AlR_3 \rightleftharpoons TiX_nAlR_3 + AlY_2P \qquad (8)$$

We have briefly indicated the catalytic complex as $(Cat)^{(+)(-)}R_c$. The chain termination, due to the insertion of the first monomer molecule into the complex occurs by process (1). The chain growth must follow a similar mechanism, process (2). It is then possible, especially when one operates at high temperatures, to obtain a spontaneous termination of the chain by transfer of an ion hydride to the complex, process (3), which can restore, by addition of a new monomer molecule,

the alkyl group bound to the active centre, and to cause the termination of a new chain having the initial reactivity, process (4).

The transfer of a hydride ion could also take place during the growth reaction, thus giving rise to an actual chain transfer with the monomer, process (5), or else a termination reaction, process (6), due to the formation of the hydride ion on the catalyst, resulting in a chain reaction.

In fact the dissociation to hydride is characterized by a strong variation of the molecular weight at high temperature. The other termination processes prevail at low temperatures. It is also possible that such an activation is generated by the heat of the addition reaction of the monomer in the short time which is necessary for the heat to be spread around. This increase of the reaction rate constant was experimentally demonstrated by one of us in other consecutive reactions (7–9).

In the presence of other ionic complexes or of simpler ionic compounds, which are inactive in the polyaddition reaction, it is also possible to obtain true ionic exchanges, process (7), which generate a new chain and an inactive macrocomplex. By operating at a high hydrogen pressure the decrease of the molecular weight can be attributed to a reaction of this type.

Another possibility exists in the substitution of the aluminium-alkyl compound, bound to a catalytically active complex containing a transition metal, process (8).

This reaction could also follow an ionic mechanism, if one considers the possible ionic dissociation of the dimers of alkyl aluminiums and an analogous dissociation of the complexes containing transition metals.

The information we have obtained so far has enabled us to understand why stereospecific polymerization processes, to which we attribute a coordinated anionic mechanism and which have led to the synthesis of stereoregular polymers, do show a kinetic behaviour very different from that of other previously known polymerization processes.

In fact the overall process could be easily interpreted as a simple polyaddition reaction which when catalysed could reach high reaction rates comparable to those of a real chain process. We believe that a deeper study on the influence exerted by several factors on the catalytic activity, on the stereospecificity of the activated crystalline surfaces and on the evaluation of the absolute number of active centres would contribute to the solution of several general problems concerning heterogeneous catalysis.

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THE CRYSTALLINE STRUCTURE OF ISOTACTIC 1,2-POLYBUTADIENE

by G. NATTA, P. CORRADINI and I. W. BASSI

(14 Dec. 1957)

[*Rend. Accad. Naz. Lincei* (8) **23**, 363 (1957)]

ABSTRACT

The crystalline structure of isotactic 1,2-polybutadiene is studied in this paper. The chain structure and the mode of packing of the chains among themselves is substantially analogous to that found by the same authors in isotactic poly-α-butene.

The only difference is in the orientation of the side group, which satisfies in both cases the principle of the maximum separation of simple bonds.

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THE STEREOSPECIFIC POLYMERIZATION OF α-OLEFINS. NOTE IV: THE POLYMERIZATION OF PROPYLENE WITH TITANIUM CHLORIDES AND DIFFERENT TRIALKYLALUMINIUMS

by G. NATTA, P. PINO, G. MAZZANTI and P. LONGI

(23 Dec. 1957)

[*Gazz. Chim. It.* **88**, 219 (1958)]

ABSTRACT

This is a study of the polymerization of propylene carried out with the aid of catalysts prepared from titanium tetrachloride or trichloride, and aluminium trialkyls. In particular the variations observed in the catalytic activity and in the stereoisomeric composition of the polymers obtained when varying the length of the alkyl groups initially bound to the aluminium have been examined.

Thus, it has been found that with the increase of the carbon atom number of the alkyl groups bound to aluminium, the catalyst obtained possesses a more and more decreasing stereospecificity. For instance, when using titanium trichloride (α modification—violet) and tri-n-octyl aluminum, it is possible to obtain polypropylenes which do not contain more than 40 per cent of a fraction nonextractable in boiling n-heptane; whereas, when using triethyl aluminium, this fraction can easily exceed 70 per cent of the total polymer.

When the length of the alkyl groups in the organometallic compounds is varied, the catalytic activity shows a practically opposite behaviour, depending on whether $TiCl_4$ or $TiCl_3$ has been used. In fact, when using tri-n-butyl aluminium, the lowest catalytic activities are

obtained by reaction with $TiCl_4$, while the highest ones were obtained by reaction with $TiCl_3$.

Moreover, the influence of the length of the alkyl groups in the aluminium alkyl compounds on the degree of polymerization of the isotactic polypropylene has been also examined.

It has been concluded that for the catalysts prepared from $TiCl_3$ and for those prepared from $TiCl_4$, the degree of polymerization gradually increases when the carbon atoms of the alkyl groups are five to six.

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APPLICATIONS OF THE ELECTRON DIFFRACTION METHOD TO THE STUDY OF POLYMER STRUCTURES

by P. CORRADINI and I. W. BASSI

(23 Dec. 1957)

[*La Ricerca Sci.* **28**, 1435 (1958)]

ABSTRACT

The application of electron diffraction methods to the study of the crystalline structure of polymers is discussed in this paper.

As an example, the unit cells of isotactic poly-alpha-butene, of isotactic polystyrene and of syndiotactic 1,2-polybutadiene, are obtained from the corresponding electron diffraction spectra.

It is observed that, in the study of polymer structures, the electron diffraction method can be performed rapidly. It gives results, which can be interpreted very easily and moreover, in the case of fibre spectra, it gives an undistorted representation of the reciprocal lattice. This allows one to draw important and immediate conclusions as far as the chain structure of the examined product is concerned, by studying the Fourier transform of each polymer molecule. We did so with regard to polyvinylisobutylether and to other isotactic polymers.

The differences existing between the intensities, as revealed by the X-ray spectra and the electron diffraction spectra, permit the observation of some interesting facts on the position of the hydrogen atoms, which show a diffraction factor higher for electrons than for X-rays (in comparison with carbon atoms).

Finally, the study of the orientation of crystals in thin films is very important both for the study of the mechanism of spherulite formation and to obtain supplementary data derived from an X-ray fibre spectrum; they are well suited to give indices to the reflections; therefore, an exact determination of the elementary unit cell is possible.

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CRYSTAL STRUCTURE OF THE COMPLEX $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$

G. NATTA, P. CORRADINI and I. W. BASSI

(26 Dec. 1957)

[*J. Amer. Chem. Soc.* **80**, 755 (1958)]

In a preceding communication to this Journal there was reported[1] the synthesis of a soluble crystallizable complex containing titanium and aluminum showing catalytic activity in the polymerization of ethylene. This fact was taken as supporting our opinion that Ziegler type catalysts are bimetallic complexes. It was also supposed that the two different metal atoms contained in the crystallizable complex were joined by bridges of the same type as the one present for instance in the monochlorodimethylaluminum dimer.[2]

To confirm the above reported hypothesis, we wish to communicate some preliminary results of an X-ray examination of single crystals of the complex $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$.

The unit cell constants are

$$a = 15{\cdot}77 \pm 0{\cdot}08 \text{ Å}; \; b = 14{\cdot}24 \pm 0{\cdot}07 \text{ Å}; \; c = 7{\cdot}54 \pm 0{\cdot}04 \text{ Å};$$
$$\alpha = \beta = \gamma = 90°$$

The number of molecules contained in the unit cell is four, and possible space groups are Pnma or $Pn2_1a$ [$(0kl)$ reflections with $k+l = 2n + 1$ and $(hk0)$ reflections with $h = 2n + 1$ being extinguished].

The space group Pnma requires that the molecule contains a mirror plane. In this case Ti and Al must necessarily lie in this plane ($y = \frac{1}{4}$).

In fact, the Patterson projection on the a–b plane of the interatomic vectors (Fig. 1) showing a concentration of the highest peaks along the lines $y = 0$ and $y = \frac{1}{2}$ supports the hypothesis that heavy atoms are contained in the $y = \frac{1}{4}$ plane.

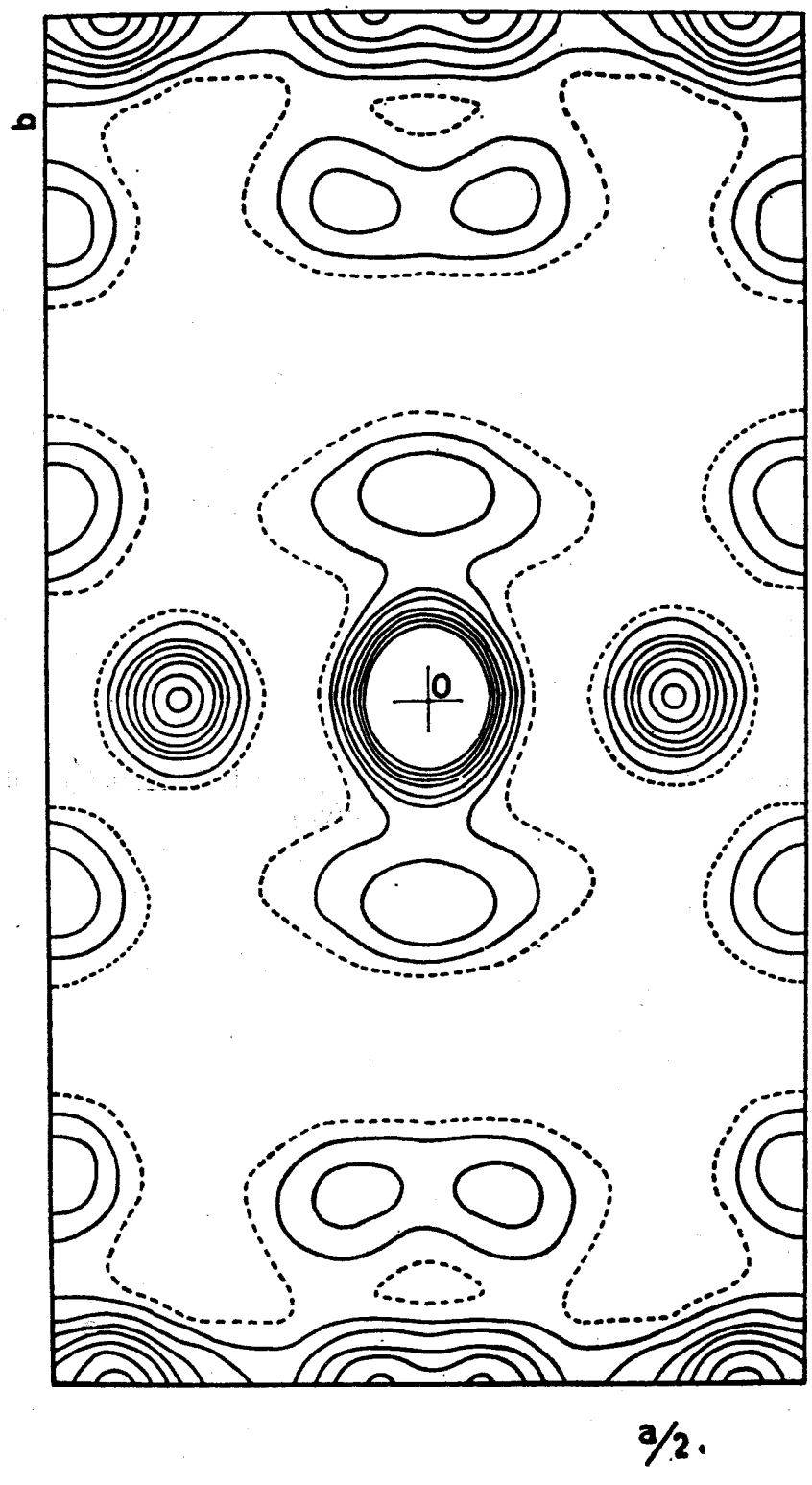


FIG. 1. Patterson projection on the a-b plane.

A complete interpretation of the Patterson projection confirms that: (1) Pnma must be chosen as the correct space group; (2) the position and the weight of the peaks appearing along the lines $y = 0$, $y = \frac{1}{2}$ may be accounted for by supposing that

$y_{Ti} = y_{Cl} = y_{Cl_{II}} = y_{Al} = \frac{1}{4}$ and $x_{Ti} = x_{Cl} = 0.021$;
$x_{Cl_{II}} = x_{Al} = 0.183$ or $x_{Ti} = x_{Cl_{II}} = 0.271$; $x_{Cl_{II}} = x_{Al} = 0.433$

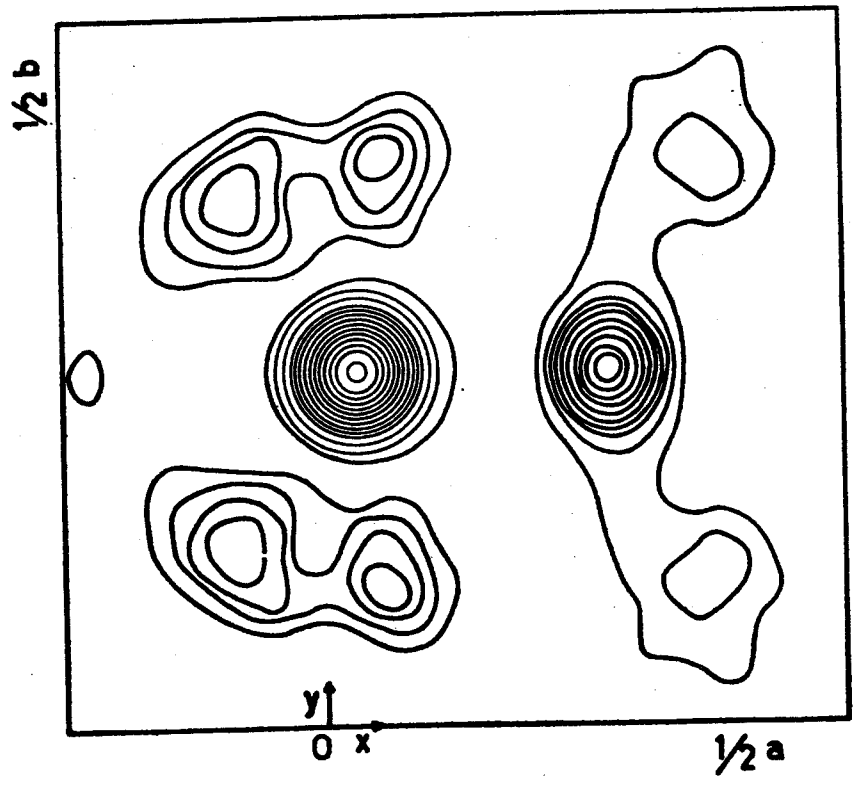


FIG. 2. Fourier projection on the a-b plane (only half contours of the heavy atoms are drawn).

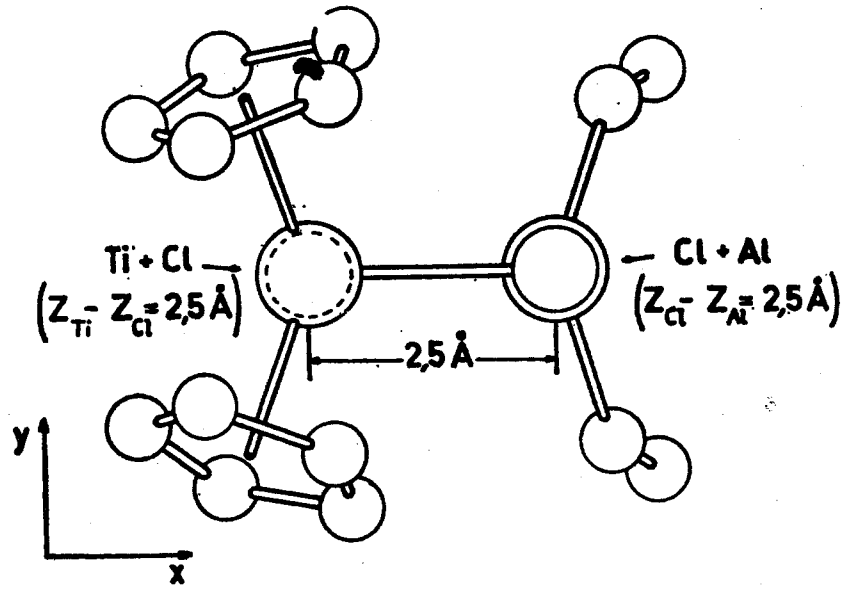


FIG. 3. Model of the molecule corresponding to the Fourier projection.

Moreover, (1) from the pseudosystematic absence of the reflections $hk3$ with $h = 2n$ it follows, with other restrictions, that $z_{Ti} - z_{Cl_I} = z_{Cl_{II}} - z_{Al_I} - \simeq 0{\cdot}333$; (2) Fourier synthesis (Fig. 2) on the ab plane shows clearly images of the cyclopentadienyl and ethyl groups, which happen to be in suitable positions.

A model of the molecule is shown in Fig. 3.

From the model, we may conclude that: (1) both Ti and Al have a tetrahedral coördination and are joined by bridges of Cl atoms forming a square ring, the Ti–Cl and Al–Cl distance being about 2.5 Å. (2) The plane of a cyclopentadienyl group is perpendicular to the line joining titanium to the center of the group, the five Ti–C distances being all equal and of the order of 2.3 Å. (3) Ethyl groups are bonded to the Al atoms. The cyclopentadienyl groups in this sandwich $\sigma\pi$-bonded complex are not parallel to each other as in ferrocene. The orientation of these groups appears dependent on the type of the hybridization of the metal atom to which they are bonded. Further structural work with this and other similar compounds is going on in our laboratory.

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KINETICS OF PROPYLENE POLYMERIZATION WITH HIGHLY STEREOSPECIFIC HETEROGENEOUS CATALYSTS. NOTE III: CHAIN TERMINATION PROCESSES DEPENDING ON CATALYST CONCENTRATION

by G. NATTA, I. PASQUON and E. GIACHETTI

(Dec. 1957)

[*Chimica e Industria* **40**, 97 (1958)]

ABSTRACT

Results are here reported on further research on the production of isotactic polymers through coordinated anionic catalysis. By operating at constant pressure and temperature, the molecular weight of the isotactic polymer, obtained with a catalyst prepared from titanium trichloride (violet modification), and trialkyl aluminum, decreases with the increase of the relative quantity of any of these two compounds.

The decrease of the molecular weight has been attributed to processes involving the termination of growing molecules, depending on the concentration of the organometallic compounds in solution.

The termination process of the polymeric chains, is interpreted as an exchange process of alkyls between the growing polymeric chains and the triethyl aluminum.

The observed processes of termination of the polymeric chains are kinetically equivalent to chain transfer reactions.

Within our limits of investigation, the molecular weights and the stereoisomeric composition of the polymer do not depend on the time of polymerization.

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KINETICS OF PROPYLENE POLYMERIZATION WITH HIGHLY STEREOSPECIFIC HETEROGENEOUS CATALYSTS. NOTE IV: INFLUENCE OF TEMPERATURE AND PRESSURE ON THE KINETICS OF GROWTH AND TERMINATION PROCESSES

by G. NATTA, I. PASQUON, E. GIACHETTI and F. SCALARI

(Dec. 1957)

[*Chimica e Industria* **40**, 103 (1958)]

ABSTRACT

By continuing the research study, which has been referred to in previous papers, we have demonstrated that in the polymerization of propylene with the aid of limited concentration of triethyl aluminum, the main process of termination of the growing chain is one equivalent to a chain transfer with the monomer.

Working with low partial pressures of propylene, a process of chain termination, independent of the concentration of the monomer and of the catalyst, was observed. The effect of this process on the lowering of molecular weights, below 80°C, is rather limited.

The mechanisms of the different processes identified (growth, transfer, and termination), which are of interest to the overall process of polymerization, are here discussed.

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CRYSTALLINE STRUCTURE OF ORGANOMETALLIC COMPLEXES CONTAINING ALUMINUM AND TITANIUM

by P. CORRADINI and I. W. BASSI

(11 Jan. 1958)

[*Rend. Accad. Naz. Lincei* (8) **24**, 43 (1958)]

ABSTRACT

The preliminary data on the structure of the complex: $(C_5H_5)_2$ $TiCl_2Al(C_2H_5)_2$ are described. It crystallizes in the rhombic system with crystallographic axes:

$a = 15.77 \pm 0.08$ Å, $b = 14.24 \pm 0.07$ Å, $c = 7.54 \pm 0.04$ Å. The choice among the possible space groups that cannot be deduced from only the systematic extinctions is made possible by the examination of the Patterson projection on the *a*–*b* plane. Therefore, we called it the *Pnma* group. By interpreting the Patterson projections and by care-

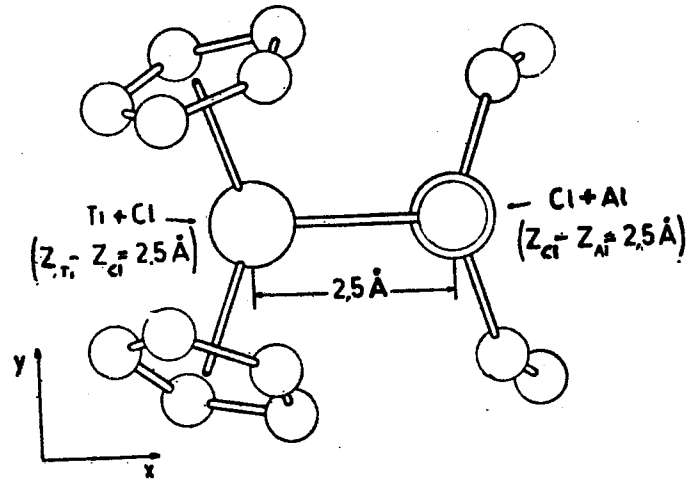


FIG. 1. Structural model of the $(C_5H_5)_2$ $TiCl_2Al(C_2H_5)_2$ molecule.

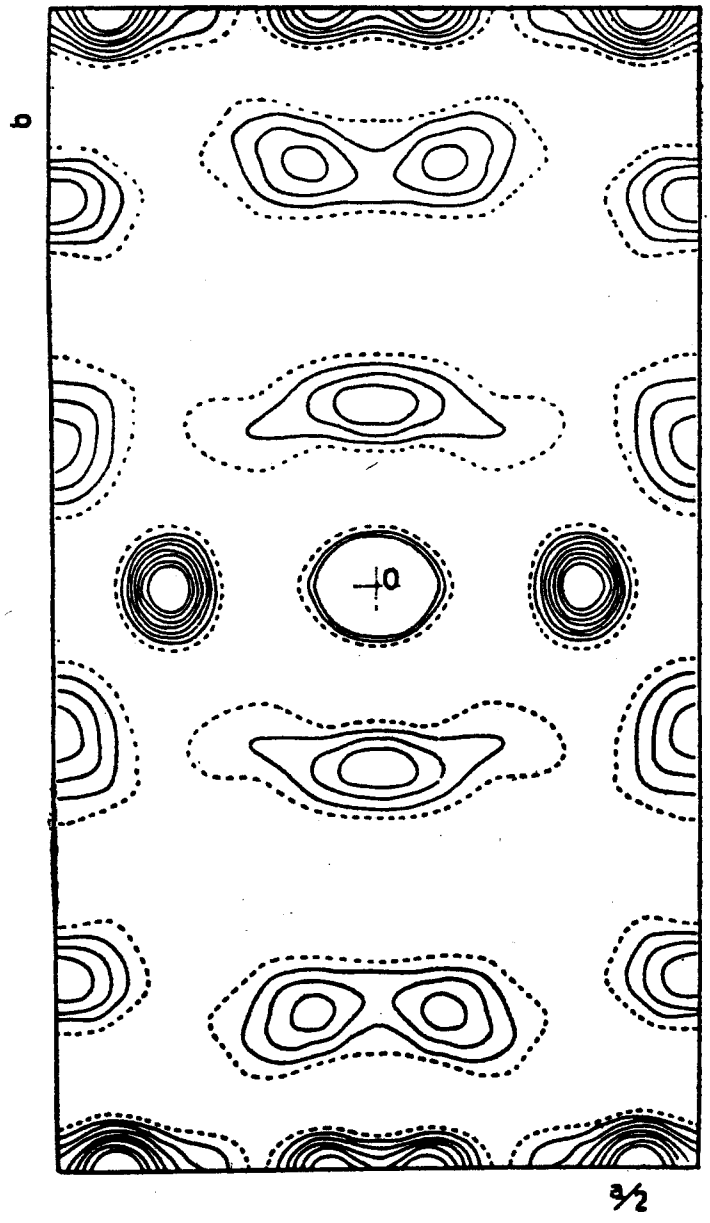


FIG. 2. Sharpened Patterson function of $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$ projected on (001).

fully analysing the *hkl* reflections, it was also possible to determine an accurate structural model of the molecule. The molecule is constituted of two different molecules, which are both electron-deficient.

Figure 1 shows the pattern of the molecule with the values of the bond distances.

Figure 2 shows the projection on the *ab* plane of the electronic density.

60

ATACTIC AND STEREOBLOCK POLYMERS OF α-OLEFINS

by G. NATTA, G. MAZZANTI and P. LONGI

(Jan. 1958)

[*Chimica e Industria* **40**, 183 (1958)]

ABSTRACT

This is a study on the variation of the stereoisomeric composition of polymers obtained with "thermally stabilized" catalysts, prepared by treating titanium halides with aluminum alkyls, as a function of the polymerization temperature and of the number of carbon atoms present in the alkyl groups initially bound to the aluminum compound.

These "thermally stabilized" catalysts were prepared by maintaining the titanium halide and the aluminum alkyl in solution for several hours at a temperature higher than that subsequently adopted for the polymerization. This stabilization procedure is necessary because of the considerable influence exerted by the temperature on the rate and on the stereospecificity of the catalyst; as shown in Table 1, the degree of this influence is determined by the higher temperature to which the catalyst is subjected, regardless of the process used (runs 1 and 2). By studying the influence of temperature on the polymerization of propylene with these catalysts, it has been noticed that an increase in the polymerization temperature causes a linear decrease of the percentage of isotactic polypropylene (insoluble in boiling n-heptane), along with an increase (which is also linear and almost proportional) of the percentage of stereoblock isotactic polypropylene, soluble in n-heptane, but insoluble in boiling ether, and which shows a low degree of crystallinity. The atactic polypropylene content increases slightly with an increase of the temperature of polymerization, when the catalytic

system used consists of triethyl aluminum and titanium trichloride (α-violet modification). On the other hand, if the catalyst is prepared from triethyl aluminum and titanium tetrachloride, the increase with a rise in the temperature is much more marked.

TABLE 1
POLYMERIZATION OF PROPYLENE WITH THE AID OF STABILIZED CATALYSTS.

Catalysts prepared by treating 0.00475 moles of $Al(C_2H_5)_3$ with 0.0032 moles of $TiCl_3$ in 150 cm³ of decalin, at a temperature of 175°C for 2 hr. Monomer concentration: 7·5 g of propylene/100 cm³ of decalin.

Run no.	*Polymerization temperature °C*	*Polymer produced g*	*Fractionation of polymer obtained*			
			ether extract %	*heptane extract %*	*residue*	
					%	$[\eta]$
1	80°C for 2 hr, then 120° for 1 hr	31	15.5	26.8	57.7	2.4
2	120°C for 1 hr, then 80° for 2 hr	30	16.5	25.1	58.4	2.5

The variation of the molecular weight of the polymers obtained has also been examined, as a function of the polymerization temperature; an almost identical behaviour can be observed when using either $TiCl_3$ or $TiCl_4$ in the preparation of the catalyst. Thus, for instance, by doubling the polymerization temperature, the value of the intrinsic viscosity is almost reduced to half.

On the basis of these results the authors dwell on the possible causes of the influence of the temperature on the formation of both isotactic and stereoblock isotactic macromolecules.

If one bears in mind that the structural differences between these two stereoisomers derive substantially from the fact that in the case of stereoblock macromolecules, the chain segments having a regular isotactic structure are rather short and alternated with chain segments which are either atactic or have an opposite configuration, whereas in the case of isotactic, high-purity macromolecules, the interruptions due to chain segments, either atactic or having an opposite configuration, are practically absent, then it would be possible to formulate two hypotheses on the formation of stereoblock polymers depending on the temperature:

1. The stereospecificity of the active centres of the catalyst decreases

with the increase of temperature. In this case each stereoblock isotactic macromolecule should be formed by segments containing monomeric units of the same steric configuration, alternated by segments having an atactic configuration.

2. The stereospecificity of the active centres does not vary with the increase of temperature; the growth of the chain with a stereoblock isotactic structure, occurs subsequently on different active centres, as a consequence of a particular transfer process of the growing chain favoured by temperature.

Because of these continuous transfers, the new segments which are being formed in the macromolecule will have the same steric configuration, statistically opposite to that of the adjacent segments.

According to the authors, the second hypothesis seems more probable since it also agrees with the experimental results obtained from the study of the influence of the organometallic compound on the stereoisomeric composition of polypropylenes.

In fact it was noticed that the percentage of isotactic polypropylene decreases, while that of the stereoblock isotactic polypropylene increases, with an increase of the number of carbon atoms (from ethyl to n-octyl) of the alkyl groups initially bound to the alkyl aluminum, and with the decrease of the ionic radius of the metal present in the metal alkyl.

Since an increase of the length of the alkyl groups and a decrease of the ionic radius of the metal favour the dissociation or the solubility of the complex, which is formed on the active centres, these factors can be also held responsible for the growing chain transfer processes, pointed out in the second hypothesis concerning the formation of stereoblock macromolecules.

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POLYMORPHISM OF CRYSTALLINE TITANIUM TRICHLORIDE

by G. NATTA, P. CORRADINI, I. W. BASSI and L. PORRI

(8 Feb. 1958)

[*Rend. Accad. Naz. Lincei* (8) **24**, 121 (1958)]

ABSTRACT

Once the existence of different stereospecific activities of $TiCl_3$ was observed depending on its method of preparation, the supposition of different polymorphous modifications of the compound could be advanced.

The methods of preparation of the three polymorphous modifications of $TiCl_3$, (a) $TiCl_3$ α, (b) $TiCl_3$ β, (c) $TiCl_3$ γ, are described here; these modifications have been subsequently analysed by X-ray methods.

The X-ray spectrum of the α-modification, as already described by Klemm and Krose, *Z. Anorg. Chem.*, 253, 209 (1947), can be interpreted on the basis of a layer lattice, which can originate from a hexagonal close-packing of the chlorine atoms, in which the titanium atoms are arranged in layers, placed at every second layer of the chlorine atoms. The elementary unit cell of this modification has constants of $a=b=6{\cdot}12$ Å, $c=17{\cdot}50$ Å, $\gamma=120°$, space group R_3, the coordinates of the chlorine atoms are 1/3; 0; 0·079; those of titanium are 0; 0; 1/3 (Fig. 1).

The X-ray spectrum of the β modification can be interpreted on the basis of a hexagonal unit cell, having constants of $a=6{\cdot}27$ Å, $c=5{\cdot}82$ Å; space group $C6/mcm$; the structure of such a modification is derived from a hexagonal close-packing of the chlorine atoms, by the gathering of the $TiCl_3$ molecules in rows which are parallel to the three-fold axis; the coordination of the halogen atoms around the titanium is still

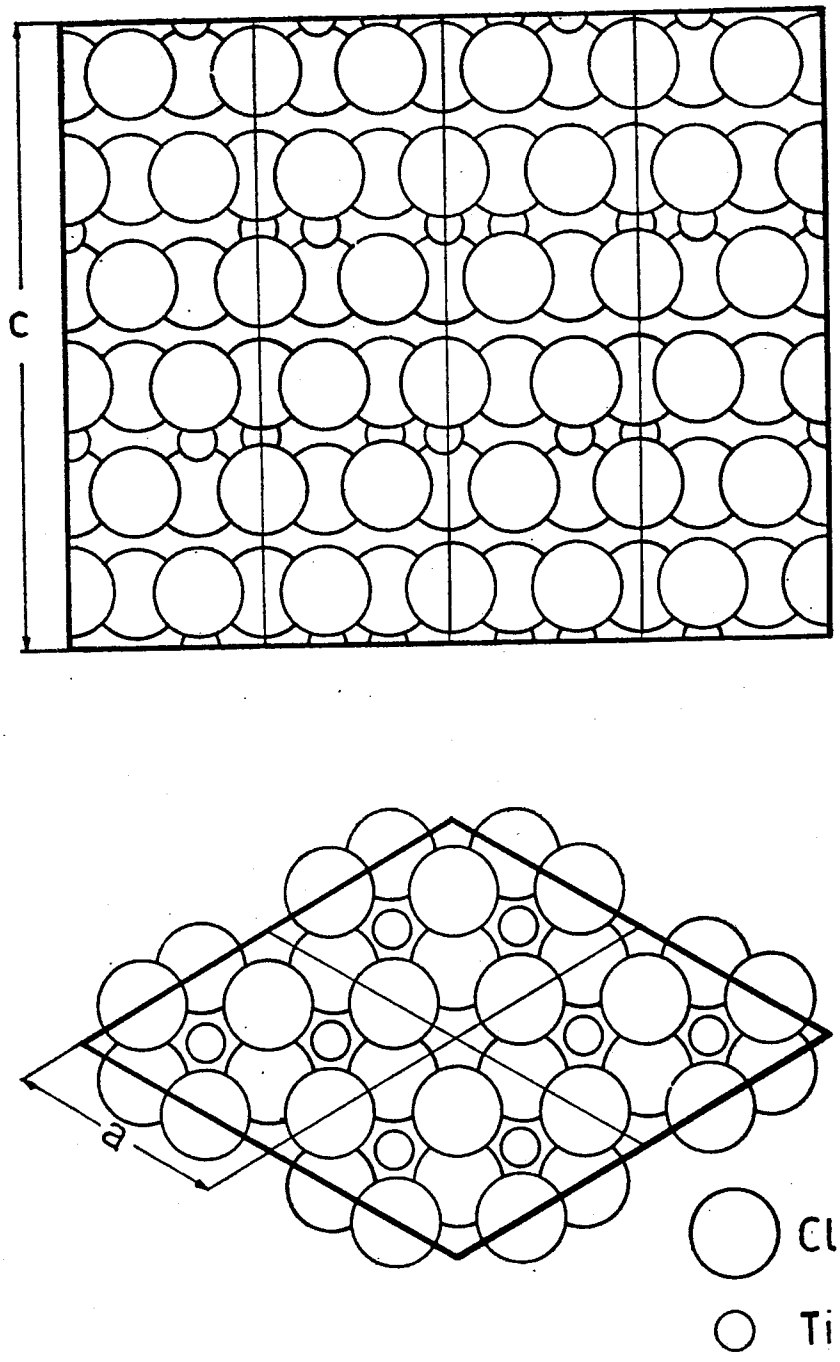


FIG. 1. Structural model of the α-modification of $TiCl_3$.

octahedral, but the way in which the titanium atoms are arranged among themselves is completely different. The coordinates of the Ti atoms were found in $X = 0$, $Z = 0$; those of chlorine in $X = 0{\cdot}315$, $Z = \frac{1}{4}$ (Fig. 2).

The X-ray spectrum of the γ modification was not interpreted in this paper; however, it may be said that it is derived as in the α-modification, from a layer lattice.

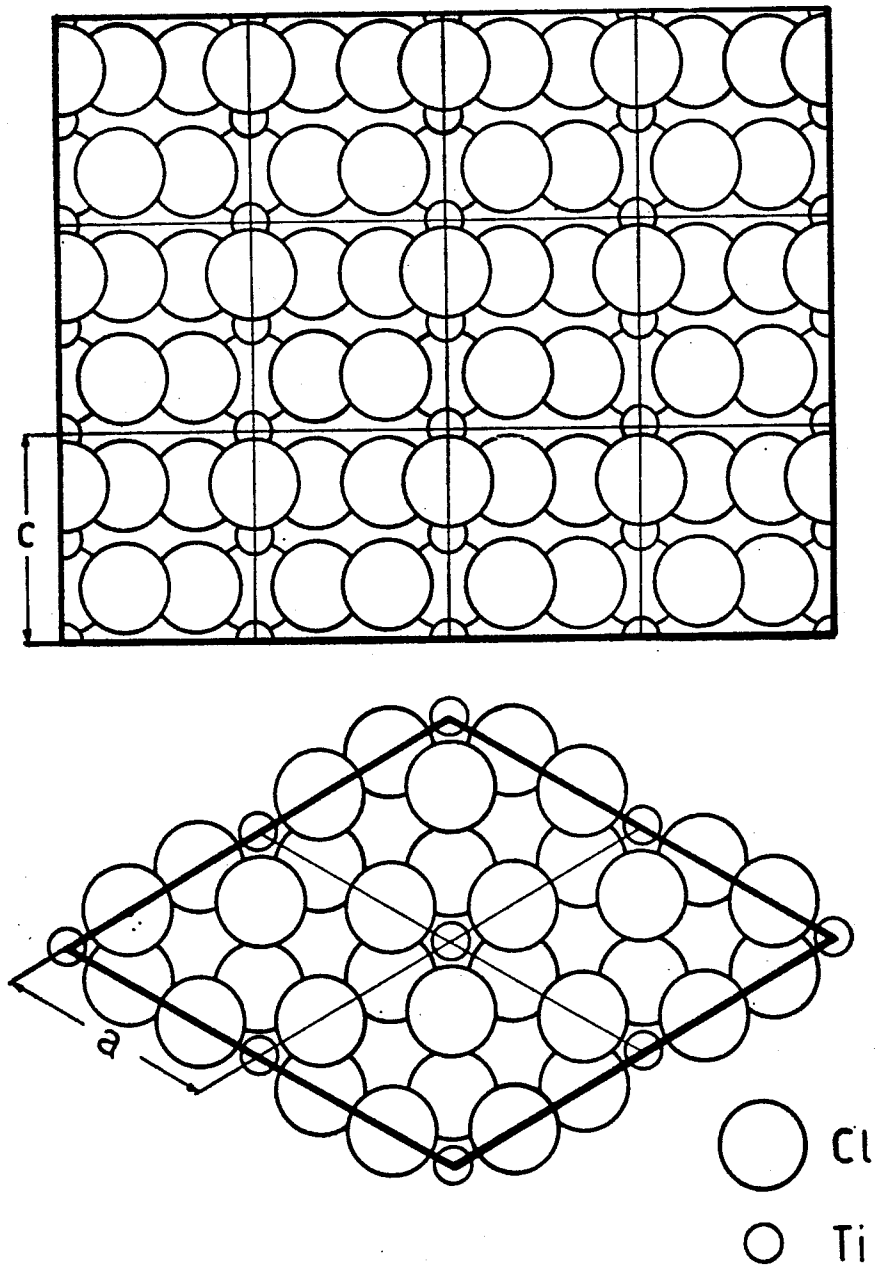


FIG. 2. Structural model of the β-modification of $TiCl_3$.

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CHROMATOGRAPHIC FRACTIONATION OF STEREOBLOCK POLYMERS

by G. NATTA, M. PEGORARO and M. PERALDO

(24 Feb. 1958)

[*La Ricerca Sci.* (7) **28**, 1473 (1958)]

ABSTRACT

It is known that amorphous polymers can be easily fractionated, from the point of view of molecular weights, by solvent extraction techniques, or by fractional precipitation. The crystalline polymers fractionation by solvent extraction is actually effective in separating molecular weights only when employed at temperatures higher than the melting temperature of the crystals. In particular, the stereoblock homopolymers are crystallizable when they contain in each molecule rather short crystallizable chain segments alternated with non-crystallizable ones of variable steric configuration.

The fractionation by means of more or less selective solvents of mixtures of poly-α-olefins of different stereoisomeric composition, was described in a previous paper (paper 31).

Here the predominant factor is the variation of solubility with temperature, closely connected with the melting temperature of the crystals, which falls with the decrease of the stereoisomeric purity of the polymers. However, in the extraction of small crystalline stereoblocks, it was observed that:

1. When the crystallinity is constant the solubility decreases with the increase of the molecular weight.

2. When the molecular weight is constant the solubility increases with the decrease of crystallinity.

Therefore, a fraction, even if it is a small one when obtained by solvent extraction, can consist of a mixture of chemical substances having very different molecular weight and crystallinity.

We fractionated by chromatographic methods, by extraction with isopropyl ether, a sample of stereoblock polypropylene, having a low degree of crystallinity and which was obtained from a mixture of stereoblock polymers. The sample was insoluble in ethyl ether and therefore free from atactic polymers. It was soluble in boiling n-heptane, thus free from highly isotactic polymers.

Further fractionation was carried out, with varying degrees of effectiveness, depending on the adsorbing substance used. For instance using silica, we first observed the extraction of products, which were not too well differentiated having only slightly different crystallinity and molecular weight. Only toward the end, did the separation of about 40 per cent of the substance occur with subsequent fractions showing increasing crystallinity and decreasing molecular weight.

We observed a more effective separation when a high-molecular-weight, highly isotactic and, therefore, highly crystalline polypropylene (a residue of a prolonged extraction in boiling n-heptane) (Fig. 1 and Table 1) was used as the adsorbing substance. In this case, stronger adsorption properties were observed for highly crystalline stereoblock polymers than for the less crystalline ones.

The strong adsorption observed must be attributed to a process of superficial interaction, whereby the isotactic parts of the stereoblock molecules are dissociated from their solutions to be attached to the

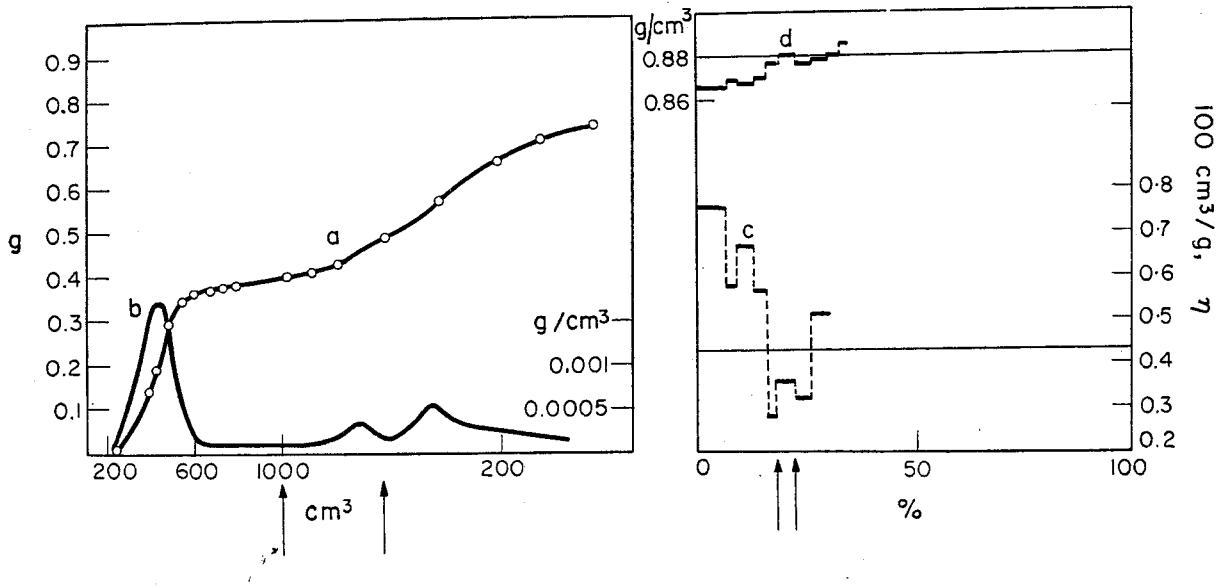


FIG. 1. Fractionation of stereoblock polypropylene on an adsorbing substance consisting of highly crystalline polypropylene (the arrows correspond to the variations of temperature indicated in Table 1): (a) Integral elution curve (b) Curve derived from the preceding one; (c) Distribution of the intrinsic viscosities of the eluted fractions; (d) Distribution of the densities of the eluted fractions.

crystalline lattice of the highly isotactic polymer used as adsorbing agent.

The stereoblock polypropylenes, with a relative density higher than 0·88 and a crystallinity higher than 20 per cent are so strongly adsorbed that it is extremely difficult to elute them, unless one operates at extraction temperatures considerably higher than those in which the adsorption is effected.

Good results were also obtained by using a highly isotactic polypropylene, previously adsorbed on an amorphous support. Also in this case the more crystalline fractions having a relative density higher than 0·882 are strongly adsorbed, independently of their molecular weight.

A mixture of stereoblock polymers with an average crystallinity of 22% and an average η of 54.1 cm^3/g was separated into fractions having a crystallinity varying continuously from 2.5 to 35 per cent.

Thus we arrived at the interesting conclusion that one of the most effective methods for the fractionation of partly isotactic stereoblock polymers, as a function of crystallinity, is adsorption, where the adsorbing substance consists of a highly crystalline high-molecular weight isotactic polymer, of the same monomer.

The method adopted in this work is effective mainly for the separation of polymers with different crystallinity, almost independently of their molecular weight. Only in the case of mixtures of substances with the same crystallinity, can the fractionation be carried out on the basis of the molecular weight. This procedure allows a better fractionation than that obtained using solvents only, but in the conditions mentioned above it is still imperfect, in that two contrasting variables exist: the molecular weight and the crystallinity.

It is probable that the procedure described in this paper can yield better results, if fractions with a narrow molecular weight distribution are subjected to a preliminary fractionation with solvents at high temperature (higher than the melting temperature of the crystals), operating independently of their crystallinity, and subsequently to chromatography on an adsorbing substance consisting of highly crystalline polymers.

Table 1. Separation, Made on a Highly Isotactic Polypropylene, of a Stereoblock Polypropylene (g 2.2; density 0.880 g/cm³, η 43.1 cm³/g). Eluting Agent: Isopropylether.

Fraction no.	*Subsequent fraction weights in % of the weight of the introduced polymer*	*eluted cm³*	*η 100 cm³/g in tetralin at 135°C*	*Density at 20°C g/cm³*	*Elution temperature °C*
1	0.1	238			30
2	6.7	393	0.754	0.865	30
3	8.7	425	0.572	0.869	30
4	13.2	485	0.666	0.868	30
5	15.9	545	0.566	0.870	30
6	16.6	605			30
7	16.9	668			30
8	17.2	728	0.277	0.877	30
9	17.3	788			30
10	18.3	1009			30
11	18.9	1131			40
12	19.8	1251	0.358	0.881	40
13	22.4	1472			40
14	26.3	1716	0.319	0.876	52
15	30.5	1982	0.508	0.878	52
16	32.8	2178		0.880	52
17	34.2	2420		0.886	52

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KINETICS OF PROPYLENE POLYMERIZATION WITH HIGHLY STEREOSPECIFIC HETEROGENEOUS CATALYSTS. NOTE V: STUDY OF THE CHAIN TRANSFER PROCESSES WITH ^{14}C LABELLED ALKYLALUMINUM COMPOUNDS

by G. NATTA, I. PASQUON, E. GIACHETTI and G. PAJARO

(Feb. 1958)

[*Chimica e Industria*, **40**, 267 (1958)]

ABSTRACT

It was observed in previous papers that the value of the viscosimetric average molecular weight of isotactic polypropylene obtained with the catalytic system α-$TiCl_3$–$Al(C_2H_5)_3$ decreased when the amount of catalyst was increased particularly when increasing the concentration of $Al(C_2H_5)_3$.

The use of ^{14}C labelled aluminum trialkyl allowed us to point out that in the polymerization of propylene, part of the termination processes of the growth of the polymeric chains, and specifically those depending on the amount of catalyst, is responsible for the introduction into the polymer of ethyl groups, derived from $Al(C_2H_5)_3$.

These processes can be compared with the alkyl exchange processes of organometallic compounds in solution, with the growing of polymeric chains on the active centres of the surface of the catalyst.

The rate of the termination process is of the order of ½ with respect to the concentration of the aluminum alkyl. This dependence had already been explained by the fact that aluminum triethyl exists as a dimer, $Al_2(C_2H_5)_6$, in hydrocarbon solutions and by the fact that $Al(C_2H_5)_3$ (in the monomeric state) participates in the termination process.

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POTENTIOMETRIC ANALYSIS OF ALUMINUM ALKYL COMPOUNDS

by M. Farina, M. Donati and M. Ragazzini

(19 Feb. 1958)

[*Annali Chimica* **48**, 501 (1958)]

ABSTRACT

The analysis of aluminum trialkyls, of aluminum alkyl mono- and dihalides is effected by their formation of complexes with Lewis bases, in particular isoquinoline, and determining their equivalence point by potentiometric methods.

The electrode system consists of two small bars of aluminum, one of which is dipped into the solution to be examined and the other in a hydrocarbon solution of triethyl aluminum, connected to the flask by means of a porous plate.

The titration must be effected under an inert atmosphere (N_2) and in an anhydrous medium. The equivalence point coincides with the highest variation of the titration curve or with the maximum point of the differential curve.

The titration is rapid and accurate in trialkyl aluminums such as: triethyl, tri-isobutyl, tri-hexyl, and in alkyl aluminum halides. Aluminum dialkyl mono-alcoholate is not titratable.

Greater difficulties are met in titrating solutions of aluminum alkyl monohydride, which forms two known complexes with isoquinnoline at a ratio 1:1 and 1:2.

The reproducibility of the analyses by this method may be of the order of 0·3–0·5 percent.

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ISOPHASIC TRANSITIONS OF POLYMERS OF n-ALIPHATIC α-OLEFINS

by G. NATTA, F. DANUSSO and G. MORAGLIO

(8 March 1958)

[*Rend. Accad. Naz. Lincei* (8) **24**, 254 (1958)]

ABSTRACT

The temperature at which a transition takes place and which is characteristic of isotactic and atactic polymers of various olefins of the n-aliphatic series was determined by dilatometric analysis in the temperature range of —60° to —10°C.

A transition with a slight inflection is seen in the dilatometric curve of each polymer. Such a transition, like similar ones which can be observed by dilatometry or by different methods, may or may not be a glass transition in the common sense.

The generical term of "isophasic transition" is introduced, for this behaviour, in antithesis to the term "phase transition".

The value of the isophasic dilatometric transition temperature, determined in this work, for polymers of the same olefin, is practically independent of the molecular weight, of the degree of crystallinity, and of the differences in the stereoisomeric structure. It, however, proves to be connected with only the transformations of the amorphous part of the polymers.

The transition temperature, in the entire homologous series, may be considered always lower than that of polyethylene. In fact, for polyethylene it is —21°C; for polypropylene —35°; polybutene —45°; polypentene —53°; polyhexene —50°; polyoctene —45°; polydecene —41°; polyundecene —37°; polydodecene —36°; polytetradecene

—32°; polyhexadecene —27°; and it varies regularly when one varies the number of carbon atoms in the side chain of the monomeric unit; moreover it assumes a minimum value for polypentene.

For the higher terms such a transition temperature asymptotically tends to reach the value of polyethylene. This can be explained by the fact that, in such a case, the properties are imposed on the polymer by the structural prevalence of the long side chains. On the other hand, these properties in the lower terms are chiefly determined by the main chain.

This two-fold aspect is also found in the structural properties of the crystalline parts of the same polymers. The first terms, in the crystalline state, have a conformation of macromolecules of the helicoidal type, whereas for sufficiently high terms the crystalline structure is imposed by the side chains which assume the zigzag planar configuration of polyethylene.*

* In this work the transition temperatures were determined on polypropylenes and polybutenes derived from some investigations on the properties of stereospecific catalysts which later turned out to be of defective composition. Further measurements on selected samples have shown that the most reliable values are —12° and —37°C for polypropylene and polybutene respectively. The behaviour of the transitions observed here has, therefore, a maximum value corresponding to polypropylene.

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A KINETIC INTERPRETATION OF THE STUDY OF THE FORMATION OF STEREOBLOCK POLYMERS

by G. NATTA

(8 March 1958)

[*Rend. Accad. Naz. Lincei* (8) **24**, 246 (1958)]

ABSTRACT

This is a study of results obtained from polymerization runs of propylene, carried out at temperatures ranging from 40 to 175°C in the presence of catalysts based on $TiCl_4$ or α-$TiCl_3$ and $Al(C_2H_5)_3$, prepared and prestabilized at 175°C before their use.

Both catalytic systems yield polymers whose steric regularity decreases when the polymerization temperature increases.

The steric irregularities observed in the polymeric chains are to be attributed to the inversion phenomena of steric configuration of the monomeric units during their polymerization. A hypothesis is proposed for such inversion phenomena to be connected with the dissociation, followed by a re-association, of the complex which consists of the transition metal and of organometallic compounds, and to which the polymeric growing chain is bound.

A method proposed for establishing the number of inversions in the polymeric chains, is based on the application of Flory's equation for determining the melting temperature of the copolymers.

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STEREOSPECIFIC POLYMERIZATION OF STYRENE. NOTE I: INFORMATION AND PROBLEMS OF CRYSTALLINE POLYSTYRENES

by G. NATTA and F. DANUSSO

(21 March 1958)

[*Chimica e Industria* **40**, 445 (1958)]

ABSTRACT

The possible developments in the field of polymers obtained by the stereospecific polymerization of styrene and, more generally, of aryl substituted vinyl monomers, are critically examined.

Isotactic polymers of styrene have been obtained so far only with the aid of catalysts acting through a co-ordinated anionic mechanism. The "Alfin" catalysts belong also to this class; however, the polystyrenes obtained in the presence of such catalysts have a limited steric order, and cannot be easily crystallized.

Crystallizable polystyrenes having a good degree of crystallinity can be obtained with catalysts containing a transition element, a strongly electropositive element with small ionic radius, and organometallic bonds.

In this case, however, in spite of the high stereospecificity of the catalysts used, the very high degree of crystallinity observed in isotactic polypropylenes and in isotactic polymers of other cyclo-alkyl or aryl-substituted vinyl monomers, has not yet been attained in polystyrenes.

The possible reasons for the limited crystallizability of isotactic polystyrene are examined and discussed as prospective grounds for

a systematic research approach. These reasons may be of a physical nature, kinetic or structural factors concerning crystallization, or of a chemical nature, in a slightly limited regularity of the polymerization.

Only results of systematic research work can be helpful in establishing some more definite conclusions.

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STEREOSPECIFIC POLYMERIZATION OF CONJUGATED DIOLEFINS. NOTE I: SYNTHESIS AND STRUCTURE OF *TRANS*-1,4 POLYDIOLEFINS

by G. NATTA, L. PORRI, P. CORRADINI and D. MORERO

(March 1958)

[*Chimica e Industria* **40**, 362 (1957)]

ABSTRACT

This paper is the first of a series concerned with the synthesis and main properties of the stereoregular polymers of conjugated diolefins, which have been synthesized since 1955 at the Institute of Industrial Chemistry of the Politecnico of Milan.

From butadiene four crystalline polymers were obtained corresponding to the four regular stereoisomers theoretically predictable: namely, *trans*–1,4, *cis*–1,4, isotactic–1,2 and syndiotactic–1,2 polybutadienes. Stereoregular polymers were also obtained from other more common diolefins, such as isoprene and 1,3–pentadiene. The new initiators have also permitted the obtainment both of amorphous polymers consisting of different-typeunits arranged at random, and of low-crystallinity polymers, which show only limited chain portions with a regular structure.

This Note refers to the preparation and properties of *trans*–1,4 polymers of butadiene, isoprene and 1,3–pentadiene. Various heterogeneous catalysts were employed for the preparation of *trans*–1,4 polydiolefins. They were obtained by treating organometallic compounds of metals of the 2nd and 3rd group of the periodic table with halides of the transition metals of 4th, 5th, 6th group, such as $TiCl_4$, violet $TiCl_3$, VCl_3, $VOCl_3$, VCl_4, $CrCl_3$, CrO_2Cl_2. The results described in this Note

concern the $AlEt_3$–VCl_3 catalytic system which is the most stereospecific among those studied by us.

The above-mentioned catalysts yielded raw polymerization products containing predominantly *trans*–1,4 macromolecules, and variable amounts, depending on the catalytic system and on the polymerization conditions, of amorphous polymers that consisted of an irregular addition of *trans*–1,4, *cis*–1,4 and 1,2 units.

The amorphous polymers were isolated from the *trans*–1,4 stereoisomers by boiling ether. In the case of polybutadienes, a complete separation of the amorphous polymers from the crystalline ones (which are left as residue to the ether extraction) was obtained with this method. In the case of polyisoprene and poly–1,3–pentadiene, the separation is not so sharp since ether also dissolves part of the crystalline polymers.

Table 1 shows the results of typical polymerizations of butadiene, carried out in the presence of the $Al(C_2H_5)_3$–VCl_3 catalyst system. (Table 1).

Raw products containing negligible amounts of ether-soluble amorphous fraction were obtained at room temperature; the residue of the ether extraction consisted of polymers having a *trans*–1,4 content of 99–100 per cent. At higher temperature (+60°C), raw polymers having a lower *trans*–1,4 content (about 90 per cent) were obtained; these polymers are nevertheless still considerably crystalline. The Al/V ratio has no appreciable influence in the 1 to 10 range. The polymerization rate is strongly influenced by temperature.

By polymerizing isoprene in the presence of the $Al(C_2H_5)_3$–VCl_3 system, polymers were obtained which consisted almost exclusively of *trans*–1,4 units, and which showed by X-ray examination the characteristic spectrum of natural guttapercha. Also, 1,3–pentadiene yielded polymers showing *trans* internal double bonds exclusively. However, in the case of this monomer, 1,2 units could also show *trans* internal double bonds, present in the side chain; therefore I.R. analysis alone is not suitable to clarify the type of addition in this case. However X-ray analysis and in particular the value of the identity period (4·85 Å), unambiguously show that the polymer has a *trans*–1,4 structure.

Figure 1 shows the I. R. spectra of *trans*–1,4 polymers of butadiene, isoprene, pentadiene. The spectra of the polymers in the solid state show, in comparison with those of the molten polymers, new bands that are characteristic of the structural regularity of the chains. The

TABLE 1. POLYMERIZATION OF BUTADIENE AT ROOM TEMPERATURE WITH THE AID OF CATALYSTS OBTAINED FROM TRIETHYL ALUMINUM AND VCl_3. SOLVENT (N-HEPTANE) cc. 100; VCl_3 g. 0.5; BUTADIENE g. 50

R (1)	*Polymerization conditions*		*Polymer obtained g*	*I.R. analysis*			*Crystallinity by X-rays % (2)*	*Fractionation*		
	temp. °C	*time hr*		*trans-1,4 %*	*cis-1,4 %*	*1,2 %*		*ether extract % (3)*	*benzene extract % (4)*	*residue to the extraction % (5)*
2	14	30	11·5	99		1	49·5	1·7	24·9	73·4
2	14	45	21	99		1	49	1·5	20	78·5
2	25	10	8·3	96·5	1	2·5	51·5	9·5	30	60·7
2	25	13	13·2	97·5		2·5	51	7·4	24·2	68·4
2	25	15	17	99		1	49·5	4·3	18·25	77·45
2	25	19	26·8	99		1	49	1·8	22·3	75·9
10	25	15	23·7	99		1	50	1·7	10	88·3

(1) Molar ratio of trialkyl aluminum to VCl_3

(2) After 1 hr of annealing crystallinity rises to 70–75%

(3) Oily — I.R. analysis { *trans*-1,4 60–70%; *cis*-1,4 3– 8%; 1,2 22–37%

(4) I.R. analysis { *trans*-1,4 > 99%; 1,2 < 1%

[η] in toluene at 30°C, 2·5–3 cm^3/g

(5) I.R. analysis { *trans*-1,4 > 99%; 1,2 < 1%

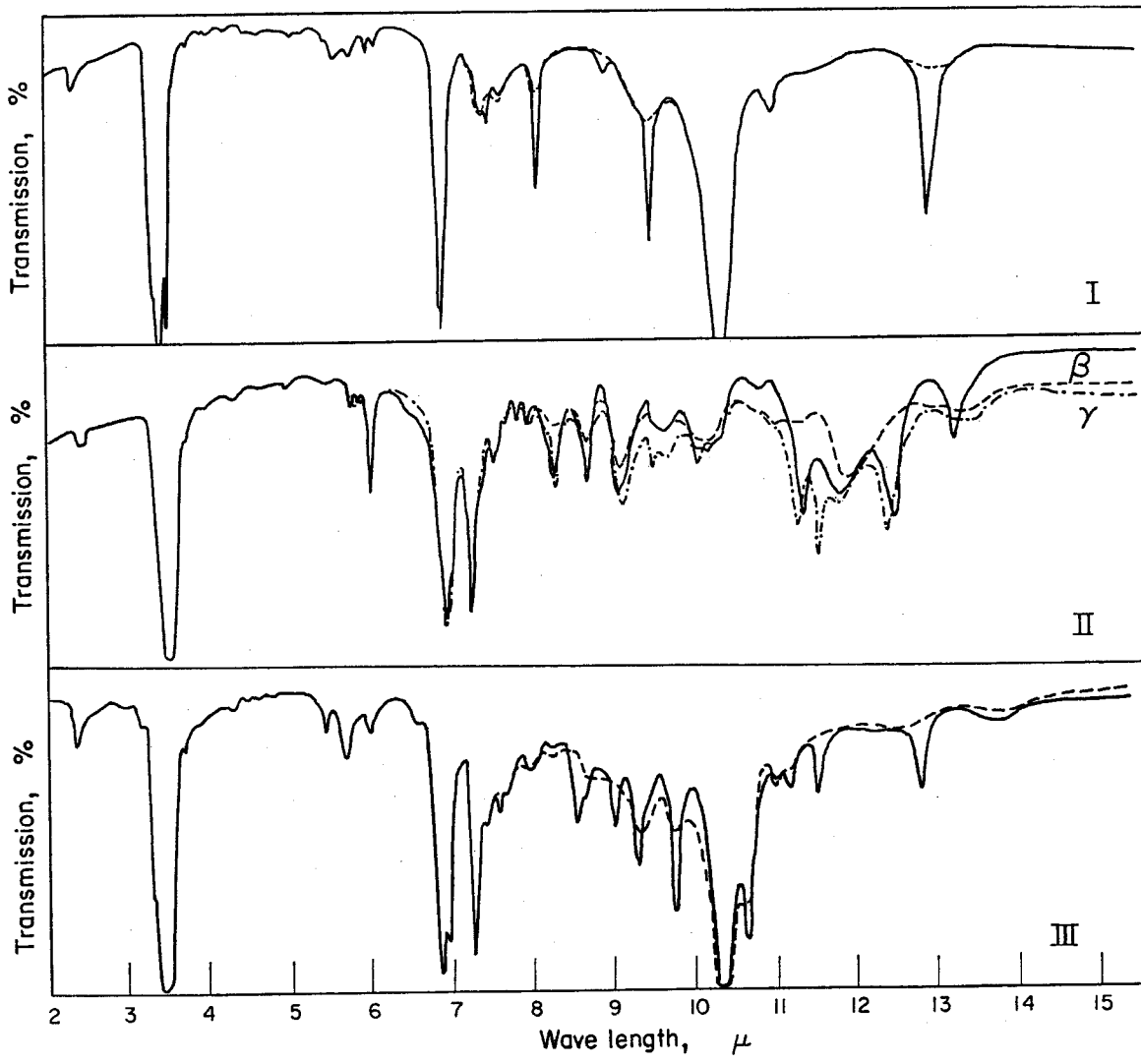


FIG. I. I. R. spectra of *trans*-1,4 polymers obtained with the aid of Al $(C_2H_5)_3$—VCl_3 catalyst.

I. Polybutadiene
——————— in the solid state
. . . . . in solution

II. Polyisoprene
——————— in the solid state, β modification
— . — . — . — in the solid state, γ modification
. . . . . in solution

III. Polypentadiene
——————— in the solid state
. . . . . in solution

spectra of natural guttapercha and of *trans*–1,4 polyisoprene obtained by synthesis are practically identical.

For the quantitative analyses of polybutadienes, the bands at 10·35 μ and 11μ were used, by assuming the values of 10×10^4 mol^{-1} cm^2 and 12×10^4 mol^{-1} cm^2 for the extinction coefficients. The percentage of *cis*–1,4 units was calculated by difference.

The X-ray spectra of *trans*–1,4 polybutadiene, polyisoprene and polypentadiene registered with a Geiger counter are reported in Figs. 2, 3, 4 respectively.

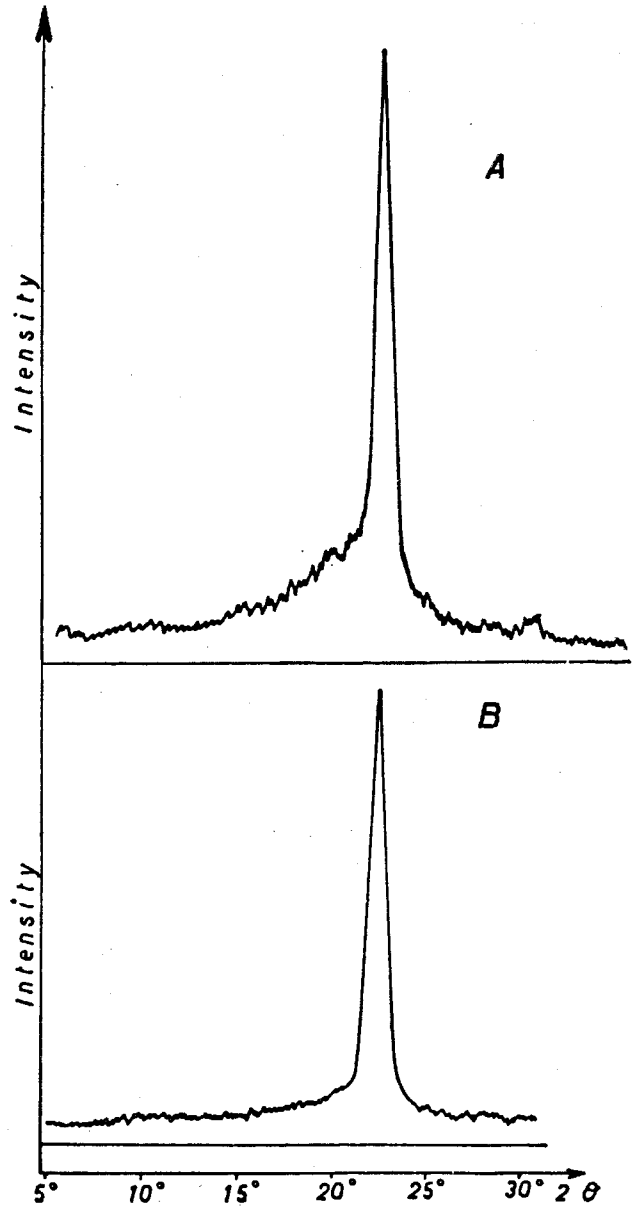


FIG. 2. X-ray spectrum (Cu$K\alpha$) registered with a Geiger counter of a *trans*-1,4 polybutadiene obtained in the presence of Al $(C_2H_5)_3$—VCl_3 catalyst, at 25°C. A, before annealing; B, after 1 hr of annealing at 110°C.

TABLE 2. SOME PHYSICAL PROPERTIES OF TRANS - 1,4 POLYMERS.

Polymer	*Relative Density*		*Identity Period* Å	*Melting point* °C
	exp.	*calc.*		
Polybutadiene	0.97	1.02	4.9	145*
Polyisoprene	0.95	1.04	8.75α 4.77β 9.2γ	64
Polypentadiene	0.92	0.98	4.82	~92

* A first order transition, with a change of crystalline phase, was observed by X-rays at about 65°C. The identity period of the new phase is 4.7 Å, while the calculated relative density, at 80°C, is 0.93.

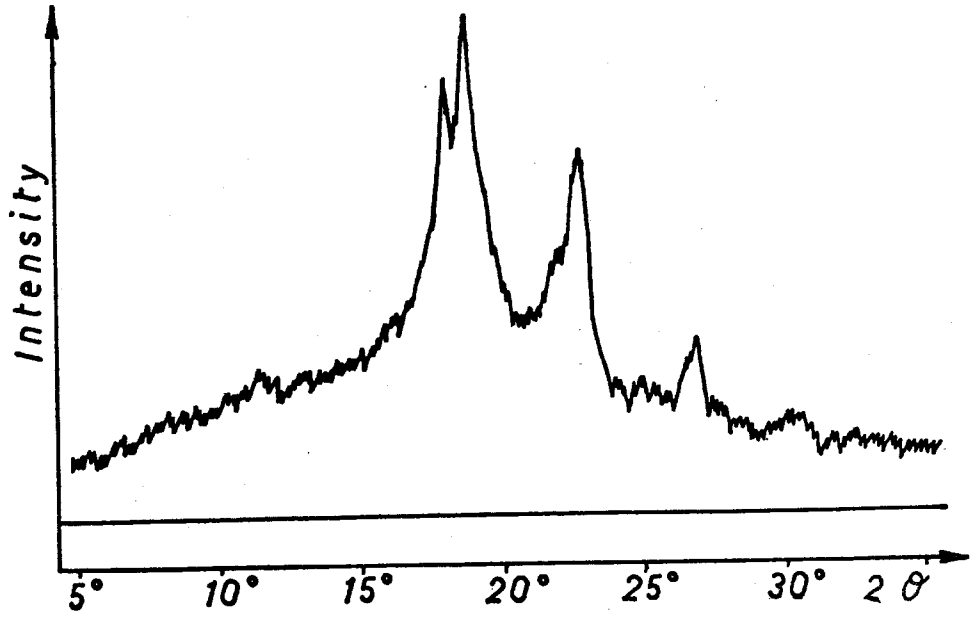


FIG. 3. X-ray spectrum (Cu$K\alpha$) registered with a Geiger counter of a *trans*-1,4 polyisoprene obtained in the presence of Al $(C_2H_5)_3$—VCl_3 as catalyst, at 25°C.

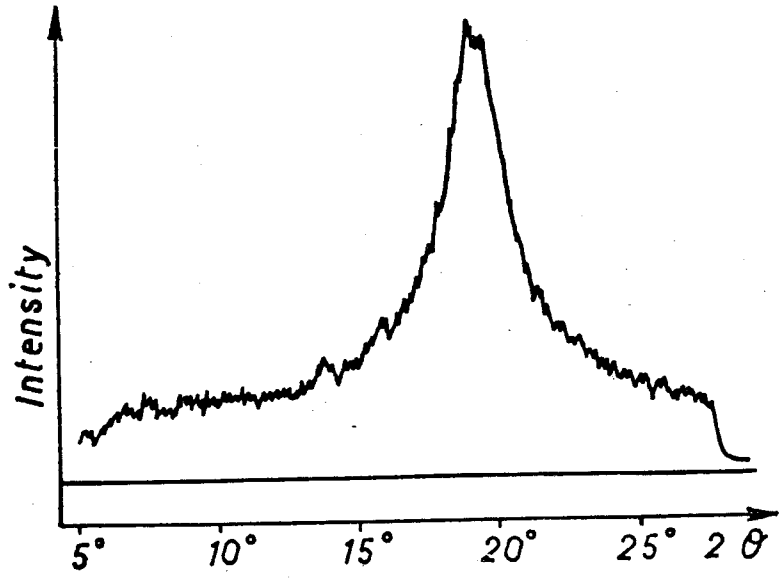


FIG. 4. X-ray spectrum (Cu$K\alpha$) registered with a Geiger counter of *trans*-1,4 polypentadiene (residue to the ether extraction) obtained with the aid of Al $(C_2H_5)_3$—VCl_3, as catalyst, at 25°C.

Raw polybutadienes, as well as the residues of the ether extraction show a crystallinity of about 50 per cent; after 1–2 hr of annealing at 100–110°C, crystallinity increases to 70–75 per cent.

Some properties of *trans*–1,4 polymers of butadiene, isoprene, 1,3–pentadiene obtained in the presence of the $Al(C_2H_5)_3$–VCl_3 system are reported in Table 2.

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STEREOSPECIFIC POLYMERIZATION OF STYRENE. NOTE II: FEATURES OF THE CATALYTIC SYSTEM $TiCl_4$–$Al(C_2H_5)_3$

by F. DANUSSO and D. SIANESI

(April 1958)

[*Chimica e Industria* **40**, 450 (1958)]

ABSTRACT

In this paper, the behaviour of catalysts obtained by the reaction of titanium tetrachloride and triethylaluminum, with regard to the polymerization of styrene, is examined.

The mode of preparation of the catalyst has an important and characteristic influence on the stereoisomeric composition and on the quantity of polymer obtained. In particular, the order in which reagents are introduced seems to be the determinant factor for both activity and stereospecificity of the type of catalysts obtained.

The dependence of activity and selectivity of the catalysts on the ratio between the quantity of the two catalytic reagents is studied in some detail. For the preparation at 40–70°C of pure isotactic polymer, a molar ratio $Al(C_2H_5)_3/TiCl_4$ higher than 2 is necessary. An optimum value is found for the ratio slightly higher than 2 depending on the purity of the catalytic reagents. For lower molar ratio values, large quantities of atactic polymer are produced, due to an acidic catalysis, which is similar, but not identical, to that of pure $TiCl_4$. By raising the temperature, atactic polymer is produced even at ratio values in which isotactic polystyrene is normally obtained, and the activity of the stereospecific catalyst is gradually reduced.

There are described a simple experimental procedure and apparatus for the preparation of the catalyst and subsequent polymerization in the same reaction vessel, in the absence of moisture and under an atmosphere of nitrogen.

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CONFORMATION OF LINEAR CHAINS AND THEIR MODE OF PACKING IN THE CRYSTAL STATE*

by GIULIO NATTA and PAOLO CORRADINI

[15 April 1958]

[*Journal of Polymer Science* **39**, 29 (1959)]

SYNOPSIS

Some general rules regarding the conformation and mode of packing of macromolecular chains in crystals are illustrated. The monomeric units occupy equivalent positions in regard to the axis of the chain. It follows that crystallizable polymers must have a type of regularity which will enable them to assume the helix- or glide-plane conformation. Energy considerations lead to other rules regarding the conformation and the mode of packing of the chains. Iso-sterism phenomena leading to statistical substitution of chains in the lattice and to the existence of planes, along which the macromolecules pack preferentially, are considered. The structures of isotactic and syndiotactic polymers, and of all four stereoisomeric polybutadienes are discussed.

The study of the crystal structure of a number of new crystalline polymers prepared for the first time in our Institute[1] allowed us to confirm some known general principles and to establish new ones concerning the shape and mode of packing of macromolecules in crystals.[2]

The importance of stereoisomerism as a determining factor of the ability of polymers to crystallize has long been recognized. Before the discovery of stereospecific polymerization processes, only a relatively small number of crystalline synthetic hydrocarbon polymers were known. Those obtained by polyaddition were generally derived from monomers such as ethylene or some vinylidene monomers, which contain at least two planes of symmetry in the molecule.

All previously known synthetic polymers of α-olefins and diolefins

*Paper presented by G. Natta at the 133rd Meeting of the American Chemical Society, San Francisco, April 15, 1958.

were amorphous. On the contrary, the structure of the molecules of most natural polymers corresponds to an architectural model showing a regular steric arrangement.

As the definition of crystal implies a three-dimensional order, a linear polymer, in order to be crystallizable, must at least show a regularity in the succession of its monomeric units. In linear crystalline polymers, in fact, the axis of the macromolecule has to be parallel to a single crystallographic axis of the crystal.

It is possible (as a simplified hypothesis) to assume that all monomeric units in a crystal occupy geometrically equivalent positions with respect to each chain axis (as this has been observed hitherto in all known structures of crystalline homopolymers). We shall refer hereinafter to this postulate as the *equivalence postulate*. It will be shown how, from the equivalence postulate, it is possible to determine the conditions which the configurations of the chains of polyhydrocarbons (e.g. polymers of α-olefins and diolefins) must satisfy in order that the corresponding polymers be crystallizable.

Let us consider a monomeric unit and define its conformation with respect to a particular axis by the coordinates of the atoms along the chain plus those of the two atoms defining the direction of its terminal bonds. It is useful to refer the coordinates of the atoms to a cylindrical coordinate system (ϱ, φ, z), with the z axis coincident with the chain axis and the origin so chosen that (say) $z_0 = 0$, $\varphi_0 = 0$. In this way, we may define intrinsic coordinates for all the monomeric units along the chain, choosing for each unit a particular coordinate system, always maintaining, however, z in the same position and direction (the position and direction of the chain axis), measuring the φ angles always (say) clockwise and taking $z_0 = 0$ and $\varphi_0 = 0$ for each monomeric unit.

Monomeric units equivalent with respect to the axis are, then, merely those of which the ith atoms have coordinates

$$(\varrho_i, \varphi_i, z_i)_{i=0}^{i=n+1},\ (\varrho_i, \varphi_i, -z_i)_{i=0}^{i=n+1},\ (\varrho_i, -\varphi_i, -z_i)_{i=0}^{i=n+1},\ \text{or}\ (\varrho_i, -\varphi_i, z_i)_{i=0}^{i=n}$$

The equivalence postulate assures us that these are the only possible building stones of a regular succession along the chain axis.

Equivalent monomeric units, differing only in the sign of *one* of their intrinsic coordinates φ_i and z_i, may be brought to coincide only by reflection and are thence enantiomorphous. Equivalent monomeric units differing in the sign of *both* their intrinsic coordinate φ_i and z_i are isomorphous, as they may be made to coincide by rotation around a straight line perpendicular to the axis.

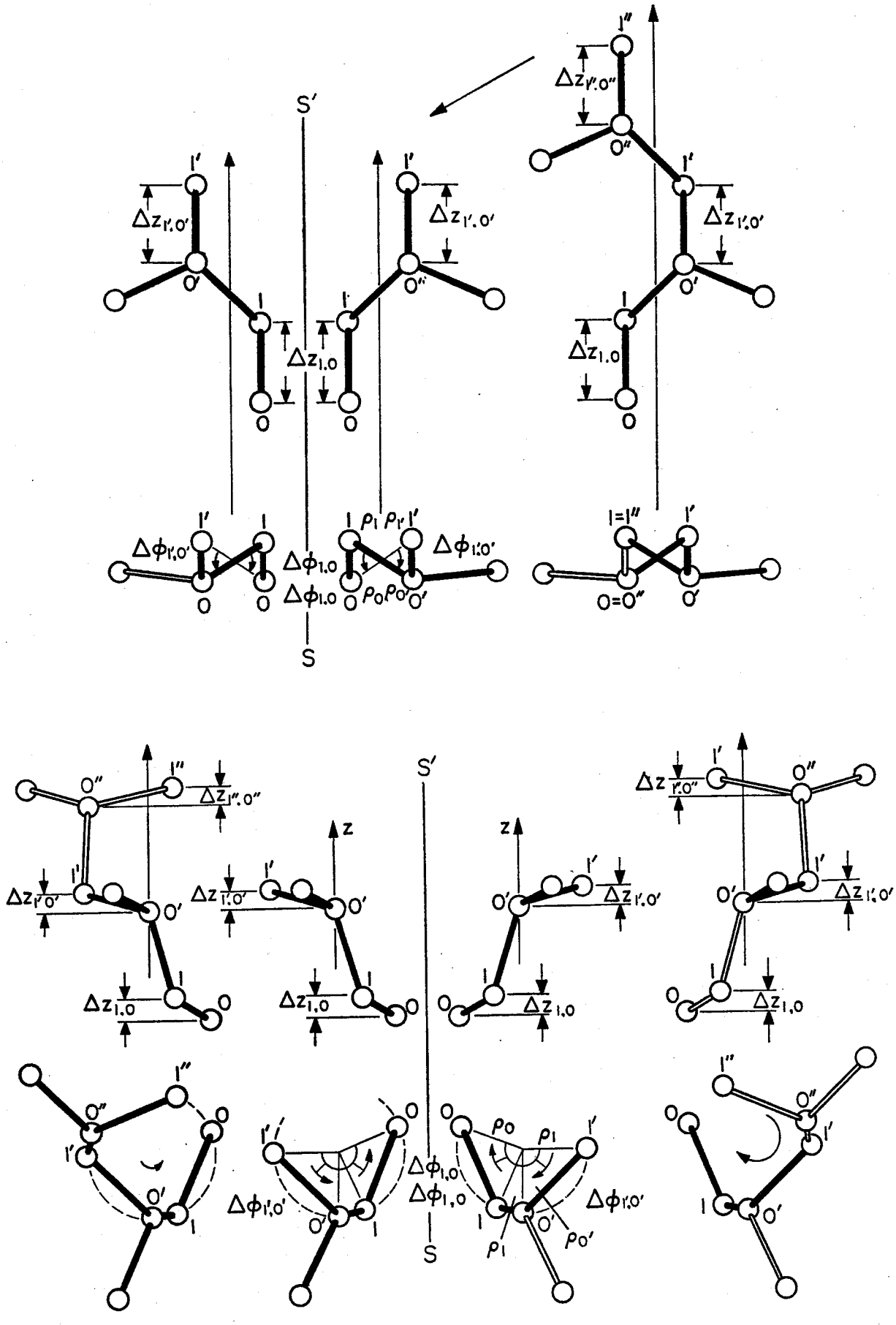


FIG. 1. Schematic diagram showing possible types of regular successions of isoclined monomeric units along an axis: (above) glide-plane succession ($\Delta\varphi_{1,0}=-\Delta\varphi_{1',0'}$) (below) helix-type succession ($\Delta\varphi_{1,0}=\Delta\varphi_{1',0'}$)

We shall define as "isoclined" those equivalent monomeric units having the same z_i coordinates and as "anticlined" those equivalent monomeric units having opposite z_i coordinates. Thence, if $(\varrho_i, \varphi_i, z_i)_{i=0}^{i=n}$ are the coordinates of a monomeric unit, we shall refer to another monomeric unit with intrinsic coordinates $(\varrho_i, \varphi_i, z_i)_{i=0}^{i=n}$ as an isomorphous isoclined unit; one with coordinates $(\varrho_i, -\varphi_i, z_i)_{i=0}^{i=n}$, as an enantiomorphous isoclined unit; one with coordinates $(\varrho_i, -\varphi_i, -z_i)_{i=0}^{i=n}$, as an isomorphous anticlined unit; one with coordinates $(\varrho_i, \varphi_i, -z_i)_{i=0}^{i=n}$, as an enantiomorphous anticlined unit.

From the equivalence postulate the following is readily seen to be true. (*a*) To permit repetition along the z axis of equivalent isoclined units (Fig. 1), the two terminal bonds must be equivalent with respect to this axis; then within the same monomeric unit,

$$\varrho_0 = \varrho_0' \tag{1}$$

$$\varrho_1 = \varrho_1' \tag{2}$$

$$z_1 - z_0 = z_1' - z_0' \tag{3}$$

and

$$\varphi_1 - \varphi_0 = \pm(\varphi_1' - \varphi_0') \tag{3'}$$

Clearly, when $\varphi_1 - \varphi_0 = \varphi_1' - \varphi_0'$, the monomeric unit involved may be bound only to an equivalent isomorphous isoclined unit, and when $\varphi_1 - \varphi_0 = \varphi_0' - \varphi_1'$, the monomer unit involved may be bound only to an enantiomorphous isoclined unit, if the monomeric units are to be equivalent with regard to the chosen axis.

From the statements under (*a*), several important conclusions follow.

(*b*) A regular succession of isomorphous isoclined units must necessarily follow an n/p-fold helix containing $n/p = 2\pi/(\varphi_0' - \varphi_0)$ monomeric units per pitch, n being the number of monomeric units and p the number of pitches contained within the identity period (helix-type succession). The ratio n/p is a rational number, and, for a particular case, it can assume the value 1 (e.g. simple repetition). An analogous hypothesis has been given by Pauling for proteins.

(*c*) A regular succession of alternatively enantiomorphous isoclined units must necessarily take place along a glide-plane with translation parallel to the axis (glide-plane-type succession).

(*d*) A regular succession of isoclined equivalent units can assume only the forms of either a helix or a glide plane succession. All head-to-tail polymers in which the two possible chain directions are intrinsically nonequivalent (i.e. a polyamide) are subjected to this condition. In

particular, a polyamide containing asymmetric carbon atoms must necessarily have a helix-type structure.

(*e*) Repetition of anticlined units (following arguments similar to those given above) may occur along helices associated with twofold axes perpendicular to z or through a translation along z associated with symmetry planes or centers.

A condition to be fulfilled by a polymer, in turn, in order to be crystallizable is that its monomeric units must have configurations which enable them to occupy equivalent positions along an axis.

On this basis we can now find which types of stereoisomers of vinyl and diene polymers may crystallize.

In the sense of what is stated above, only two types of regular sequences, intrinsically different, may be expected for vinyl head-to-tail crystallizable polymers. Isotactic vinyl polymers are those capable *per se* of assuming a helix-type crystalline structure. Syndiotactic vinyl polymers are those capable *per se* of assuming a glide-plane structure in the crystalline state. As the two possible chain directions are intrinsically equivalent in head-to-tail vinyl polymers, their chain may also be built up in the crystal state by a succession of anticlined units. For example, in theory a syndiotactic polymer may also achieve a helical chain structure associated with twofold axes perpendicular to z. Isotactic and syndiotactic polymers may be considered also as the *cis* and *trans* geometrical stereoisomers, respectively, of the same polyvinyl chain of infinite length. Analogous reasoning leads to various possibilities for regular, crystallizable, diene polymers. Figure 1 of paper 19, shows isotactic and syndiotactic main chains lying ideally in a plane.

We should like now to discuss briefly two more useful postulates related to the shape and mode of packing of macromolecules in crystals.

Provided the equivalence is satisfied, the conformation of the chain in a crystal may be assumed to approach the conformation of minimum potential energy for an isolated chain oriented along an axis. We shall refer to this as the *minimum energy postulate*.[3] Lateral packing effects (between neighboring chains) are also important in determining the conformation of the chain, but these generally play a less important role compared to the packing effects inside the chain. The following rules should generally be satisfied in the conformation of the polymer chain.

1. Constancy of bond lengths.

2. Coplanarity of certain groups of atoms (for instance the amide group).

3. Constancy of bond angles.

4. Staggered single bonds.

5. Van der Waals distances between non-bonded atoms within the chain of such a magnitude as to permit unstrained packing. .

When the rules outlined above cannot be satisfied simultaneously, we may, in general, expect:

1. Deformation of bond angles to values exceeding the normal values (e.g., more than 110° for the C—C—C angle).

2. Slight deviations from the principle of staggered bonds.

3. Distances between certain atoms of the chain which are slightly less than normal van der Waals distances.

All the above-mentioned deformations take place in general, but to different degrees for various types of chains, so that (according to the minimum energy postulate) a minimum potential energy for the isolated chain is approached. In actual structures, however, the necessity for filling space uniformly may slightly modify the form ; for instance, in the case of a helix, the form corresponding to the minimum energy postulate for the free chain can be modified, giving smaller n and p values or slightly different n/p ratios. This follows from the fact that, in a crystal, the chains arrange themselves so that they are parallel to each other and spaced at an intermolecular distance so that they fill as much as possible any gap between them similar to that found in low molecular weight compounds. With this limitation, as many elements of symmetry of the isolated chain as possible are maintained in the lattice, and therefore, equivalent atoms of different monomeric units along an axis tend to assume equivalent positions with respect to the atoms of neighboring chains. The role of this postulate, which we call the *packing postulate,* will now be discussed.

Sometimes not all statements of the packing postulate can be satisfied simultaneously; in such a case, in a manner analogous to that discussed for the minimum energy postulate, a compromise is achieved in actual structures for filling space uniformly. In many cases both of the pair of anticlined molecules ("up" and "down" molecules) are present in the unit cell of the crystal of a head-to-tail polymer. Moreover, when a given monomeric unit may give rise to equivalent right- or left-handed helices (for example, in the case of a monomer containing no asymmetric carbon atoms, such as propylene), both are generally represented in the crystal lattice.

In isotactic polymers containing helices of the order of $n>2$, each right-handed helix tends to face a left-handed helix. Whenever only one type of helix, either left-handed or right-handed, is possible, formation of a super helix of the chain may occur to provide a better filling of the space; this is the case with proteins.

Frequently, nearly isosteric equivalent chains, i.e., chains with a similar steric bulkiness (such as enantiomorphous isoclined chains, isomorphous anticlined chains, or enantiomorphous anticlined chains) may be substituted for each other in the same lattice site. This phenomenon was observed for the first time by Nyburg[4] in natural rubber and was observed by us in some isotactic polymers.[5]

In packing, the polymer molecules generally tend to maintain, at least partially, the symmetry of the chain. In the structure of polymers made up of chains of the glide-plane type, for instance, the glide plane is usually maintained in the lattice. This fact occurs in natural rubber, polyvinyl chloride, 1,2- (syndiotactic) and *cis*-1,4-polybutadiene, and in rubber hydrochloride.[6]

Another interesting feature of some crystalline polymers is that it is possible to recognize in their structure layers of molecules along planes, containing the fiber axis and generally the smallest equatorial translation, such that the crystal may be imagined to be formed by the parallel or antiparallel association of them. In many polymers which we have examined, it was observed that the two translations determining such planes are only very slightly affected by thermal movements. From the results of the study of some types of spherulites, it appears likely that the polymer crystals grow best along the equatorial translation contained in the said above planes (principal planes) (which are parallel to the spherulite radius).[7]

Let us now see how these principles may justify the experimentally found structures of some new polymers.

ISOTACTIC POLYMERS[8]

Isotactic polymers are the *cis* stereoisomers of vinyl head-to-tail polymers as we have shown above. The bulky dimensions of lateral groups do not permit these polymers to assume a planar chain conformation. A planar structure is, indeed, impossible. For instance, in the case of polypropylene, a planar structure would result in a distance of only 2·5 Å between the nuclei of the two carbon atoms of successive methyl groups, which is very unlikely, because certain hydrogen atoms

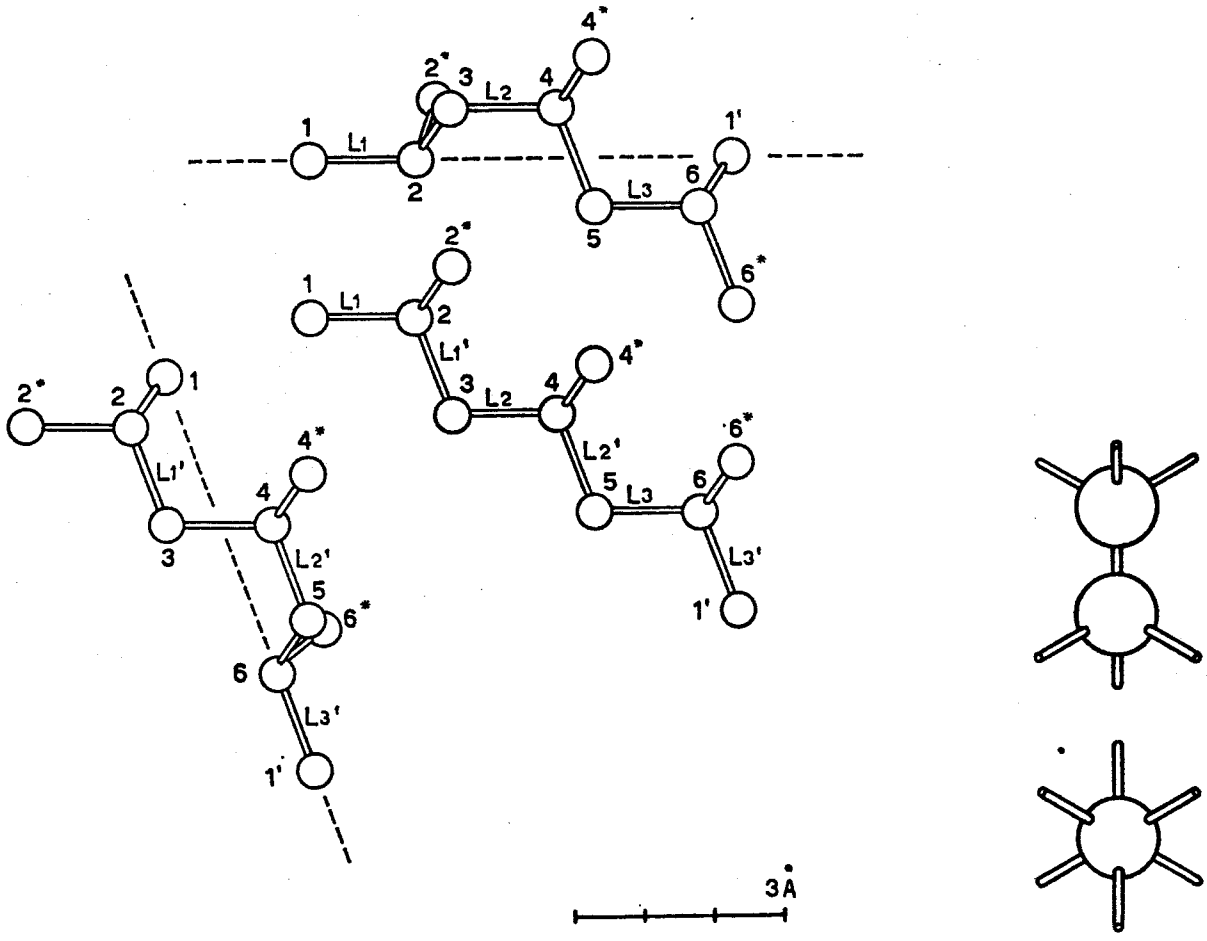


FIG. 2. Genesis of right- and left-handed isotactic helices from a planar chain.

of the methyl groups would be, as a result, too near to each other, and this situation conflicts with the requirements of the minimum energy postulate. (The nature of the strain may be easily understood when we consider that the large resonance energy of linear crystalline polyacetylene, which, according to unpublished data, has a planar structure, is destroyed in polyhexyne, whose chain structure is nonplanar; the net loss, according to our calculation, is about 10 kcal. per monomeric unit, something like what happens in the case of benzene and cyclooctatetraene).

A suitable accomodation of the methyl groups according to the equivalence postulate and the principle of staggered bonds, may be achieved in a helical structure only when the successive monomeric units are arranged on a threefold helix.

This structure may be easily derived from the planar one shown in Fig. 2, by clockwise or counterclockwise rotations of 120° around the 1–2, 3–4, 5–6 bonds or around the 2–3, 4–5, 6–1′ bonds, thus generating a left- or right-handed helix. The separation of the methyl groups

achieved in this way (>4 Å), assumes a value comparable with the van der Waals distance, and there is no conflict with the principle of staggered bonds. As the planar configuration is very unlikely from the point of view of thermodynamics, no interchange of enantiomorphous helices appears to be possible, at least at low temperatures, and we believe that left- and right-handed helices can be considered to be true optical stereoisomers. Optical activity is not observed because of the presence of equal amounts of the two forms.

When built up with normal bond lengths (1·54 Å.) and angles (109° 30′), the isotactic threefold helix should have an identity period of 6·2 Å. Actually, the periods are 6·5–6·65 Å. A slight increase in the C—C—C angles along the chain appears to be the reason for this, as this arrangement permits a better accomodation of the hydrogen atoms of the chain at separations of the order of van der Waals distances. The bulkiness of side groups, and more precisely, the steric hindrance of side groups near the chain axis, is the reason for the four-fold helix structure of 3-methyl-substituted polyolefins in the crystalline state and the 3,5-fold helix conformation of 4-methyl substituted polyolefins (Fig. 6 of paper 24). The principle of staggered bonds no longer holds strictly, but valence angles along the chain tend to approach normal values once again, so that there should be only very low differences in energy between a threefold or fourfold helix. Indeed, polybutene-1 has been observed to crystallize in both forms, the fourfold helix, however, being the more unstable. This form is the first to appear on crystallization from the melt or from a solution. Therefore, we can deduce that, in the liquid state, there is sufficient freedom to permit rotation around single bonds in the chain at a low energy level; this leads to a slight despiralization of the helix.

It is interesting to note that crystals with the fourfold helix of polybutene-1 are transformed immediately to crystals with threefold helix by drawing, and that this transformation takes place much more slowly on standing.

Chains slightly different in form from those discussed above may also appear in other isotactic polymers and have been found, for example, in substituted polystyrenes; their stability is attributed to better packing of lateral groups within the chain and between different chains.

The complete determination of the crystal structure of polypropylene and polybutene-1 permits at this point a discussion of the mode of packing of the chains of these polymers in crystals.

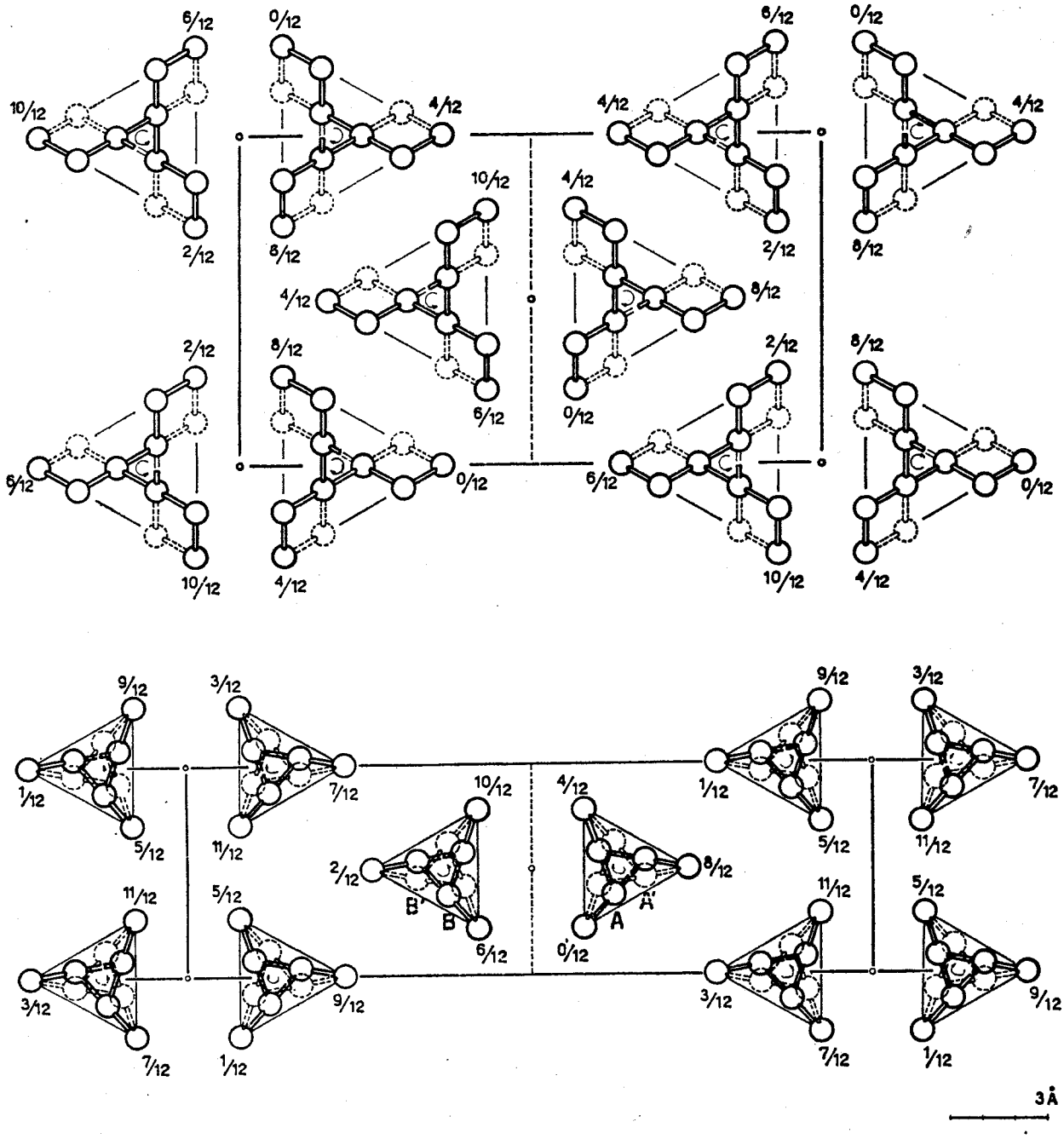


FIG. 3. Comparison between the crystal structures of polypropylene and polybutene-1 projected along the fiber axis.

According to the requirements just explained, we found that in all these polymers enantiomorphous chains face each other in pairs. Close packing is obtained through the operation of a glide plane with translation parallel to the fiber axis.

The anticlined isomorphous chains of these two polymers are nearly isosteric with respect to the bulkiness because of the lateral groups. As the intermolecular contacts, that is, the closest approaches of the chains are between these lateral groups, anticlined isomorphous chains

can, in theory, replace each other in the same lattice site, and, at least partly, they do it.

Polybutene-1 crystals are able to maintain the complete symmetry of the chain, so that three glide planes at angles of 120° to each other and related by a threefold helix are easily recognizable in the rhombohedral structure of this polymer.

Assumption of a similar structure also for polypropylene would yield a too loose mode of packing. The glide plane through which two enantiomorphous facing chains are related is, in this case, a principal plane. Evidence that the *a–c* plane can be considered a principal plane in polypropylene is found in the close packing realized along this plane of the groups of two enantiomorphous symmetry-related chains (Fig. 3). This is in accordance with the shortness of the *a*-axis, its orientation parallel to the spherulite radii and its very low thermal expansion in comparison with that taking place along the *b* axis.

We believe that the main features of the structure of other isotactic polymers may be explained following these lines.

SYNDIOTACTIC POLYMERS[9]

Syndiotactic polymers may be defined as the *trans* stereoisomers of vinyl head-to-tail polymers. Their chain structure should be, according to the equivalence postulate, of the glide-plane type, and hence repetition should be achieved along the fiber axis every two (in Greek *σύν δύο*) monomeric units or of the helix type associated with twofold axes. Two polymers are now known to possess a syndiotactic chain structure, i.e., polyvinyl chloride and one of the two crystalline stereoisomers found for 1,2-polybutadiene.

The bulkiness of the side groups does not hinder a planar or nearly planar conformation of the chains as was the case for isotactic polymers. A slight deviation from a completely zigzag planar structure of the chain has been supposed, but not proved, to exist in polybutadiene as a result of steric repulsion between successive lateral vinyl groups; the perpendicular orientation of these side groups with respect to the chain axis obeys the principle of staggered bonds (Fig. 4). In every case it is easily seen that no distinction is possible between "up" and "down" molecules, and therefore only one type of chain must be accommodated in the lattice.

The glide-plane is maintained in the three-dimensional structure of these polymers, so that the closest packing of these molecules occurs in

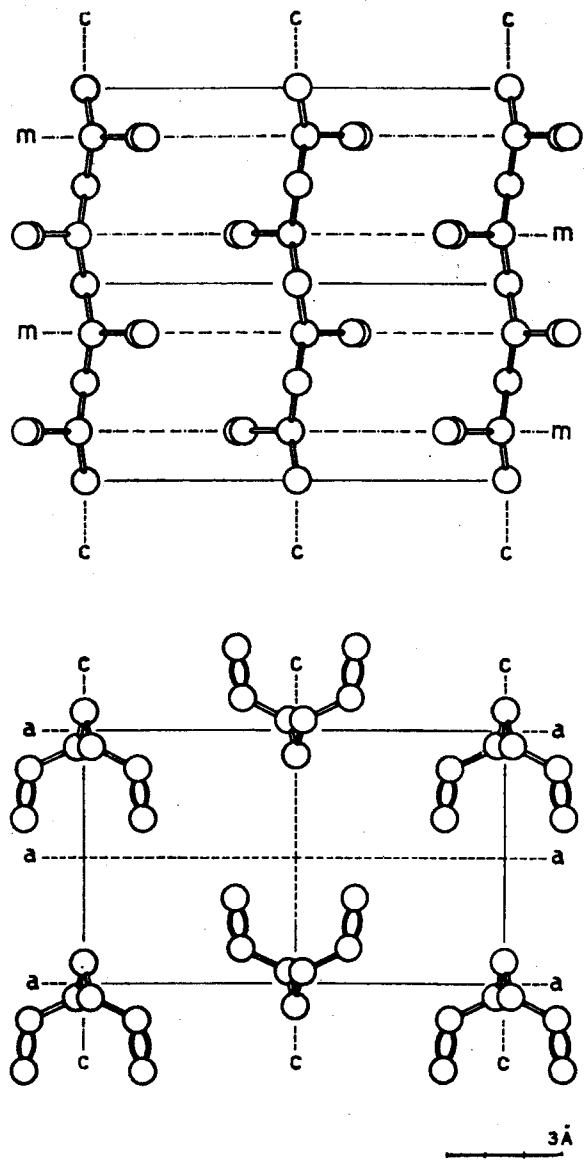


FIG. 4. Crystal structure of syndiotactic 1,2-polybutadiene.

layers along this plane; different layers pack among themselves in an antiparallel way.

Thermal expansion in syndiotactic 1,2-polybutadiene is almost completely in a direction perpendicular to the glide plane *c*, a phenomenon which is believed to be associated with the existence of a principal plane of packing.

CRYSTALLINE 1,4-POLYDIENES[10]

Under the headings of isotactic and syndiotactic polymers we have dealt with the known structures of stereoisomeric 1,2-polydienes. In this section we shall deal with the known structures of crystalline

1,4-polydienes. The synthesis of all four stereoisomeric crystalline polybutadienes effected in the Institute of Industrial Chemistry of the Polytechnic of Milan, and the study of their structure have enabled us to give a full idea of stereoisomeric phenomena in the field of polydienes.

Natural rubber is a regular head-to-tail polymer built up of *cis*-1,4-isoprene units. Its chain structure may be expected to be a glide-plane or a helix-type succession only. However, on the basis of the equivalence postulate only, it is not possible to establish which of the two forms will actually be assumed by the macromolecule on crystallization, as neither can be correlated with intrinsic differences in the configuration of the chain. This may be easily seen on considering that, by permitted rotations around single bonds, the completely planar structure (I), corresponding to a set of equal units (which may be considered a one-fold helix) may be transformed to the planar glide-plane type structure (II) (Fig. 5).

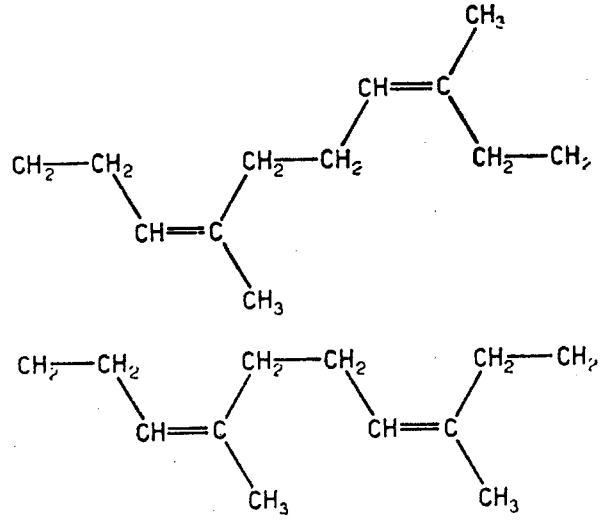


FIG. 5. Possible structures of a polyisoprene chain considered stretched in a plane: (above) II; (below) I.

Actually, a glide-plane, nonplanar structure is found for the chain of crystalline *cis*-1,4-polyisoprene. Indeed, we should expect on the basis of the minimum energy postulate that: (1) the five atoms of each monomeric unit should be in a plane; (2) in accordance with the principle of staggered bonds, the direction of the CH_2—CH_2 bond should take each of the three positions outlined in Figure 6, positions 3 and 3′ having to be discarded because of too short van der Waals contacts; (3) the directions of the two CH_2—CH_2 bonds on the two sides of the

isoprene unit should be in opposite and parallel direction; i.e., the enantiomorphous conformations 1,1′-and 2,2′ are the most likely to be realized; (4) repetition of a monomeric unit with such a conformation, owing to the fact that $\Delta_{\varphi 1,0} = \pi = \Delta_{\varphi 1',0'} = -\Delta_{\varphi 1',0'}$ may be achieved in a helix type or a glide plane type succession. The first possibility may be discarded because of unlikely van der Waals contacts, and therefore only the glide plane type conformation may be admitted.

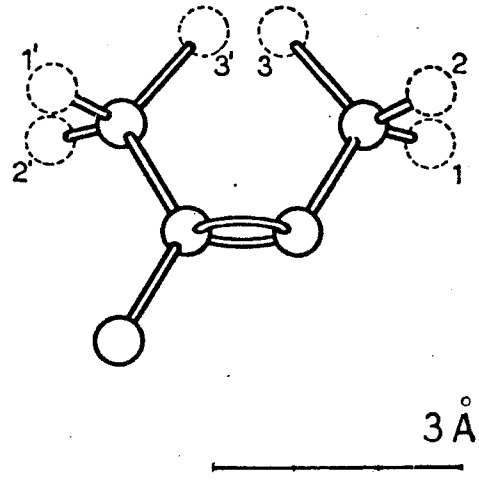


FIG. 6. Possible conformations of an isoprene monomeric unit.

The glide plane is maintained in the lattice so that close packing of molecules is expected along this plane; also, alternatively anticlined molecules should be represented along this plane.

As contacts lateral to the so realized principal plane are due only to methyl groups, we find that, in the actual structure, successive parallel or antiparallel principal planes are able to pack themselves at random (Fig. 7). It is possible to see from Figure 7 that a layer of molecules such as ABAB can be followed statistically by a layer such as CDCD or C′D′C′D′.

A great similarity of structure is to be expected between *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene, and actually a similar conformation of the chain is found; in both of these, enantiomorphous monomeric units repeat along a glide-plane. No further distinction, however, is possible in *cis*-1,4-polybutadiene, between "up" and "down" molecules as is the case with *cis*-1,4-polyisoprene; also, an identity period is found which is slightly longer than the one foreseeable on the basis of the principle of staggered bonds. This fact is probably due to repulsions between hydrogen atoms of two CH_2 groups in opposite positions with respect to the double bond, which tend to lengthen

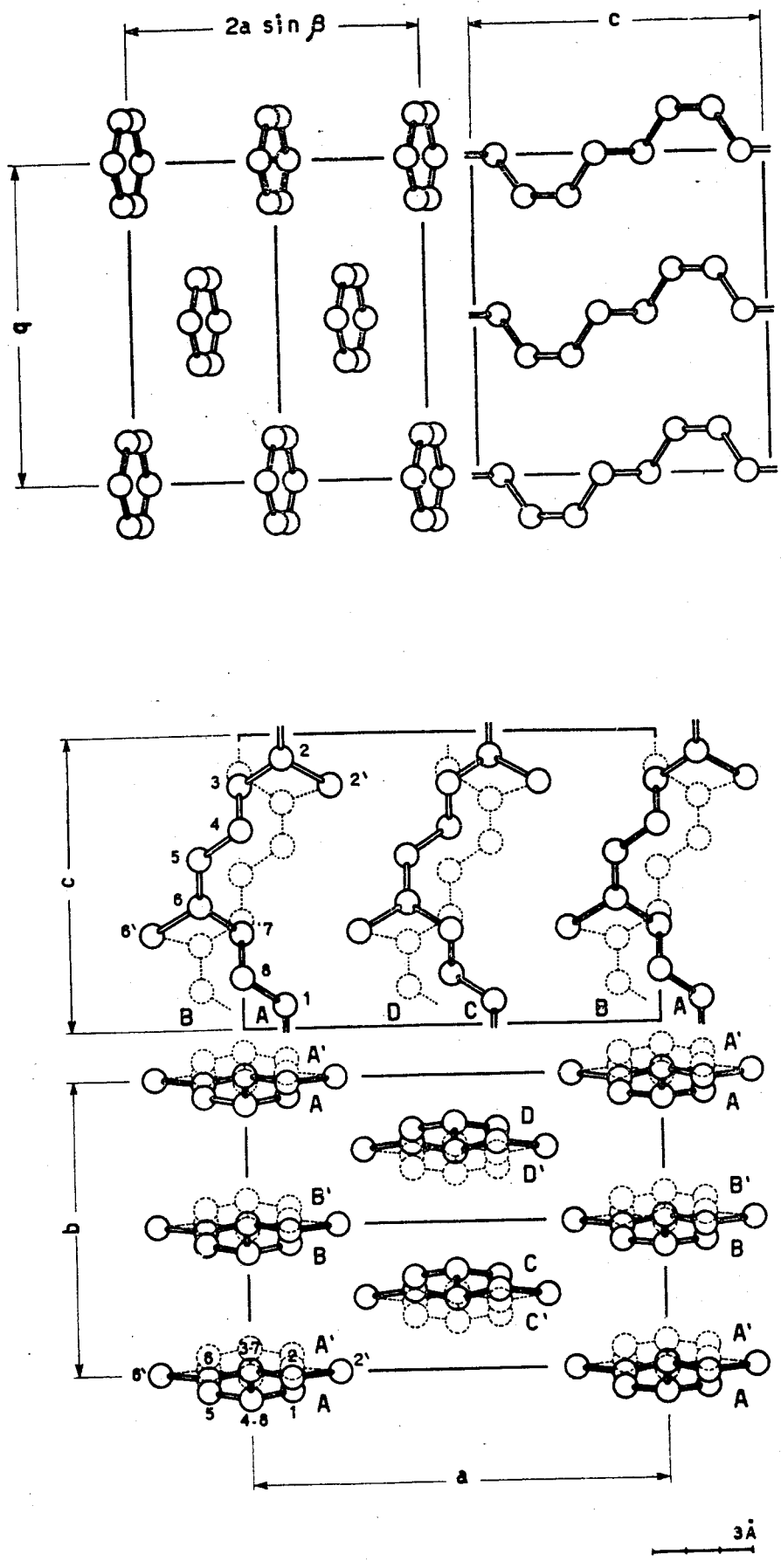


FIG. 7. Comparison between the crystal structures of *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene.

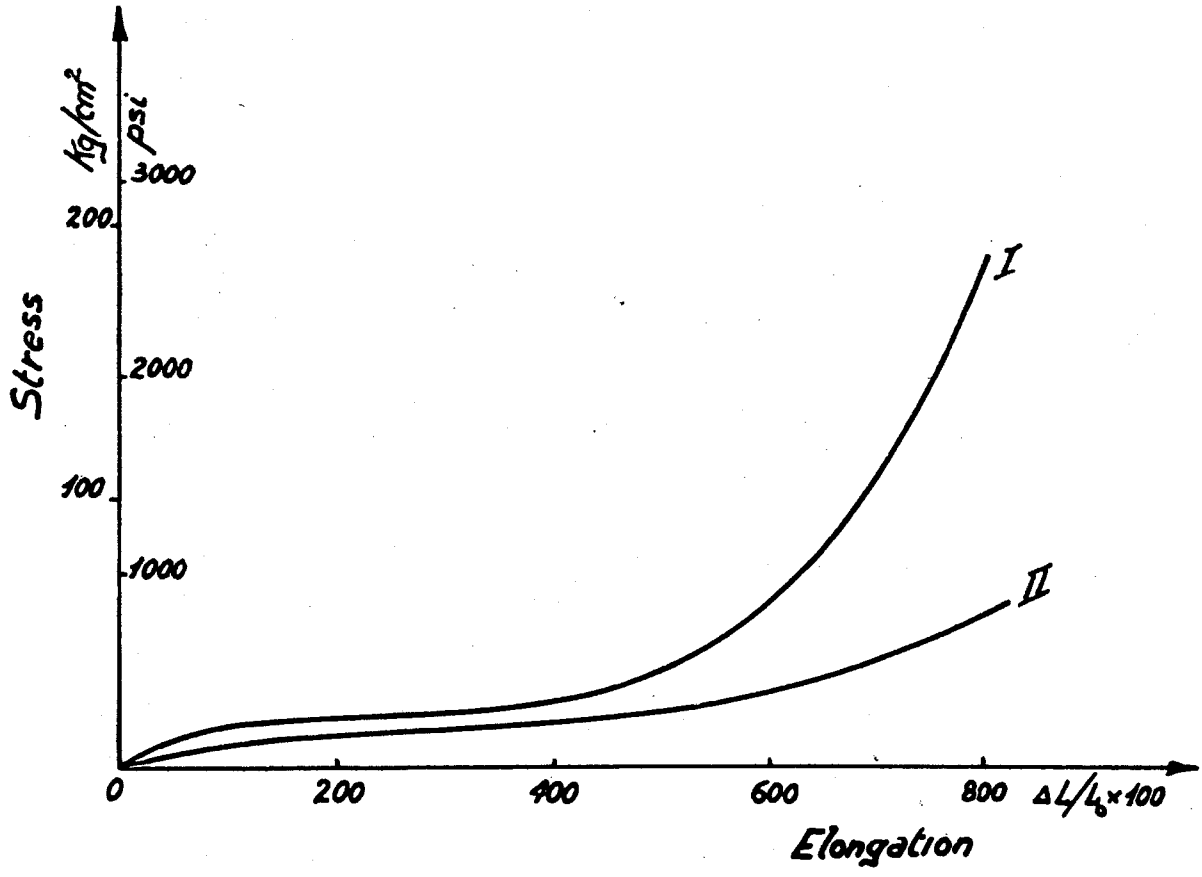


FIG. 8. Stress-strain curves for *cis*-1,4-polybutadienes of different stereoisomeric purity: (I) > 95% *cis;* (II) 85—90% *cis*.

the chain. These repulsions cannot be eliminated in the case of polyisoprene because of steric hindrance due to the methyl groups.

The glide plane is also a principal plane in polybutadiene and determines a mode of packing of the macromolecules in the crystalline state which is very similar to but simpler than the one realized in the structure of polyisoprene. In fact, because of the absence of side groups, there is no longer need for accommodation of "up" and "down" molecules, nor for a statistical distribution of successive antiparallel or parallel layers of molecules developed on the principal plane.

Along with the strong similarity of structure between *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene there is a correspondingly strong similarity between their physical and mechanical properties.

Only when we could prepare a *cis*-1,4-polybutadiene with a high degree of stereoisomeric purity, i.e., equal to that of natural rubber, was it possible to compare in a quantitative way their physical properties.

Undrawn *cis*-1,4-polybutadiene has a melting point of about 0°C. The melting entropy should have a low value as in polyisoprene, because

melting points for drawn samples of polybutadiene were 80°C higher than the melting point in the undrawn state.

The stress-strain curve shows a very low initial modulus, which rises suddenly at elongation, depending on the sterical purity at which crystallization begins. This crystallization, which in *cis*-1,4-polybutadiene having a purity higher than 95 per cent *cis*, begins at 400–500 per cent elongation, causes an increasing of the tensile strength in the polymers of high molecular weight cured with 0·5–1 per cent S to values of about 3000 psi. Figure 8 shows a stress-strain curve of vulcanized samples of *cis*-1,4-polybutadienes of different steric composition.

In the crystal state at room temperature *trans*-1,4-polybutadiene shows a chain structure (with an identity period $c = 4{\cdot}92$Å) very similar to that of β gutta-percha. The nearly cylindrical shape of its molecules favors packing of the chains in a pseudo-hexagonal array with $a = 4{\cdot}54$Å. At 67°C., a first-order transition takes place in the solid state. The structure of the high-temperature phase corresponds to a mode of packing in which the chains, always remaining parallel to each other, should be relatively free to move and oscillate around the chain axes. The phase change is accompanied by a decrease in the density of more than 9 per cent. The low-density phase possesses a pseudo-hexagonal array with $a = 4{\cdot}88$ Å and $c = 4{\cdot}68$ Å. In a drawn fiber, this transformation gives rise to a sudden, reversible contraction process, which is analogous to that taking place in living muscle.

The dimensional change is of the same order as the change in the c dimension ($\sim$5 per cent). We believe this is the first time that a similar phenomenon, related to a first-order crystal-crystal transition, has been observed in synthetic fibers.

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STEREOSPECIFIC POLYMERIZATION OF CONJUGATED DIOLEFINS WITH CATALYSTS CONTAINING DIFFERENT $TiCl_3$ MODIFICATIONS

by G. NATTA, L. PORRI and L. FIORE

(May 1958)

[*Gazz. Chim. It.* **89**, 761 (1959)]

ABSTRACT

At least three different crystalline modifications, indicated by the authors α, β, γ respectively, are possible for titanium trichloride. The α modification is obtained by reduction of $TiCl_4$ with H_2 at high temperature; its colour is violet and it is characterized by a layer lattice. The β modification, which is brown and characterized by a fibre lattice can be obtained: (a) by treating $AlEt_3$ at room temperature with $TiCl_4$ (Al/Ti molar ratio 1) or $AlEt_2Cl$ with $TiCl_4$ (Al/Ti$\geqslant$ 1) in hydrocarbon solution; (b) by decomposition of $TiCl_3$ mono alkyls in hydrocarbon solution; (c) by the action of dark charges at room temperature on a gaseous mixture of H_2 and $TiCl_4$, according to the process described by Böck and Moser in 1912 (*Monatsh.* **33**, 1407, 1912).

By heating the β modification above 200°C, a violet modification with layer lattice was obtained, which, however, is not similar to α—$TiCl_3$; this new modification has been indicated as γ-$TiCl_3$.

Catalysts prepared from aluminum trialkyls or aluminum dialkylhalides and $TiCl_3$ show a different stereospecificity in the polymerization of conjugated diolefins, depending on the modification of $TiCl_3$ used. The AlR_3-α-$TiCl_3$ or -γ-$TiCl_3$ systems give, in the polymerization of butadiene, crystalline polymers, which are chiefly *trans*-1,4. In the

case of isoprene, these systems yield polymerizates, the crystalline fraction of which is practically identical, by I.R. and X-ray analyses, with natural guttapercha.

The systems obtained from AlR_2Cl and α-$TiCl_3$ or γ-$TiCl_3$ respectively show the same stereospecificity as those obtained from AlR_3. On the contrary the catalytic systems obtained from aluminum alkyls and β-$TiCl_3$ show a quite different behaviour.

In the polymerization of butadiene the $AlEt_3$-β-$TiCl_3$ system ($Al/Ti \geqslant 1$) yields polymerization products consisting of a mixture of products amorphous at room temperature with chiefly *cis*-1,4 arrangement, and of crystalline products which are substantially *trans*-1,4 (>90 per cent). The $AlEt_2Cl$-$\beta TiCl_3$ system independently of the Al/Ti ratio, yields products which are predominantly 1,4 (>90 per cent), and which appear to be *cis*-1,4 and *trans*-1,4 copolymers.

In the polymerization of isoprene, the $AlEt_3$–β-$TiCl_3$ and $AlEt_2Cl$ –β-$TiCl_3$ systems yield polymers which are prevailingly *cis*-1,4 (>90 per cent), and which exhibit properties similar to those of natural rubber. No appreciable difference was observed between the systems prepared from β-$TiCl_3$, obtained in the $AlEt_3$-$TiCl_4$ reaction and according to Böck and Moser respectively.

The results obtained when using catalysts prepared from different modifications of $TiCl_3$ are interpreted by admitting that, due to the different crystalline structure, different catalytic complexes are formed on the surface of the $TiCl_3$ crystals, in the reaction with aluminum alkyls.

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POLYMERIZATION OF ETHYLENE WITH SOLUBLE CATALYSTS

by M. FARINA and M. RAGAZZINI

(May 1958)

[*Chimica e Industria*, **40**, 816 (1958)]

ABSTRACT

The use of soluble catalytic systems formed by $Al(C_2H_5)_3$ and $Ti(O\text{-}iC_3H_7)_4$ in the polymerization of ethylene, yields different results depending on the ratios of the components and on their methods of preparation. When solutions of the two components are mixed, at room temperature and under inert atmosphere (N_2), followed by the addition of ethylene to the brown-black solution formed, a linear high-molecular-weight polyethylene is mainly obtained, together with variable amounts of butene-1. The butene to polyethylene ratio is a function of the Al to Ti ratio (it decreases when the latter increases), and of the reaction time; in fact butene-1 is formed essentially during the first stage of the reaction.

If the preparation of the catalytic mixture is made in the presence of ethylene, a high yield of butene-1 is obtained. With Al/Ti ratios of about 10, it may reach 95–99 per cent, of the reacted ethylene, with conversion rates of 150–200 g of butene per g of $Al(C_2H_5)_3$ per hour (pressure, 25 atm; temperature, 70°C).

The content of butene-1 present in the gases given off is very high. The fraction C_4 shows amounts of only 1–3 per cent of butene-2 and negligible amounts of higher homologues.

The polyethylene obtained is highly linear, as shown by the melting point (higher than 135°C) and by the I.R. spectrum, in which the

methyl bands at $\sim$7-25 μ are not present. Therefore, one can assume it is not an ethylene-butene copolymer.

The n-heptane soluble fraction consists of a mixture of linear alpha-olefins having a molecular weight of some thousands and a high order of crystallinity, as revealed by X-ray examination.

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ISOTACTIC POLYMERS OF METHYL-SUBSTITUTED STYRENES

by D. SIANESI, G. NATTA and F. DANUSSO

(May 1958)

[*Gazz. Chim. It.* **89**, 775 (1959)]

ABSTRACT

The stereospecific polymerization of some monomers, methyl derivatives of styrene, is examined in this paper with special emphasis on the nature of the products which can be obtained.

The possibility of obtaining from these monomers, depending on their structure, linear polymers with an ordered structure, some of which are isotactic and crystallizable to a high or medium degree of crystallinity, while some others are not crystallizable at all, is particularly interesting.

The influence exerted by the position of the substituents on the polymerization rate and on the structure of the polymer may be related to the effect that the substituent itself has on the electronic configuration of the monomer, and also to the effects of steric nature on the possible packings of the macromolecules in the solid state.

The exceptionally high melting points and, in some cases, the ease of orientation of the crystals lead us to expect interesting applications for the crystallizable products (see also paper 98).

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X-RAY CHARACTERIZATION OF SOME NEW ISOTACTIC POLYMERS

by G. NATTA, P. CORRADINI and I. W. BASSI

(May 1958)

[*Gazz. Chim. It.* **89**, 784 (1959)]

ABSTRACT

The results of the X-ray characterization of some new isotactic polymers are reported here. They include also some fluorinated polymers which can yield fibres:

(a) Poly-para-fluorostyrene (identity period 8·30 Å; helix 4_1)
(b) Poly-ortho-fluorostyrene (identity period 6·63 Å; helix 3_1)
(c) Poly-ortho-methyl-para-fluorostyrene (identity period 8·05 Å; helix 4_1)
and poly-α-vinylnaphthalene (identity period 8·10 Å; helix 4_1)
and polyallyltrimethylsilane (identity period 6·50 Å; helix 3_1).

The reasons why the above-mentioned polymers assume different conformations are also reported. The shape of their chains and their helix type having ternary or quaternary symmetry, depending on the hindrance and the mode of packing in the crystalline lattice, confirms their isotacticity and the stereoselectivity of their method of preparation.

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THE INTERPRETATION OF THE I.R. SPECTRUM OF ISOTACTIC POLYPROPYLENE*

by M. PERALDO

(May 1958)

[*Gazz. Chim. It.* **89**, 798 (1959)]

ABSTRACT

The I.R. spectrum of isotactic polypropylene, reported for the first time by G. Natta[1] was studied by examining crystalline samples which were either non-oriented or oriented mono-dimensionally. By considering the X-ray structure of polypropylene[2] we thought, as a first approximation, that its chain vibrates like an isolated three-fold helix, even though it does not maintain this kind of symmetry in the crystal. As a consequence of this we made an analysis of the normal modes of vibration, considering the group of points C_3, isomorphous with the factor group of the isolated chain C_3.

Vibrations are classified, to a first approximation, with respect to the particular internal coordinates and to their groups with due reservations for the strong couplings which could be expected and actually are observed in some deutero derivatives.

If one takes into account the fact that some bands may pass unobserved and one excludes also those bands which are attributable to the amorphous and to the imperfect orientation of the polymer, the number of bands observed, particularly in the very significant range between 1370 and 650 cm^{-1}, becomes very similar to that which can be expected from the hypothesis that the infrared spectrum of polypropylene

* Paper presented at the 8th National Congress of Chemistry held jointly with the London Society of Chemical Industry—Turin, May 27—June 2, 1958.

should be essentially the spectrum of an isolated threefold helix. The vibrations of type A are parallel to the threefold helix, while those of type E are perpendicular to it.

Some considerations are made by having taken into account previous data, on the deuterated polypropylenes: $CH_3—CH=CD_2$ and $CH_3—CD=CH_2$. After the observation that strong displacements of all the non-internal frequencies occur in the spectra of poly(propylene 1,1-d_2) and of poly(propylene $2d_1$), we defer the discussion of this topic, and the description of these types of vibrations to subsequent papers[3].

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ISOTACTIC POLYMERS OF SILICON-CONTAINING VINYL MONOMERS

G. NATTA, G. MAZZANTI, P. LONGI and F. BERNARDINI

(16 May 1958)

[*J. Polymer Sci.* **31**, 181 (1958)]

The polymerization of silicon-containing vinyl monomers by means of conventional processes yields only low molecular weight polymers. In fact, such monomers with radical initiators, even if very high pressures in the range of 5000 atm are employed, yield only low polymers, e.g. tetramers or hexamers.[1] Similarly, with cationic catalysts only liquid oily polymers were obtained from allyltrimethylsilane[2].

High molecular weight polymers from monomers containing one vinylic unsaturation and one silicon atom have now been prepared by using heterogeneous catalysts which act according to a mechanism of coordinated anionic catalysis. Such polymers contain linear, head-to-tail macromolecules having regular structure, and are crystallizable.

Monoallylsilane has been polymerized at 60–70°C in the presence of catalysts prepared from violet titanium trichloride and triethyl aluminum. The polymer thus obtained is highly crystalline, melts completely at 127–128°C near the melting point of polybutene–1[3] and, when freshly prepared, is completely soluble in boiling n-heptane. This polymer, owing to the presence of Si—H bonds, can be easily cross-linked by oxygen at 70–80°C or by water or alcohols in suitable conditions.

By polymerization of allyltrimethylsilane in heptane solution at a temperature of 70–80°C. in the presence of catalysts prepared by reaction of triethyl aluminum with titanium tetrachloride (moles $Al(C_2H_5)_3$/moles $TiCl_4$ = about 2), crude polymers having high molecular weight have been obtained with good yields.

TABLE 1. FRACTIONATION AND PHYSICAL PROPERTIES OF POLYALLYLTRIMETHYLSILANE PREPARED AT 80°C. IN THE PRESENCE OF CATALYSTS OBTAINED FROM $Al(C_2H_5)_3$ AND $TiCl_4$

Reference no.	*I* *Acetone extractable fraction, %,*	*II* *Ether extractable fraction*			*III* *Heptane extractable fraction*				*IV* *Xylene extractable fraction*				*V* *Residue (highly crystalline by X-rays)*			
		%[a]	η[b]	d^{30}	%[a]	η[b]	d^{30}	*m.p.*, °C[c]	%[a]	η[b]	d^{30}	*m.p.*, °C[c]	%[a]	η[b]	d^{30}	*m.p.*, °C[c]
1	9.4	13.1	0.47	0.863	1.9	0.25	0.870	125	2.8	0.28	0.875	140	72.8	0.53	0.876	360
2	15.0	10.6	0.06	0.856	3.6	0.21	0.866	123	4.8	0.34	0.870	170	66.0	0.49	0.874	351

[a] Weight percentage of polymer, extractable with boiling solvents.
[b] Intrinsic viscosity in tetralin at 135°C.
[c] Melting temperature, determined by polarizing microscope, by heating at a rate of 1°C/min.

The crude polymers, obtained from allyltrimethylsilane, have a silicon content of 24·35% (calculated for $(C_6H_{14}Si)_n$, Si 24·56%) and an intrinsic viscosity in tetralin at 135°C of about 0·5.

They were fractionated by extraction with solvents, employed at their boiling point, in the following sequence: acetone, ether, n-heptane, xylene. In Table I the results of fractionation are reported, as well as some physical properties of the several resulting fractions. Fractions III and IV prove to be crystalline under X-rays and possess higher specific gravity and lower solubility than the corresponding fractions I and II, which are amorphous.

As previously found for the crystalline fractions and for the amorphous, noncrystallizable fractions of poly-α-olefins, the solubility of the different fractions depends mainly on their steric structure.[4]

The highly crystalline fractions possess a very high melting point (350–360°C) and can be extruded, in the melted state, in filaments and then stretched.

The X-ray fiber spectra indicate a helix structure with a ternary symmetry, and an identity period of 6·5 Å of the chain, attributable to an isotactic structure.

The fractions possessing higher solubility show lower crystallinity, lower specific gravity, and lower melting points than those of the highly crystalline isotactic polymers. The very low melting point of some fractions may depend not only on the lower molecular weight, but also on the presence of steric irregularities along the chains (stereoblock polymers).

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RADIOCHEMICAL DETERMINATION OF THE NUMBER OF ACTIVE CENTRES IN STEREOSPECIFIC POLYMERIZATION CATALYSTS

by G. NATTA, G. PAJARO, I. PASQUON and V. STELLACCI

(17 May 1958)

[*Rend. Accad. Naz. Lincei* (8) **24**, 479 (1958)]

ABSTRACT

An analytical method of isotopic dilution was used to determine the nature and the number of active centres in stereospecific polymerization catalysts.

Adsorption measurements of $Al(C_2H_5)_3$ and of $Al(C_2H_5)_2Cl$ were effected on α-$TiCl_3$ at various temperatures, labelling the ethyl radical of the organometallic compounds with ^{14}C.

Tests were performed as follows:

(a) A certain amount of $TiCl_3$ at a given temperature was treated with a solution of a labelled organometallic compound.

(b) The solid was filtered and washed with the same solvent used in test (a).

(c) Addition of an exactly measured amount of an inactive Al alkyl to the residue.

(d) Decomposition of the carbon–metal bond with 10% H_2SO_4, followed by oxidation of the gases and measurement of the radioactivity.

This type of measurement gives the value of the total adsorption of the organometallic compound on $TiCl_3$, provided one takes care that the adsorption is complete at the given temperature and the washing is carried out at the same temperature.

TABLE 1. DETERMINATION OF THE NUMBER OF ACTIVE CENTRES ON A SAMPLE OF GRUND α-$TiCl_3$, FROM ADSORPTION RUNS OF ^{14}C LABELLED ALUMINUM ALKYL COMPOUNDS

Aluminum compound	*Adsorption temperature °C*	*Adsorption period hr*	*Solvent*	*Washing temperature °C*	*—C_2H_5 labelled groups per mole of α-$TiCl_3$*	
					Total number of —C_2H_5 groups left on $TiCl_3$ after washing	*Number of the —C_2H_5 groups present on the active centres*
$Al(C_2H_5)_3$	—18	1/2	n-heptane	—18	$17{\cdot}0\times10^{3}$	not determined
$Al(C_2H_5)_3$	—18	3	n-heptane	—18	$45{\cdot}0\times10^{-3}$	$9{\cdot}3\times10^{-3}$
$Al(C_2H_5)_3$	20	1/2	benzene	20	$48{\cdot}2\times10^{-3}$	$10{\cdot}1\times10^{-3}$
$Al(C_2H_5)_3$	46	1/2	benzene	46	$17{\cdot}7\times10^{-3}$	$10{\cdot}5\times10^{-3}$
$Al(C_2H_5)_3$	70	1/2	benzene	20	$10{\cdot}5\times10^{-3}$	$10{\cdot}8\times10^{-3}$
$Al(C_2H_5)_3$	70	1/2	benzene	70	$6{\cdot}2\times10^{-3}$	$6{\cdot}7\times10^{-3}$
$Al(C_2H_5)_3$	100	1/2	toluene	100	$3{\cdot}0\times10^{-3}$	$3{\cdot}0\times10^{-3}$
$Al(C_2H_5)_2Cl$	70	1/2	n-heptane	20	$3{\cdot}0\times10^{-3}$	$3{\cdot}1\times10^{-3}$

If one polymerizes ethylene or propylene and does not decompose the catalyst as in (d), a certain amount of radioactivity, due to the end groups inserted in the polymer, is found in the isolated polymer, purified by precipitation.

From the data summarized in Table 1, one can conclude that two types of adsorption exist: a reversible, and an irreversible one. The former does not apparently participate in the polymerization process, while the latter is responsible for the polymerization, and it is entirely found in the polymer.

The number of ethyl groups present in the polymer were conventionally considered equal to the number of the active centres of the catalyst.

The values of these adsorptions depend on the type of $TiCl_3$ (α, γ, δ), on the size of the crystals and on the type of aluminum alkyl used.

It has been found that the number of active centres is about constant when operating in this way and at a temperature range of 18° to +70°C.

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KINETICS OF PROPYLENE POLYMERIZATION WITH HIGHLY STEREOSPECIFIC HETEROGENEOUS CATALYSTS. NOTE VI: DETERMINATION OF THE ACTIVE CENTRES BY KINETIC METHODS

by G. NATTA, I. PASQUON, G. PAJARO and E. GIACHETTI

(26 May 1958)

[*Chimica e Industria* **40**, 556 (1958)]

ABSTRACT

The catalytic complexes, which are active in the stereospecific polymerization of α-olefins, prepared from α-$TiCl_3$ and $Al(C_2H_5)_3$, or $Al(C_2H_5)_2Cl$ contain initially ethyl groups, derived from the aluminum alkyl, bound to a metal. During the polymerization, the monomeric units are inserted on these metal–carbon bonds: therefore, the first polymeric chain which is formed on the catalytic complex, contains a terminal ethyl group. The growth of the polymeric chains is terminated by processes, which can be compared to the chain transfer ones. Not all these processes regenerate the catalytic complexes containing ethyl groups. It follows that by increasing the period of polymerization and by operating at constant pressure and temperature and in the presence of a catalyst having a constant activity, the ratio of the terminal ethyl group to the polymerized monomer should decrease.

Polymerization runs of propylene, carried out with α-$TiCl_3$ and $Al(C_2H_5)_2Cl$ containing ^{14}C, have allowed us to prove this hypothesis, and moreover to evaluate the amount of catalytic complexes present in the system under consideration (in the order of a few "moles" per thousands of α-$TiCl_3$).

The results obtained also indicate that the overall propagation rate of the sterically less pure macromolecules is lower than that of the more stereoregular ones.

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STEREOSPECIFIC POLYMERIZATIONS AND CATALYSIS*

by G. NATTA

(27 May 1958)

[*Gazz. Chim. It.* **89**, 52 (1959)]

Two important branches of chemistry, namely kinetics and catalysis, assume particular aspects when applied to the field of macromolecules.

When the chemist first started working in the field of organic macromolecules, where nature has produced so many examples, the most salient results were obtained by using catalytic methods different from those usually adopted in the synthesis of low molecular weight substances.

Heterogeneous catalysis represented the most important and fertile branch of catalysis, leading to the most outstanding results in the synthesis of low molecular weight products. The macromolecular synthesis had instead a higher development through homogeneous catalytic processes (at least in its initial phase); in particular, processes initiated by free radicals, improperly called catalytic processes.

Highly exothermic processes initiated by free radicals have made it possible to produce from simple monomers most of the polymeric macromolecules, having molecular weights of hundreds of thousands, or of millions, which have led to the production of thermoplastic resins on an industrial scale. If we compare macromolecules produced by chemists with the products of nature, we note a fundamental differ-

* Lecture held at the 8th National Congress on Chemistry jointly with the London Society of Chemical Industry—Turin, May 26—June 2, 1958.

ence. Natural products often correspond to a precise pattern, also sterically regular in their constitutive elements, while synthetic products mostly have a sterically irregular and disordered chemical structure. An exception is given by some synthetic polymers such as nylon, prepared by polycondensation of monomers having a simple, unbranched structure containing the reactive groups in terminal position and by some other polymers, such as polyisobutylene, obtained by polyaddition of monomers having highly symmetric molecules. In other cases, polymers with a non-regular structure obtained both by polyaddition and by polycondensation are incapable of crystallizing.

The chemist, although having at his disposal stronger means of activation (from very high temperatures to very high energy radiations) compared to those of natural biochemical processes, has been incapable of mastering and controlling them and to arrange the single asymmetric monomer molecules in regular associations corresponding to a pre-established model also from the steric standpoint.

Many natural macromolecules, such as natural rubber, cellulose, silk and many protein substances, show, on the contrary, regular arrangements of their monomeric units. Such arrangements correspond not only to a regularity of their chemical composition, but also to the steric configuration of the single units. Natural macromolecules correspond to a constantly reproducible model with the same configuration.

The difference between synthetic and natural products is evident in the field of diolefinic polymers.

Hevea rubber, on one hand, and guttapercha, on the other, represent products whose monomeric units are repeated with the same steric configuration, *cis*-1,4 and *trans*-1,4 respectively. The former is, at ordinary temperature, the best elastomer; the latter represents one of the first known linear macromolecules with thermoplastic properties. They can both crystallize; the first at low temperature or if oriented by stretching, the other in several polymorphous forms at room temperature or just slightly above.

Until 4 years ago all synthetic products obtained by diolefin polymerization were, on the contrary, amorphous.

Over 40 years of research on diolefin polymerization had not made it possible to obtain polymers showing all the elastic properties of natural rubber.

G. NATTA

Synthetic Polymers having Sterically Regular Structure

A cause of irregularity in the structure of macromolecules is the steric configuration of their carbon atoms.

While in nature there are polymers containing asymmetric atoms in which all monomeric units have the same steric configuration (crystallizable proteins, cellulose), all synthetic polymers, obtained by polyaddition of vinyl asymmetric monomers (of $CH_2=CHR$ or $CH_2=CR'R''$ type), contained, in their main chains, carbon atoms with different steric configurations arranged in an irregular manner. They were incapable of crystallizing unless the size of R was only slightly different from the size of H (that is to say provided R was isomorphous with H). Only in the cationic polymerization of isobutyl-vinylether, did Schildknecht obtain mixtures containing two different types of polymers, one of which was crystalline and consequently structurally ordered.[1]

The discovery of stereospecific catalysis processes achieved in the Polytechnic School of Milan, at the beginning of 1954, allowed the synthesis of linear head-to-tail polymers with sterically ordered structures in case of α-olefin and diolefin polymers.[2] In the field of α-olefin polymers, isotactic ones could be produced in which all the tertiary carbon atoms of long sections of chain show the same steric configuration. Perfectly linear crystalline products were thus obtained with high melting temperatures and with physical properties entirely different from the previously known polymers.

From diolefin monomers, moreover, other crystalline polymers have been obtained in which crystallinity is due to a regular alternation of units having opposite steric configuration.

I had to apply two new attributes to define in a simple way these two types of crystalline polymers: *isotactic* and *syndiotactic*, respectively.[2,3] The amorphous polymers, on the other hand, having an irregular distribution of the monomeric units with opposite steric configurations, have been called atactic. Subsequently Mark proposed to use the name *eutactic*, which defines all regularly structured polymers, regardless of their type of steric structure.

The new syndiotactic and isotactic structures correspond to characteristic chain structures which do not exist in natural hydrocarbons. Isotactic polymers have helix shaped chains, built up of structurally equal monomeric units. Syndiotactic polymers have chains along which the repetition of successive units is achieved by means of a translation

TABLE 1. MELTING POINTS AND CRYSTALLINITIES OF POLYPROPYLENES WITH DIFFERENT STEREOISOMERIC COMPOSITIONS

Solvent employed for the extraction	*Fractionation of polypropylene obtained with $TiCl_4$ and $Al(C_2H_5)_3$ catalyst; R = 2.5: T = 90°C [P_{INIT}] = 21 at*			*Fractionation of polypropylene obtained with $TiCl_4$ and $Al(C_2H_5)_3$ R = 2.8; T = 35°C: P_{COST} = 3.3 at*			*Fractionation of polypropylene obtained with $TiCl_3$ and $Al(C_2H_5)_2Cl$: R = 3; T = 70°C; [P_{INIT}] = 21 at*			*Fractionation of polypropylene obtained with $TiCl_3$ and $Al(C_2H_5)_3$ R=2.5; T = 80°C; P_{COST} = 6 at*		
	[η] 100 cm^3/g	*crystallinity %*	*melting point °C*	*[η] 100 cm^3/g*	*crystallinity %*	*melting point °C*	*[η] 100 cm^3/g*	*crystallinity %*	*melting point °C*	*[η] 100 cm^3/g*	*crystallinity %*	*melting point °C*
Pentane	0·51	27	114	1·12	11	114	0·35	15	106	0·42	27	110
Hexane	0·61	37	130	1·13	29	135	0·67	25	110	0·55	36	127
Heptane	0·68	54	159	0·92	41	159	0·90	41	147	0·63	52	159
2-ethyl-hexane	1·22	64	170	1·01	52	168	1·12	53	168	0·86	62	170
Octane	2·08	68	174	3·11	60	174	1·63	62	174	1·32	64	174·5
Residue	—	—	—	—	—	—	3·50	64	174	2·97	66	174·5

and a mirror reflection: so that adjacent monomeric units are structurally enantiomorphous.

Although in nature isotactic polyhydrocarbons do not exist, nevertheless a certain structural analogy is observed of certain crystalline proteins (α-keratin) (Fig. 3 of paper 42) and certain spiralized polysaccharides with isotactic polymers.

In such polymers, chains have a helix structure with regular successions of monomeric units with the same relative steric configuration. In the case of alpha-keratin, tertiary carbon atoms are linked to groups with a different chemical constitution; therefore, they are optically active. However in the case of linear head-to-tail α-olefin polymers the tertiary carbon atoms are included between two equal methylenic groups. Therefore the phenomena of stereoisomery, due to the asymmetry of tertiary carbon atoms, in rather long chains, derive only from the relative configuration of each monomeric unit with respect to the preceding or the following one.

In very long macromolecules, in fact, we can neglect the effects due to the diversity of the terminal groups and to differences in length of the main chain sections linked to a tertiary carbon atom.

The differences in the properties of isotactic and atactic polymers are really remarkable. Isotactic polymers are crystalline, capable of giving highly resistant films, textile fibers and stiff, hard shaped articles with a high melting temperature. Atactic polymers may be considered viscous liquids and can lead to elastic rubbers if their molecular weight is sufficiently high.

Between isotactic and atactic polymers a whole series of intermediate products having a lower melting temperature than the corresponding isotactic polymers has been isolated.[4]

Such polymers, in which sections of isotactic chains having a certain configuration alternate with others of opposite configuration or with atactic sections, are called stereoblock polymers (Fig. 19 of paper 24).

Steric irregularities along the chains lower the melting temperature in the same way as chemical irregularities. It is thus possible to obtain stereoisomeric polymers, whose melting temperatures vary in a continuous way according to their steric irregularities (Table 1). For polymers having very high molecular weight the melting point may drop from 175° C for totally isotactic polypropylene to almost 100°, due to the decrease of the average length of the individual isotactic sections present in stereoblock polymers (Table 2).

TABLE 2. FRACTIONATION OF RAW POLYMERS OBTAINED WITH DIFFERENT CATALYSTS PREPARED FROM TITANIUM CHLORIDES AND TRIETHYL ALUMINUM AT TEMPERATURES BETWEEN 35° AND 90° C

Fraction	*Soluble in*	*Insoluble in*	*Crystallinity %*	*Melting point*	*Steric Irregularity %**
I	—	trichloroethylene	75–85	176	0
II	—	n-octane	64–68	174–175	0,4– 0.8
III	n-octane	2-ethyl-hexane	60–66	174–175	0.4– 0.8
IV	2-ethyl-hexane	n-heptane	52–64	168–170	2.5– 3.4
V	n-heptane	n-hexane	41–54	147–159	7.2–12.2
VI	n-hexane	n-pentane	25–37	110–135	17.3–27.8
VII	n-pentane	—	15–27	106–114	26.1–29.5

(*) Supposing that ideal crystalline polymer melts at 176°.

A decrease of the average molecular weight below 5,000 leads to a strong lowering of melting temperature. This is also valid for pure isotactic polymers, since the end groups cause irregularities in the crystals. Such irregularities have an effect similar to the one caused by internal irregularities in stereoblock polymer chains.

Stereospecificity of Polymerization Processes

Polyaddition processes used in the past were processes acting with free radical mechanism. They were considered catalytic processes; but in fact they are not, because the so-called catalysts (peroxides, hydroperoxides, peracids and their derivatives, diazo-compounds) are substances which do not remain unaltered after the reaction, as they should if they were true catalysts. These are indeed initiators and act because of their decomposition into free radicals, which are used up during polymerization.

The high reactivity of free radicals, their position mostly confined to the free end of a growing chain, and the possibility of transfer in other sites of the chains or in other molecules, are the causes of the great irregularities in the structure of polymers obtained by free radical processes:

1) Irregularities of chemical nature such as branchings in polymeric chains, inversions in the head-to-tail structure, telomerizations due to chain transfer with solvent molecules or due to coupling with other free radicals.

2) Steric irregularities due to the different possible steric configurations of the asymmetric monomeric units.

The only obstacle to irregularities in steric configuration can derive from the bulkiness of the functional groups. Functional groups can in the addition of each monomeric unit, favour its presentation with an opposite configuration with respect to the one of the previous unit. This causes, in some vinyl polymers (polyvinyl chloride and polyacrylonitrile), a greater probability of syndiotactic successions.

Cationic processes, in general, yield polymers having low molecular weight and chemically and sterically irregular structure. This is due to the facility with which chain transfers occur, unless one operates at extremely low temperatures with particular monomers showing a certain symmetry (isobutylene).

A third polymerization mechanism is given by anionic catalytic processes which, in the past, has had a quite negligible importance, if one excludes the production of synthetic rubber by the polymerization of butadiene with sodium as catalyst in Russia before the war. Such polymerization proved to be neither chemically nor sterically specific, since polymers thus obtained are constituted of monomeric units with different linkages, in part 1-2 and in part *cis*–1,4 and *trans*–1,4.

Processes of truly stereospecific catalyses of alpha-olefins and di-olefins were discovered only at the beginning of 1954.

These processes (to which we attribute an anionic co-ordinated mechanism) take place in the presence of catalytic complexes containing low valency transition metal compounds and organometallic derivatives of highly electropositive elements having small ionic radius.

These enabled us to obtain in Italy the first isotactic and syndiotactic polymers and the four different pure, highly crystalline polybutadiene stereoisomers (two with 1,2 linkage isotactic and syndiotactic, and two with 1,4 linkage *cis* and *trans*).

Anionic processes, using organometallic compounds of lithium, developed in U.S.A. allowed the preparation of the first synthetic rubbers from isoprene having predominantly *cis*-1,4 configuration, like natural rubber.

Behaviour of different monomers in stereospecific catalysis.

The response towards ionic catalysts and, in particular, to anionic co-ordinated catalysts chiefly depends on the chemical nature of the monomer. For instance, the presence in the monomer molecule of electron-releasing or electron-attracting groups near the double bond determines its tendency to polymerize with a certain catalytic mechanism.[5]

It is known that the monomers which react better with cationic polymerization contain electron-releasing substituents.

The data concerning the classical polymerizations of anionic type were rather scarce and concerned a small number of monomers. These data show that the monomers which polymerize better by cationic processes do not polymerize by anionic processes. Only the monomers in which the double bond is conjugated with other double bonds or with aromatic groups, may polymerize, because of their greater polarizability, both by anionic and cationic processes.

The new coordinated anionic polymerization processes seem apparently to disagree with old schemes, because they act with monomers (like α-olefins) containing electron-releasing groups (which normally polymerize only with cationic mechanism) and do not polymerize the monomers containing electron-attracting groups which normally polymerize with anionic catalysts.

This is due to the instability of the coordinated anionic catalytic systems and their high sensitivity not only towards substances containing mobile hydrogen, capable of supplying hydrogen cations (a property which is common to all anionic catalytic processes), but also towards substances which contain atoms with "lone electron pairs". These last easily react with the catalysts containing organometallic electron-deficient complexes, stopping their catalytic activity. The consequence is that the most typical monomers, which are polymerized by catalysts considered as basic or nucleophilic (acrylonitrile, methyl methacrylate, etc.) are not polymerized by the most typical coordinated anionic catalysts. Only when electropositivity of the coordinating metal atom in the complex is reduced, is it possible to polymerize monomers containing oxygen, chlorine or other halogens with catalysts constituted by complexes containing transition metals. Such catalysts having in some respects a character intermediate between the cationic and anionic catalysts can also, but only in special cases, act stereospecifically (Table 3).

Schemes in which monomers are arranged according to their response to the different types of catalysts (cationic and anionic) or to radical initiators were proposed by various authors. In the scheme reported in the table, we have tried to summarize the coordinated catalysis characteristics.

In the case of hydrocarbons the presence of electron releasing groups (for example CH_3) enables the monomers to polymerize with typical Friedel and Crafts cationic catalysts. The α-olefins and the vinylidene

TABLE 3.

Monomers	*Substituent action*	*Response to the reactions*	
		ionic simple	*with complexes containing transition metals*
$CH_2=CH-CN$	electron releasing — inductive effect	anionic polymerization	reaction of substituents with very electron deficient complexes
$CH_2=CH-COOR_1$			
$CH_2=CH-F$			
$CH_2=CH-Cl$			
$CH_2=CH-Br$			
$CH_2=CH-O-CH_3$			
$CH_2=CH-O-CH(CH_3)_2$			
$CH_2=CH-O-CH_2(CH_3)$			
$CH_2=CH-CR=CH_2$	conjugative effect	cationic polymerization	possible co-ordinated polymerization non anionic
$CH_2=CH-C_6H_4-F$			
$CH_2=CH-C_6H_5$			
$CH_2=CH-C_6H_4-CH_3$			
$CH_2=CH-C_6H_4OCH_3$			
$CH_2=CH_2$			highly stereospecific polymerizations
$CH_2=CH-CH_3$	electron attracting — inductive effect		anionic co-ordinated polymerization with very electron deficient complexes
$CH_2=CH-CH_2-CH_3$			
$CH_2=CH-CH(CH_3)_2$			
$CH_2=C(CH_3)_2$			
$CH_2=CR(CH_3)$			

hydrocarbons polymerize, therefore, easily by non-stereospecific cationic processes, but do not polymerize with typical anionic catalysts.

The stereospecificity seems, in general, to be connected with the use of a type of catalyst acting with a mechanism which is different from the one that would normally be preferred on the basis of the chemical nature of the monomers. A too high reaction rate would render the polymerization sterically uncontrollable. The use of anionic catalysts is, in fact, necessary for the stereospecific polymerization of monomers which ordinarily polymerize more easily by cationic processes and, inversely, the use of cationic catalysts should be preferable for the stereospecific polymerization of monomers containing electron attracting groups which polymerize easily with anionic processes.

In the case of cationic polymerization processes, which are in general sterically uncontrollable, it was possible to make them stereospecific, by adopting conditions which reduce the catalytic activity (low temperature, complexing of the electron-deficient catalysts with substances containing lone electron pairs, etc.).

The first partially stereospecific polymerization of vinyl monomers was carried out by Schildknecht with catalysts of cationic type by complexing BF_3 with ether and operating at low temperature.

The α-olefins, which do not polymerize with the most typical anionic catalysts, polymerize on the contrary with coordinated anionic catalysts and, preferably, with heterogeneous catalysts. On these catalysts a chemisorption of the monomer takes place, involving a particular double bond activation. In this way the polymerization of monomers which do not polymerize by homogeneous anionic catalysis becomes possible. Ordered structures in the solid phase of catalysts cause their stereospecificity in isotactic α-olefin polymerization.

In the case of monomers containing electron attracting groups (for instance vinylethers, vinylchloride, etc.) the cationic polymerization is less easy than with monomers containing electron releasing groups. However, the use of complexes, containing transition metals, the electropositivity of which is reduced with regard to the typical Ziegler catalysts, permits the polymerization of such monomers too. We have obtained, for instance with some complexes containing transition metals, aluminum and halogen atoms, high yields of polymers of vinyl-alkyl-ethers, having high molecular weight and a higher crystallinity than the polymers obtained by Schildknecht with catalysts constituted by boron fluoride-etherates, not containing transition metals (Table 4.).

TABLE 4.

BUTYLVINYLETHER POLYMERIZATION WITH CRYSTALLIZABLE COMPLEXES CONTAINING TITANIUM AND ALUMINUM

Complex	*Activity of the catalyst*	*Characteristics of the polymer*
$(C_5H_5)_2TiCl_2Al(C_2H_5)_2$	none	—
$(C_5H_5)_2TiCl_2AlC_2H_5Cl$	moderate	isotactic
$(C_5H_5)_2TiCl_2AlCl_2$	high	isotactic

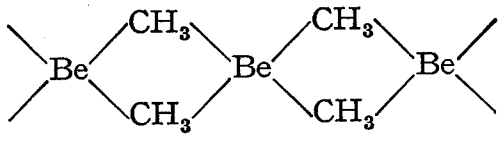
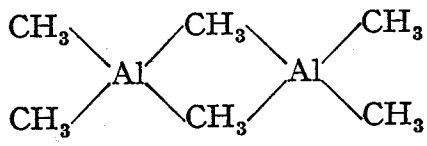
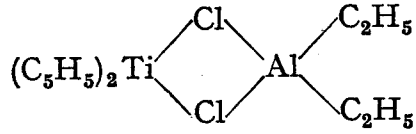
Co-ordinated Anionic Catalysis and its Stereospecificity

More than four years of research work enabled us to clarify stereospecific catalysis as well as the possible causes of stereospecificity.

Co-ordinated anionic polymerization occurs when the organometallic complex contains very electron-positive atoms linked to carbon atoms and at least one transition metal atom.

The incompleteness of the *d* orbital of the transition metal may cause a first association of the vinyl group with the complex. The vinyl group tends however, because of the polar environment, to polarize itself and to be oriented with the less substituted carbon towards the electropositive metal and the more substituted carbon towards the negative group previously linked to the metal complex. All stereospecific catalysts consist of electron-deficient bimetallic complexes.

TABLE 5.

	Angle M—C—M	*Distance C—M* Å	
		bridge	*terminal*
	66°	1.93	—
	70°	2.24	1.99
	90°	~2.5 (Ti—Cl)	—

In these catalysts electronegative atoms constitute bridge-bonds between very electropositive metal atoms of very small diameter.

Alpha-olefin polymerization takes place only when atoms, capable of supplying ions with very small diameter and with high charge, cause a close co-ordination of the anions (and consequently also the carbon anion) in the complex. The presence of two different metal atoms creates a lack of symmetry in the complex, which causes a decided orientation of the monomer molecule during its transformation in monomeric unit.

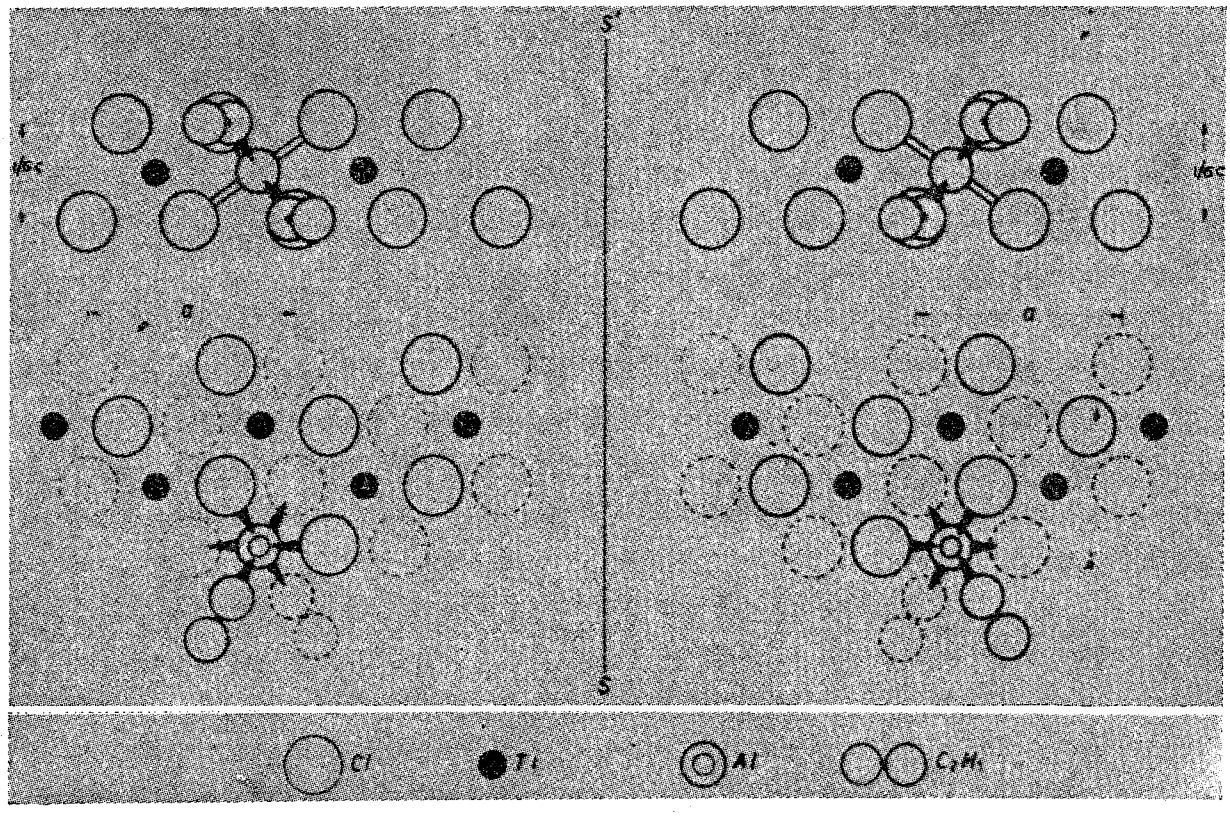


FIG. 1. Schematic model of how an epitactic adsorption of $AlCl(C_2H_5)_2$ on the border of the base plane of a crystal of $TiCl_3$ ($a = 6.12$ Å, $c = 17.50$ Å) may give rise to enantiomorphous active centers.

In our stereospecific catalysts the stereospecificity is in relation to the ionic diameter of the metal. Each active centre causes the synthesis of macromolecules containing sequences of hundreds or thousands of monomeric units having the same relative steric configuration.

Each active centre causes therefore an asymmetric synthesis.

In the case of α-olefin polymers, isotactic chains thus obtained assume, with regard to crystals, regular helical conformations. It is possible

that these conformations continue to exist also in the state of free molecules (melted or dissolved), although with a certain variation in the helical radius and pitch. Such helices may be built either in a left handed or in a right handed sense. The lack of optical activity is due to the fact that the effect of the two spiralization senses are mutually compensated.

TABLE 6. DEPENDENCE OF THE STEREOSPECIFICITY ON THE IONIC RADIUS OF THE METAL CONTAINED IN THE CATALYTIC COMPLEXES

Metal of the metal organic compound	*Ionic radius of the metal*	*% of polypropylene non-extractable by boiling n-heptane*
Be	0.35 Å	94–96%
Al	0.51 Å	80–92%
Mg	0.66 Å	78–85%
Zn	0.74 Å	30–40%

The growing polymeric chain is linked to the complex by a carbon anion and it can be separated by thermal dissociation with formation of a vinylidenic end group. It can also be separated by transfer of hydride ion, from the CH adjacent to the chain end group, to the catalytic complex or to a monomer molecule.[6]

The inductive action of alkyl groups linked to the tertiary carbon atom favours the separation of the hydride ion. This explains the lower polypropylene and polybutene molecular weight with respect to polyethylene and polystyrene (Table 7).

TABLE 7. INTRINSIC VISCOSITY IN TETRALIN OF ISOTACTIC POLYMERS, PREPARED WITH CATALYSTS OBTAINED FROM $Al(C_2H_5)_3$ AND TITANIUM CHLORIDES AT 60-80 °C

Monomers	*Titanium chloride*	*Moles $Al(C_2H_5)_3$/ moles $TiCl_n$*	*Highly crystalline fraction, insoluble in boiling:*	*Intrinsic viscosity*
Styrene	$TiCl_4$	2.5	methyl-ethyl-ketone	3–4
Propylene	$TiCl_4$	2	n-heptane	2–2.5
Butene-1	$TiCl_4$	2	diethyl ether	1.5–2
Styrene	$TiCl_3$	2	methyl-ethyl-ketone	3–4
Propylene	$TiCl_3$	2	n-heptane	2.5–3
Butene-1	$TiCl_3$	2	diethyl-ketone	2–2.5

Nature of the Surface of the Solid Catalysts

One of the more intensively studied problems in heterogeneous catalysis is the determination of the number and nature of active centres on the catalyst surfaces.

In the literature one can find hundreds of papers on the determination of the number and nature of active centres, their variations with respect to temperature and their behaviour in catalysis.

For a long time, it has been admitted that not all the surface of a catalyst is active and that not all the sites where the chemisorption takes place are equally efficient with regard to catalysis.

Stereospecific polymerizations enable us to examine a very interesting aspect in catalysis, namely its stereospecificity. Moreover, since every active centre presents the property of producing a chain of reactions of a given type, it is now possible to differentiate the active centres in terms of the composition and structure of the produced polymers.

The fact that a layer lattice crystalline catalyst is activated by the action of an organometallic compound raises the problem whether the activation is due to a reversible or irreversible adsorption or to a reaction with irreversible modification of the superficial structure of the support.

The problem has been faced, as for heterogeneous systems including a solid phase having a layer lattice, by using organometallic compounds containing labelled carbon. In Table 8 the quantity of alkyls adsorbed at different temperatures is indicated.

From the data of Table 8 it is proved that only part of the adsorbed alkyls are efficient in catalysis.

The ratio between the two absorbed quantities approximately corresponds to the ratio between the surface of the base of the crystals and the surface of the more irregular lateral facets of the hexagonal prisms.

We believe that also chemisorption is connected with the formation of bridge-bond complexes with Ti atoms (similarly to what happens with soluble complexes) coming out on the lateral surface and being incompletely coordinated with the crystalline lattice.

Kinetics of the Growth Processes and Determination of the Number of Active Centres of the Catalyst

The true catalytic nature of the violet $TiCl_3$—$Al(C_2H_5)_3$ systems, has been demonstrated by us on the basis of kinetic measurements carried out using metal alkyls marked with ^{14}C.

These measurements have demonstrated:

1. The existence of two types of adsorption, one of which is reversible, of the $AlEt_3$ on $TiCl_3$.

2. The adsorption, which is not reversible at low temperature, and which can be considered as due to a surface chemical reaction, gives rise to the active centres in the catalysis (observed in the order of magnitude of 1×10^{-3} active centres /g$TiCl_3$).

3. Each active centre maintains (in the absence of impurities) an activity which is constant with time.

4. The first polymeric chain which is formed on an active centre starts with an alkyl deriving from $AlEt_3$; since its life is very short (normally no more than a few minutes) the successive molecules of the polymer, which are initiated on the same active centre, are formed by successive processes of chain termination and of chain transfer.

5. The molecular weight of the polymer depends on several processes (Table 9):

(*a*) a termination process which takes place at high temperature by dissociation of the catalytic complex to hydride, followed by the initiation of a new polymeric chain, due to the formation of an alkyl group by reaction between such a hydride and the monomer;

(*b*) a chain transfer with the monomer;

(*c*) a chain transfer in which some alkyls present in solution take part by at least two possible catalytic mechanisms. One of them is independent of the polymerization rate and depends only on the square root of the aluminum alkyl concentration. The other one depends on the polymerization rate and also on the quantity of titanium compound present.

In Table 9 the catalytic complex was written in a simplified ionic form. It is an electron-deficient complex in which the R group is inserted between two metals (i.e. Ti and Al).[7]

The chain transfer processes connected with alkyls exchange prevail when operating with relatively high concentrations of alkyls in solution. In this case the rate of these processes may represent more than 50 per cent of the total chain transfer and termination processes.

TABLE 8 DETERMINATION OF THE NUMBER OF ACTIVE CENTRES ON A GROUND SAMPLE OF α-$TiCl_3$, FROM ADSORPTION DATA OF ^{14}C LABELLED ALUMINUM ALKYL COMPOUNDS, FOLLOWED BY POLYMERIZATION OF PROPYLENE

$TiCl_3$: 0.5 g; aluminum alkyl compound: 0.5 cm^3; solvent: 30 cm^3 n-heptane

Aluminum compound	*Adsorption temperature °C*	*Time of adsorption h.*	*Solvent*	*Washing temperature with anhydrous solvent. °C*	*Moles of C_2H_5 adsorbed per mole of $TiCl_3$*	
					Total number of pre-adsorbed alkyl groups remaining on $TiCl_3$ after washing	*Number of alkyl groups adsorbed on active centres (pre-adsorbed alkyl groups found in the polymer)*
$Al(C_2H_5)_3$	—18	1/2	n-heptane	—18	$17{\cdot}0\times10^{-3}$	n.d.
$Al(C_2H_5)_3$	—18	3	n-heptane	—18	$45{\cdot}0\times10^{-3}$	$9{\cdot}3\times10^{-3}$
$Al(C_2H_5)_3$	20	1/2	benzene	20	$48{\cdot}2\times10^{-3}$	$10{\cdot}1\times10^{-3}$
$Al(C_2H_5)_3$	46	1/2	benzene	46	$17{\cdot}7\times10^{-3}$	$10{\cdot}5\times10^{-3}$
$Al(C_2H_5)_3$	70	1/2	benzene	20	$10{\cdot}5\times10^{-3}$	$10{\cdot}8\times10^{-3}$
$Al(C_2H_5)_3$	70	1/2	benzene	70	$6{\cdot}2\times10^{-3}$	$6{\cdot}7\times10^{-3}$
$Al(C_2H_5)_3$	100	1/2	toluene	100	$3{\cdot}0\times10^{-3}$	$3{\cdot}0\times10^{-3}$
$Al(C_2H_5)_2Cl$	70	1/2	n-heptane	20	$3{\cdot}0\times10^{-3}$	$3{\cdot}1\times10^{-3}$

The determination of the number of the active centres has made it possible to evaluate also the average life-time of each macromolecule which is of the order of minutes. Since each molecule contains, on an average, hundreds of monomeric units, it follows that the chain growth through successive "stepwise addition" stages, corresponds under certain conditions to times of the order of seconds for each addition of a monomeric unit.[8,9]

The formation of a macromolecule thus results in a relatively slow process with respect to the normal formation of macromolecules by free radical processes.

TABLE 9. REACTION SCHEMES FOR THE PROPYLENE POLYMERIZATION PROCESS WITH STEREOSPECIFIC CATALYSTS

(a) *Initiation and propagation*

$$[Cat]^{(+)}\text{—}^{(-)}R + CH_2{=}CHCH_3 \rightarrow [Cat]^{(+)}\text{—}^{(-)}CH_2CHCH_3R$$

$$[Cat]^{(+)}\text{—}^{(-)}CH_2CHCH_3(CH_2CHCH_3)_{n-1}R + CH_2{=}CHCH_3 \rightarrow$$
$$\rightarrow [Cat]^{(+)}\text{—}^{(-)}CH_2CHCH_3\,(CH_2CHCH_3)_nR$$

where: R=H, C_2H_5, C_3H_7 or other polymeric alkyl groups

(b) *Chain transfer and termination*

(1) Monomolecular termination process

$$[Cat]^{(+)}\text{—}^{(-)}CH_2CHCH_3(CH_2CHCH_3)_nR \rightarrow$$
$$\rightarrow [Cat]^{(+)}\text{—}^{(-)}H + CH_2{=}CCH_3\,(CH_2CHCH_3)_nR$$

(2) First order chain transfer process with respect to the monomer

$$[Cat]^{(+)}\text{—}^{(-)}CH_2CHCH_3(CH_2CHCH_3)R + CH_2{=}CHCH_3 \rightarrow$$
$$\rightarrow [Cat]^{(+)}\text{—}^{(-)}CH_2CH_2CH_3 + CH_2{=}CCH_3\,(CH_2CHCH_3)_nR$$

(3) Chain transfer process depending on aluminum alkyl concentration

$$[Cat]^{(+)}\text{—}^{(-)}CH_2CHCH_3(CH_2CHCH_3)_nR + R_1AlR_2 \rightarrow$$
$$\rightarrow [Cat]^{(+)}\text{—}^{(-)}R_1 + R_2AlCH_2CHCH_3(CH_2CHCH_3)_nR$$

or:

$$TiCl_nY_2AlP + AlR_3 \rightarrow TiCl_nAlR_3 + AlY_2P$$

where Y=alkyl and P=polymeric chain

Since the catalytic activity is constant with time, it follows that when one uses very pure reagents, each active centre in the course of a some-day polymerization, can lead to thousands of macromolecules, containing altogether millions of monomeric units.

Heteroblock Copolymers of Alpha-olefins

By introduction of different monomers in the growth reaction we succeeded in obtaining macromolecules consisting of a succession of different monomeric units in the same macromolecule, that is, block polymers of the type:

... AAAAAAABBBBBBBAAAAAAABBBBBBB ...

In order to achieve this result, we operated with catalysts containing catalytic centres active for both monomers and at a temperature at which the average life-time of each macromolecule becomes sufficiently long.[10]

Operating at room temperature with stereospecific catalysts based on α-$TiCl_3$, the process was carried out as follows:

1. Polymerization of monomer A at a reduced pressure for a short time (5 min);
2. Complete elimination of the unreacted monomer A from the system (e.g. by evacuating or stripping with an inert gas);
3. Introduction of monomer B and polymerization for 5 minutes, at a reduced pressure;
4. Complete elimination of unreacted monomer B.

These four steps can be repeated at will with the same or with different monomers.

The average length of each block of monomeric unit A (or B) depends on the duration of each phase and on the polymerization rate of each monomer. Blocks of equal length can obviously be obtained by adjusting the concentration of the monomers and the time.

The crude polymers, obtained by successive polymerization of ethylene and propylene, show with X-rays the presence of crystals, some of

them having the structure of polyethylene, others having the structure of polypropylene. Amorphous portions join the portions of chains having different structure which belong to different crystals.

In Table 10 the results of the extraction of a crude block copolymer (propylene-ethylene) is compared with the extraction of crude polyethylene or crude polypropylene, obtained in similar conditions (alternating polymerization and evacuation steps, but operating with only one monomer).

The field of block copolymers of alpha-olefins with more or less long sections of certain monomeric units with a regular structure, is a new field of research which shows some very interesting aspects especially from a steric point of view.

Random Copolymers of Alpha-olefins

The properties of the random copolymers of alpha-olefins present some analogies with those of stereoblock homopolymers.

TABLE 10.

Polymer	*Fraction extractable by boiling ethylether* %	*Fraction extractable by boiling n-heptane* %	*Fraction extractable by boilin n-octane* %	*Residue from extraction* %
Ethylene-propylene copolymer	1	16.5	30.5	52
Polyethylene	2	4	65	29
Polypropylene	12	6	20	62

Small quantities of a different monomer introduced into an isotactic polymer reduce its crystallinity and lower the melting point, as happens for the presence of sterically different units in stereoblock homopolymers. Higher quantities (e.g. higher than 20–25 per cent) make the copolymers amorphous.

As a rule, by using some typical Ziegler catalysts one obtains products containing mixtures of macromolecules comprising copolymers having a very large range of composition, together with homopolymers. Instead the products obtained by continuous polymerization, either with certain catalysts containing only one type of highly stereospecific, active centres, or with certain non-stereospecific catalysts

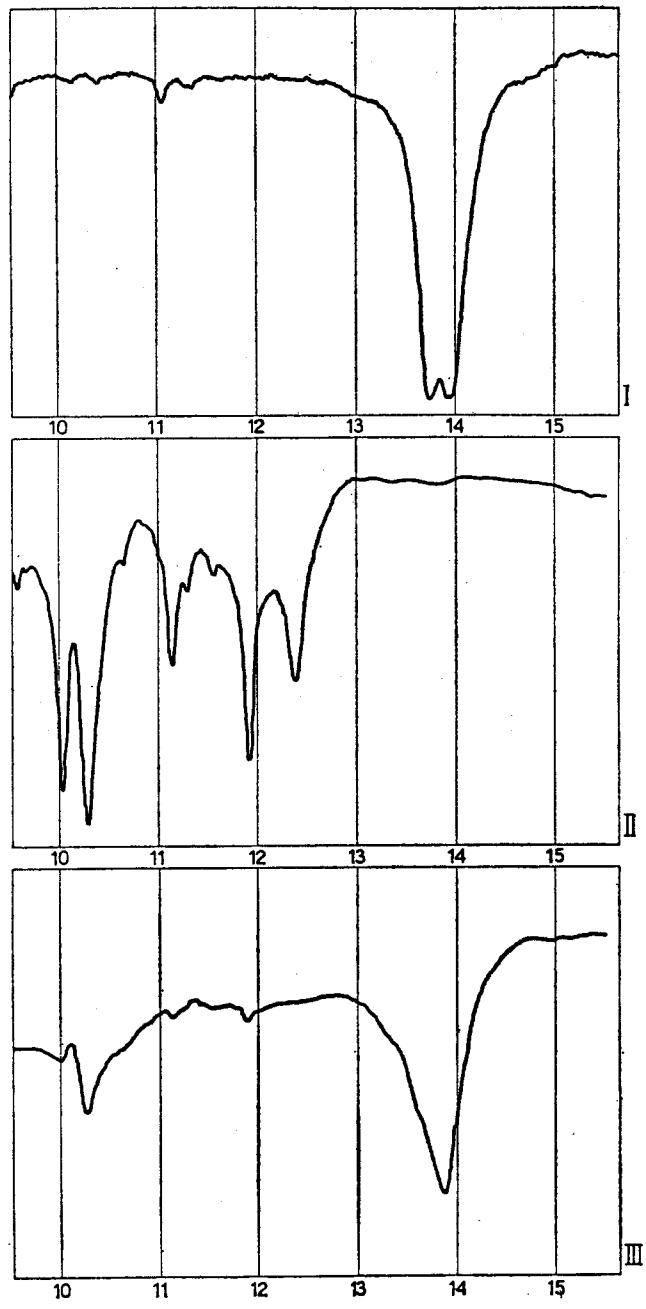


FIG. 2. Comparison of I. R. spectra, between 9.5 and 15μ, of a linear polyethylene (I), of a fraction of polypropylene insoluble in ether but extractable in n-hexane (II), and of a corresponding fraction of ethylene–propylene copolymer containing 60 mol % of ethylene (III). Thickness of the samples 0.1 mm.

(e.g. those obtained from VCl_4 and trihexyl aluminum), are constituted only of copolymers and are free of homopolymers.

The above mentioned facts have been demonstrated by us by carrying out some accurate fractionations of the copolymerization products and examining the properties of the different fractions.[11]

The amorphous copolymers of ethylene with propylene (obtained with VCl_4 and $Al(C_6H_{13})_3$ are completely soluble in boiling n-heptane. On the other hand, the polyethylene obtained using the same catalyst is

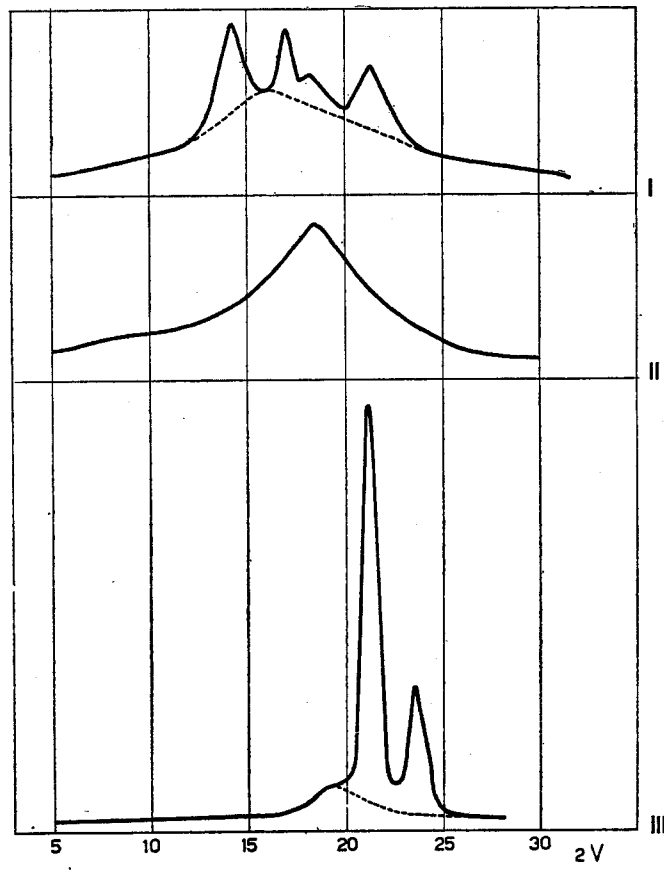


FIG. 3. Comparison of X-ray diffraction spectra of a fraction of polypropylene insoluble in ether, but extractable with boiling hexane (I), of a corresponding fraction of ethylene–propylene copolymer containing 60 per cent of ethylene (II), and of a linear polyethylene (III).

almost completely insoluble and the polypropylene is partially insoluble in boiling n-heptane.

The infrared spectra of the copolymer fractions isolated by different solvents, differ remarkably from the spectra of the corresponding fractions of propylene homopolymers and of pure polyethylene (Fig. 2).

The infrared spectrum of all the copolymer fractions show, for instance, absorption bands between 13.4 and 13.8 μ which can be attributed to the presence of sequences of methylene groups having different lengths.

Also, the X-ray examination confirms the nature of the copolymers prepared by us. The fractions which can be isolated by ether extraction are amorphous; the maximum in the diffraction intensity appears at a diffraction angle different both from that corresponding to the maximum for amorphous linear polypropylene, and from the maximum value which can be predicted for an amorphous polyethylene.

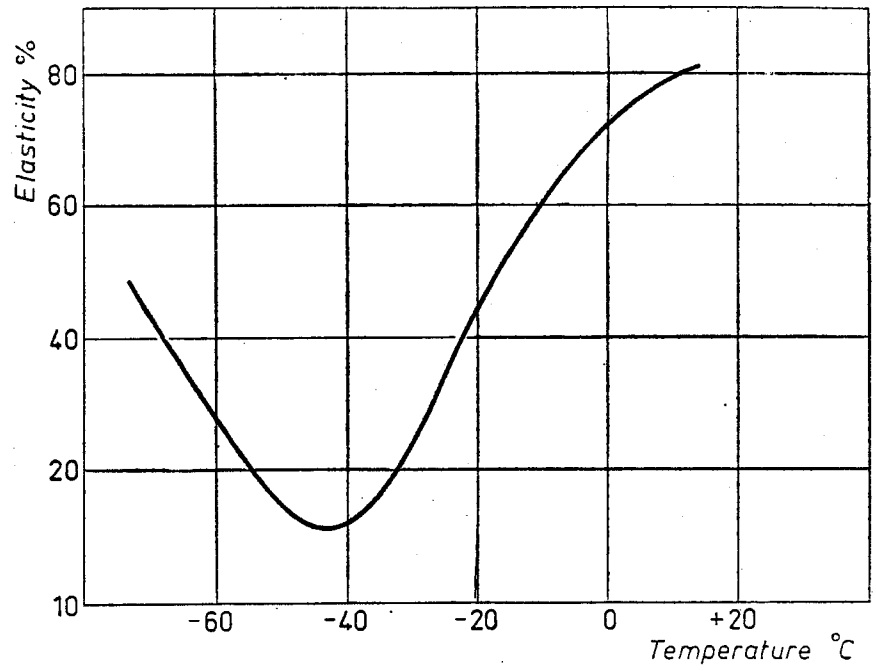


FIG. 4. Per cent of rebound versus temperature of an ethylene–propylene copolymer.

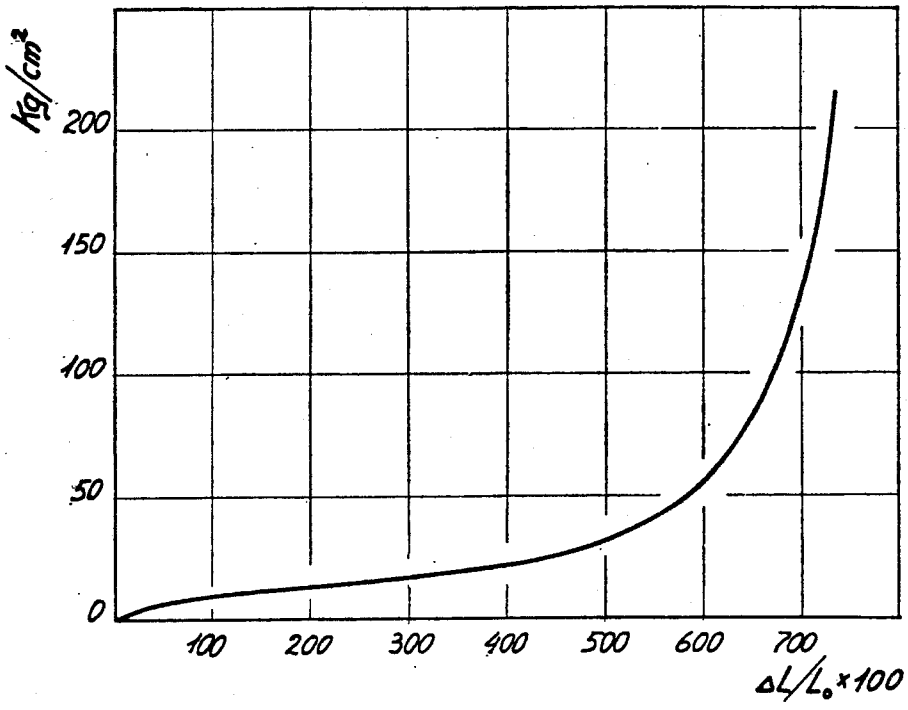


FIG. 5. Stress–strain curve of vulcanized ethylene–propylene copolymer without reinforcing agents.

Further, the fractions extractable by boiling hexane and heptane are, in general, amorphous by X-rays, while on the contrary, the analogous fractions obtainable from the propylene homopolymers present a remarkable crystallinity (between 30 and 50 per cent).

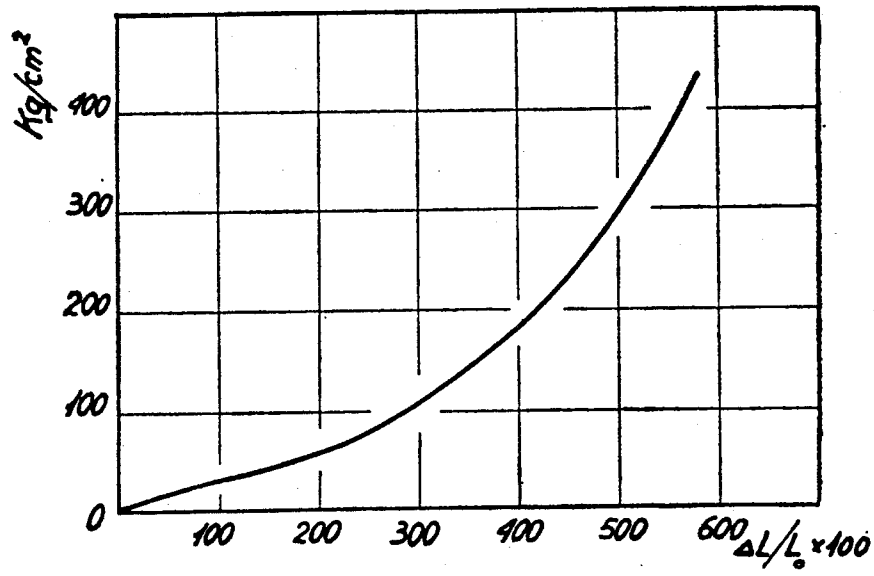


FIG. 6. Stress–strain curve of vulcanized ethylene–propylene copolymer with 45 parts of EPC black.

As an example, Fig. 3 shows a comparison between the X-ray spectra of a linear polyethylene, of an ethylene-propylene copolymer fraction, insoluble in ether but extractable by hexane, and of a corresponding fraction obtained from pure polypropylene.

The mechanical properties of the copolymers prepared by us are different from those of the homopolymers and from those of their physical mixtures. Amorphous copolymers can be used as raw materials for the production of good elastomers.[11-12]

Ethylene-propylene copolymers are in fact constituted of long linear hydrocarbon chains containing short sequences of methylene groups, having no tendency to crystallize in the unstretched condition.

These sequences confer a great flexibility on the chain. In the non-crystalline state the polyethylenic chain can, in fact, rotate around the CH_2—CH_2 bond. This rotation, at least for small angles with respect to the position of minimum potential energy, is hindered only by a low energy barrier.

The non-vulcanized polymers show, in fact, a visco-elastic behaviour which is very similar to that of the natural rubber and have a low second order transition temperature. They show low initial elastic moduli and high ultimate elongations. The temperature at which the resilience decreases, to reach a minimum, is near to that shown by natural rubber (Fig. 4).

The crosslinking of the ethylene-propylene copolymers can be suitably achieved by different methods and leads to vulcanized products

having excellent chemical resistance, high tensile strength and good elastic properties (Fig. 4).[13]

They can be reinforced with active fillers (such as carbon-black, and silica) or mixed with conventional plasticizers (Fig. 6). A 50 per cent propylene — ethylene copolymer having an intrinsic viscosity about 4, reinforced with 45 parts of carbon-black, shows, after vulcanization, tensile strengths of 300–400 kg/cm^2, ultimate elongations of 500–600 per cent, hardness of 60–70 degrees (Shore A) and a rebound, at room temperature, of 60–70 per cent.

In comparison with other elastomers, the ethylene-propylene copolymers, being constituted of substantially saturated macromolecules, have a high resistance to oxidation and aging; furthermore, they resist quite well the attack of many chemical reagents such as sulphuric acid, nitric acid, etc.

Influence of the Steric Structure on the Properties of the Diolefin Polymers

I shall briefly summarize the properties of the sterically regular polymers of diolefins, because the high number of the possible isomers and the great influence of the steric purity on the mechanical properties of the polymers enable us better to understand the great importance of stereoisomerism in the field of macromolecular chemistry (Table 11).

By stereospecific polymerization of butadiene we have been able to obtain, with different catalysts, the isotactic and syndiotactic polymers with 1,2 arrangement. They are both crystalline, but the syndiotactic polymers have a higher melting temperature.[3] The bulkiness of the lateral groups imposes a deformation on the zig-zag planar form of the main chain. Therefore one can predict a lesser stability of planar configuration for the syndiotactic polymers of butene and of the higher alpha-olefins, with respect to the stability of syndiotactic polybutadiene, on account of the larger size of the lateral saturated groups in comparison with the vinyl groups.

A decrease in the steric purity leads, both with isotactic and syndiotactic polymers, to a lowering of the melting point.

A fractionation of the isotactic and syndiotactic butadiene polymers yields a series of products in which both crystallinity and melting point decrease with decreasing steric regularity.

Generally, both the prevailingly isotactic or syndiotactic crude polybutadienes contain amorphous parts separable by ether extraction. It

is interesting to point out that the amorphous fractions in both cases show the same properties, corresponding to the properties of an atactic polymer with a 1,2 arrangement. In fact, an ideal atactic polymer corresponds to an ideal statistical distribution of the equally probable sterically opposite units. It may be considered as an intermediate case between the ideal isotactic polymer (ratio between inversion rate and chain growth rate equal to zero) and syndiotactic polymers (ratio equal to 1).

The atactic polymers with 1,2 arrangement are rubbers presenting a lower resilience than 1,4 polymers of the same monomer. They have, however, a higher resilience compared to head-to-tail linear polybutene. It must be noted that the isotactic polymers of butene are very similar, as far as concerns their structure and physical properties, to isotactic polybutadiene.[14]

The typical catalysts used for the synthesis of 1,2-polymers are those obtained from chromium soluble complexes having a coordinated bulky group containing oxygen (acetylacetonate) or nitrogen (carbylamines). The formation of isotactic and syndiotactic polymers depends on the molar ratio between aluminum alkyl and chromium complex used.

A comparison between the properties of the *trans*–1,4 and *cis*–1,4 butadiene stereoisomers, which differ from each other much more than the corresponding isoprene 1,4 stereoisomers, may be very interesting.

Trans–1,4 polybutadiene which can be obtained with a very

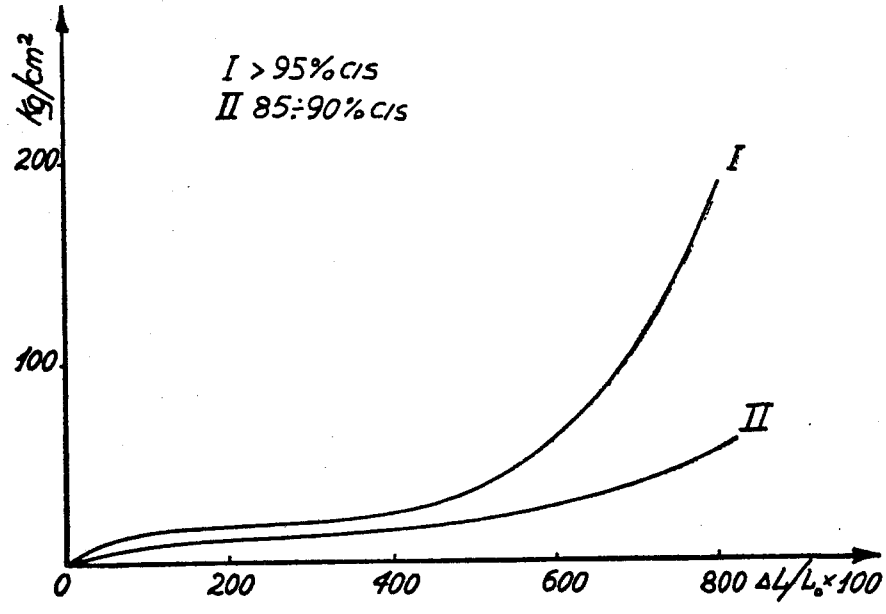


FIG. 7. Stress–strain curve of two vulcanized *cis*-1,4 polybutadienes.

high purity, with catalysts prepared from VCl_3 and aluminum alkyls, has a melting temperature of about 140° and another first order transition temperature, due to polymorphism, at 65° C.[15]

When the stereoisomeric purity decreases, the melting temperature decreases to values lower than 100°, and the other transition temperature reaches values which are lower than 65°. The *trans*–1,4 polybutadiene when extruded into filaments can be cold-stretched. The highly crystalline and oriented filaments thus obtained present properties which are similar, from some points of view, to those of the protein fibres of the muscles. In fact the reversible transformation of the crystals into other equally oriented crystals, by heating at a temperature of 65° C, is accompanied by contraction in the length of the chains identity period and, consequently, in the length of the fibres and may be accompanied by the production of mechanical work.

Samples of *cis*–1,4 polybutadiene with a steric purity of 95–97 per cent have a melting temperature of about 0° C, crystallize under stretching (400 per cent) and are still crystalline at a temperature of 80° C. They show properties which are very similar to those of natural rubber.

Figure 7 shows the stress–strain curves, for two polybutadienes, one having a purity of 96 per cent, the other of 87.5 per cent. The infrared

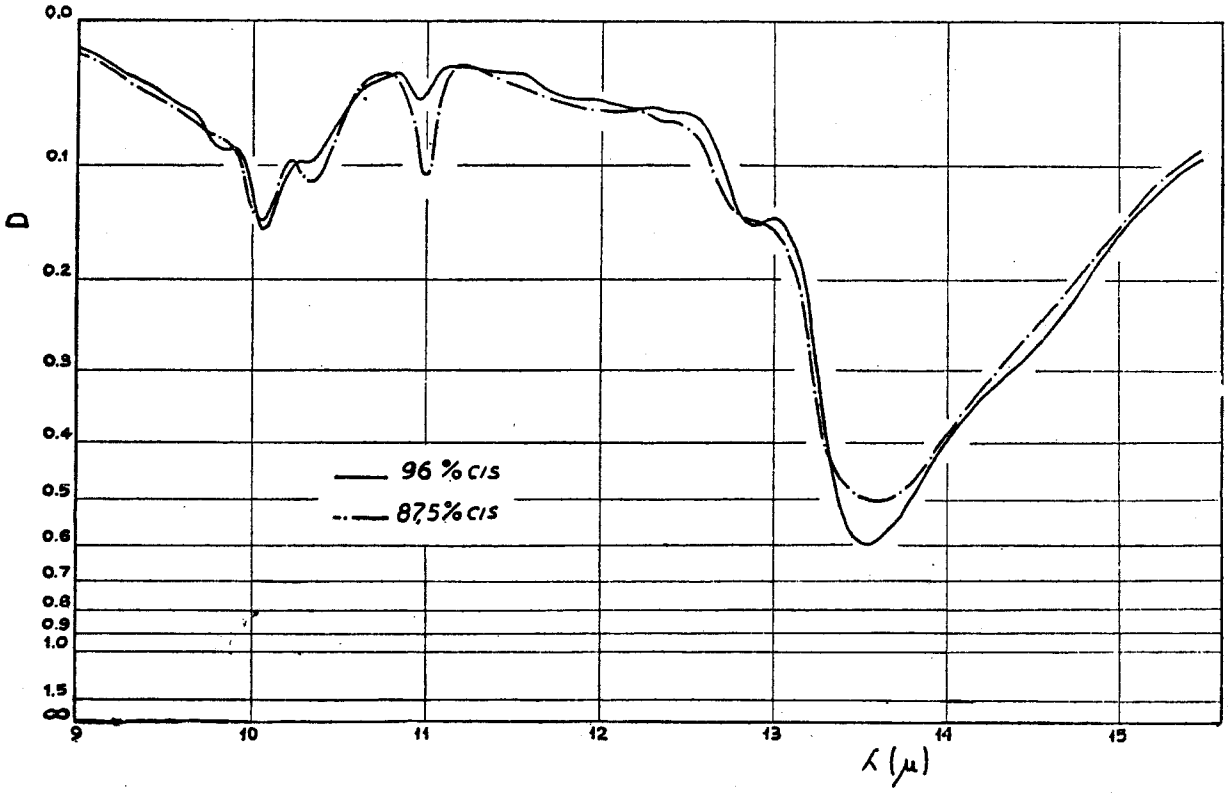


FIG. 8. Infrared spectra of two polybutadienes having high *cis*-1,4 content.

spectra of the two polymers are shown in Fig. 8. The coefficients used for the determination of the composition are different from coefficients used by other authors.[16] When adopting these last with the polymer prepared by us, a *cis*–1,4 percentage of 95 would result for the 87.5 per cent *cis*–1,4 polymer.

The different mechanical behaviour and the high tensile strength are due to the higher stereoisomeric purity which leads to a higher crystallinity under stretching and to a higher melting point.

New Plastics

Considerable importance is attached to stereospecific catalysis due to possible applications for several stereo-ordered polymers in the field of plastics. This is due to the fact that such catalysis makes it possible to investigate a vast new branch of macromolecular chemistry and to produce new classes of linear and highly crystalline polymers, so far unknown.

The practical difference between the crystalline polymers with very high molecular weight and the non-crystalline polymers (conventional polystyrene, polyvinyl chloride, etc.) is that these last polymers are brittle below the second order transition temperature and are rubber-like above this temperature. The crystalline polymers maintain high mechanical characteristics over the range between the 1st order transition temperature and second order transition temperature and, when oriented, even below this last temperature (Fig. 5 of paper 42).

From the practical point of view the most interesting polymers are highly crystalline polypropylene (m.p. 175° C) and poly-butene-1 (m.p. 136–140°C), because of the low cost of the monomers, immense amounts of which are available in the petroleum cracking gases, or cheaply available by pyrolysis of petroleum fractions or of natural gases.

Certain linear isotactic and low crystalline stereoblock polymers having high molecular weight are of particular interest, owing to their higher elasticity compared with that of the highly crystalline polymers.

They consist of macromolecules containing isotactic chain sections interspersed with atactic sections or with isotactic sections of opposite steric configuration. They show properties which can be varied gradually, depending on their stereoisomeric composition, from the properties of a hard, highly crystalline thermoplastic material, having a high tena-

TABLE 11. X-RAY DATA ON CRYSTALLINE POLYBUTADIENE–STEREOISOMERS

Polymer	*Space group*	*Number of monomers per unit cell*	*Cell dimensions* Å *a*	*b*	*Chain axis* Å *c*	α	β	γ	*X-Ray density*	*X-Ray melting point*
trans-1,4	(pseudohexagonal)	(1)	(4.54)		4.9				1.02	148°C
cis-1,4	*C*2/*c* (monoclinic)	4	4·60	9·50	8·60	90°	109°	90°	1·01	0°C
syndiotactic-1,2	*Pacm* (rhombic)	4	10·98	6·60	5·14	90°	90°	90°	0·96	155°C
isotactic-1,2	*R* 3*c* (hexagonal)	13	17·3	17·3	6·50	90°	90°	120°	0·96	125°C

city, to those of a less crystalline material, having mechanical properties like leather, and thence to still more elastic rubberlike materials (Fig. 9).

It is to be expected that, among the unlimited number of isotactic polymers obtainable from various vinyl monomers, practical interest will concentrate particularly on those whose monomers are more widely available or the synthesis of which will be possible at low cost.

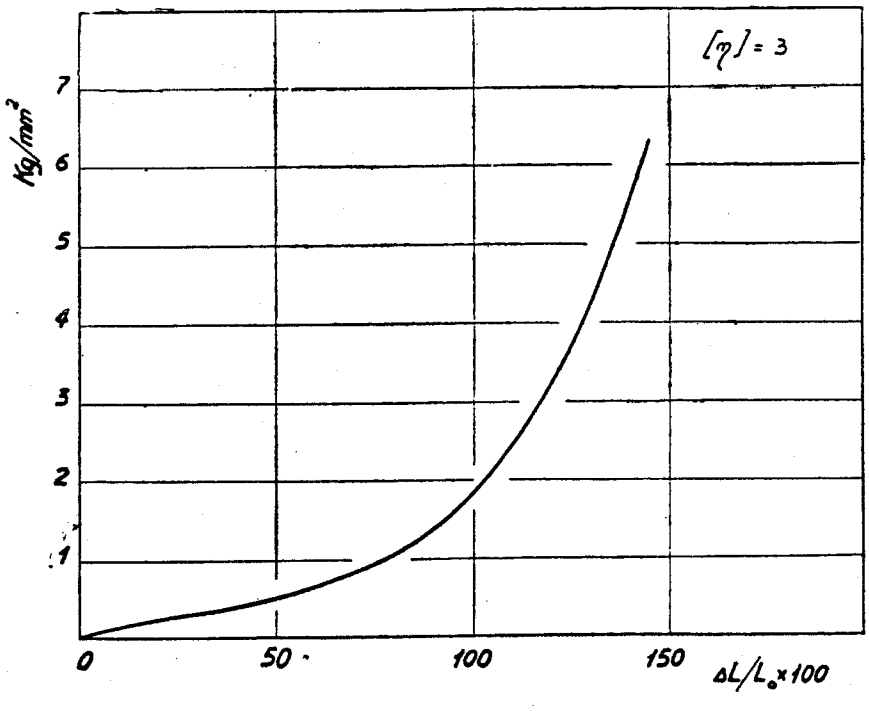


FIG. 9. Stress–strain curve of a stereoblock polypropylene (having intrinsic viscosity of 3) preoriented by cold stretching to an elongation of 700 per cent.

In the field of films, transparent crystalline products were obtained, both in the non-oriented and in the oriented state.

New Textile Fibres

Considerable practical interest is attached to the new field of possible application of isotactic polymers for production of textile fibres.

In the past the presence of hydrogen bonds or polar groups, which by association could oppose the viscous flow of the macromolecules, was believed to be a necessary condition for obtaining high strength fibres.

The discovery of highly crystalline isotactic polymers has shown that very high tenacity fibres can be obtained from macromolecules of pure hydrocarbons, free of hydrogen bonds and polar groups (Fig. 22 of paper 24).

The low cost of propylene, probably less than that of any other vinyl monomer, the high yield and ease of the low pressure polymerization, the direct production, by polymerization, of a highly crystalline material which, without any fractionation, can give directly by extrusion in the molten state filaments with a high strength, all these factors will make possible the production on a commercial scale of textile fibres whose production cost is likely to become, in the future, less than that of any other synthetic fibre, and of the main natural fibres.

The great lightness of polypropylene and the possibility of obtaining extremely soft staple fibres, provided with high thermal insulating property, but with a much higher mechanical strength than wool, open up wide possibilities of use for this new and very interesting textile material.

New Synthetic Elastomers

Another important applicative field of the anionic coordinated polymerization processes concerns, as already mentioned, the production of new synthetic rubbers.

The diolefin polymers with *cis*–1,4 arrangement may give rise to rubbers having very good elastic properties, and high resilience: *cis*–1,4 polyisoprene, synthesized in U.S.A., is practically equal to natural rubber. *cis*–1,4 Polybutadiene stereoisomers which crystallize under stretch, as natural rubber does, were prepared long since at the Polytechnic of

Milan. Subsequently products of high stereoisomeric purity have been obtained at the "Donegani" Research Institute of Novara. These polymers yield elastomers which show excellent elastic properties at very low temperatures and high tensile strength. The lower cost of butadiene in comparison with the cost of isoprene lets us foresee interesting possibilities for these new polymers.

A very different and entirely new class of synthetic elastomers, which will surely have a great future, is the one of the ethylene-propylene copolymers. Rubbers prepared from these copolymers show very low elasticity hysteresis values which approach closely those shown by natural rubber, and a very high tensile strength together with high elastic elongation.

The very low cost of the olefins from petroleum makes this new class of elastomers of distinct interest for the production of synthetic rubbers.

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PROBLEMS CONCERNING THE VISCOSITY OF POLYPROPYLENES IN SOLUTION

by G. MORAGLIO and F. DANUSSO

(27 May 1958)

[*Annali Chimica*, **49**, 902 (1959)]

ABSTRACT

Viscosimetric values and behaviours of polypropylene solutions are normal for polymers directly derived by synthetic routes. By fractionating raw samples, however, it is possible to separate polymers having fairly high intrinsic viscosities, for which deviations from Newtonian behaviour might occur.

The influence of the velocity gradient on the viscosity of polypropylene fractions in dilute solution, has been examined. For this purpose, a new viscometer was constructed, which enabled us to perform measurements more easily than with other analogous apparata proposed so far.

On the basis of the viscosimetric data, a study was made to establish the suitable order of solvents power in polypropylene solutions.

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STEREOSPECIFIC POLYMERIZATION OF ACETYLENE

by G. NATTA, G. MAZZANTI and P. CORRADINI

(10 June 1958)

[*Rend. Accad. Naz. Lincei* (8) **25**, 3 (1958)]

ABSTRACT

The polymerization of acetylene with $AlEt_3$ and violet $TiCl_3$ yields a mixture of products which are partly oily and soluble in acetone, and partly consist of an almost insoluble solid polymer with a weak order of crystallinity, shown by X-rays (Table 1).

The hydrocarbon soluble catalysts, prepared from alcoholates of transition metals and from organometallic compounds, polymerize acetylene to high yields (98.5 per cent). The percentage of oily products is very low when operating with high ratios of catalyst to monomer. From the runs reported in Table 2 it results that:

(1) the yields of polymer with respect to the catalyst are of the order of 2g/g of catalyst.

TABLE 1. TYPICAL POLYMERIZATION RUNS OF ACETYLENE WITH CATALYSTS PREPARED FROM TRIALKYL ALUMINUM AND FROM SEVERAL MODIFICATIONS OF TRANSITION METAL TRIHALIDES HAVING A LAYER LATTICE

Halide		$Al(C_2H_5)_3$ *moles*	*n-heptane* cm^3	*Time hr*	*Temperature* °C	*Polymers Obtained g*	*Acetone extractable products %*
type	*moles*						
α-$TiCl_3$	0·05	0·05	400	10	35–40	21	18
α-$TiCl_3$	0·05	0·05	400	20	35–40	24	20
VCl_3	0·04	0·10	500	10	40–45	25	65

TABLE 2. POLYMERIZATION OF ACETYLENE WITH CATALYSTS PREPARED FROM HYDROCARBON-SOLUBLE ORGANOMETALLIC COMPOUNDS AND TITANIUM ALCOHOLATES

Organometallic compound		*Titanium alcoholate*		*Solvent*		*Polymerization conditions*		*Polymer obtained g*	*Acetone-extractable Oily Products: %*
type	*moles*	*type*	*moles*	*type*	*cm³*	*T, °C*	*Time, hr*		
$Al(C_2H_5)_3$	0·1	$Ti(OC_3H_7)_4$	0·04	n-heptane	500	45	15	35·5	4·5
$Al(C_2H_5)_3$	0·1	$Ti(OC_3H_7)_4$	0·04	"	500	75	15	48·5	11·1
$Al(C_2H_5)_3$	0·1	$Ti(OC_3H_7)_4$	0·04	"	500	—20	10	4	3·5
$Al(C_6H_{13})_3$	0·05	$Ti(OC_4H_9)_4$	0·025	"	300	50	15	35	10·0
LiC_5H_{11}	0·14	$Ti(OC_3H_7)_4$	0·02	"	250	60	20	6·4	18

(2) with the use of triethyl aluminum or trihexyl aluminum or n-pentyl lithium, the type of polymer obtained does not vary, but the yields are lower when the lithium alkyl is used.
(3) the reaction rate increases with the increase in temperature from —20° to 80°C.

The X-ray spectrum of the polymer shows a typical band of crystallinity and it lacks those characteristics of strongly cross-linked polymers. The infusibility and insolubility of the acetylenic high polymers prevented the preparation of oriented fibres.

A strong peak, for a lattice distance $d_1 = 3.65$ Å, was observed in the powder spectrum of polyacetylene in addition to less-defined broad bands attributable to an amorphous substance. Since a pitch for a lattice distance $d_2 = 2.11$ Å ($d_1 = \sqrt{3d_2}$) is observed in higher angular regions, one can suppose that those reflections derive from lattice planes perpendicular to the axes of the linear chains, packed in a pseudo-hexagonal lattice, having relative distances of 4.22 Å $= 2/\sqrt{3d_1} = 2d_2$.

On the basis of calculation of the average periodicity along the chain axis for monomeric unit, using the value of the experimental density (about 1.10g/cm^3), one can expect that the bonds along the chain are chiefly of the *trans*-type.

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STRUCTURE OF LINEAR LOW POLYMERS OF ACETYLENE

by E. LOMBARDI and L. GIUFFRÈ

(10 June 1958)

[*Rend. Accad. Naz. Lincei* (8) **25**, 70 (1958)]

ABSTRACT

This is a study of the structure of linear low polymers of acetylene obtained by solvent extraction from polyacetylene prepared with the aid of catalytic systems similar to those generally used in the stereospecific polymerization of alpha-olefins.

The u.v. adsorption spectra of polymers obtained in the various runs resulted to be practically equal among themselves. An analogy was also observed with some polyenes of the type: CH_3—$(CH=CH)_n$—CH_3.

This evidence, supported also by the chemical behaviour of the examined low molecular-weight polyacetylenic fractions, allowed us to conclude that these polymers contain chains with conjugated double bonds, of the type: $(—CH=CH—CH=CH—CH=CH—)_n$.

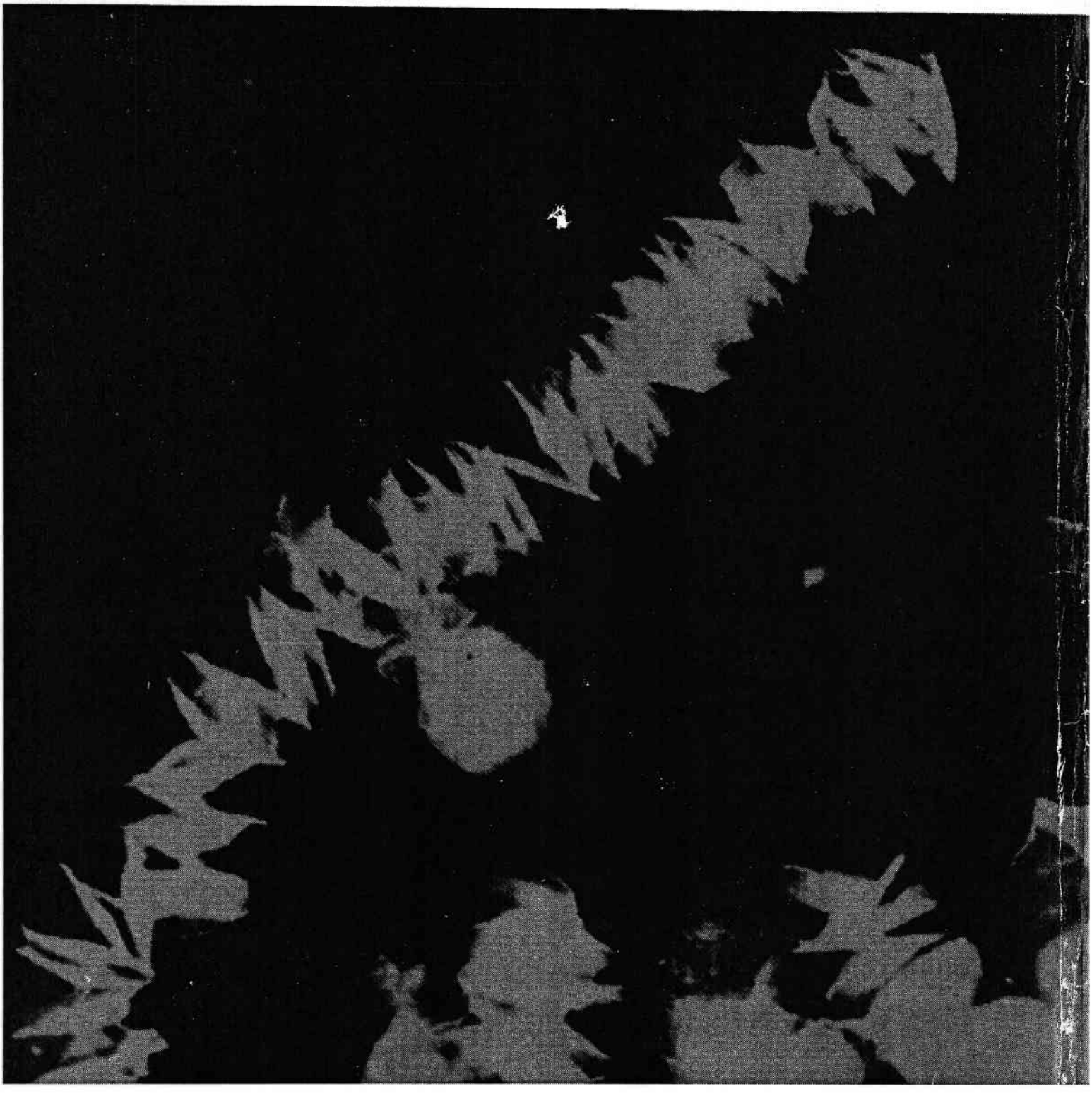
Stereoregular Polymers and Stereospecific Polymerizations

The Contributions of Giulio Natta and his school to Polymer Chemistry

Volume 2

Edited by G. Natta and F. Danusso

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83

SPHERULITIC AND POLYHEDRITIC STRUCTURES OF ISOTACTIC POLYSTYRENE

by F. DANUSSO and F. SABBIONI

(26 June 1958)

[*Rend. Ist. Lomb. Sci. e Lettere* **A92**, 435 (1958)]

ABSTRACT

The morphology of some crystallite aggregates that can be obtained from isotactic polystyrene by melting and cooling was studied by means of a hot-stage polarizing microscope.

Depending on the crystallization conditions, isotactic polystyrene, recently obtained by stereospecific polymerizations, crystallizes yielding either aggregates of the spherulitic type or other polyhedral bodies for which the term "polyhedrites" is proposed. The spherulites observed were of the type already known in other crystalline polymers having a needle-like structure; this can be either achieved with simply radiating needles or sometimes with concentric rings arising from a secondary rearrangement.

Polyhedrites are aggregates similar to spherulites in dimensions, but limited by a polygonal contour, either hexagonal or star-shaped dodecagonal. Polyhedrites have never been observed before in the organic high polymers. They have the following properties: (a) they are formed into isotactic polystyrenes having a medium molecular weight, when the length of the polymeric chains is of the order of magnitude of the longitudinal dimensions of the crystallites; (b) if well shaped (single crystals?) they are optically empty when observed by polarized light with crossed Nicols; (c) they reach forms consistent with the symmetry of

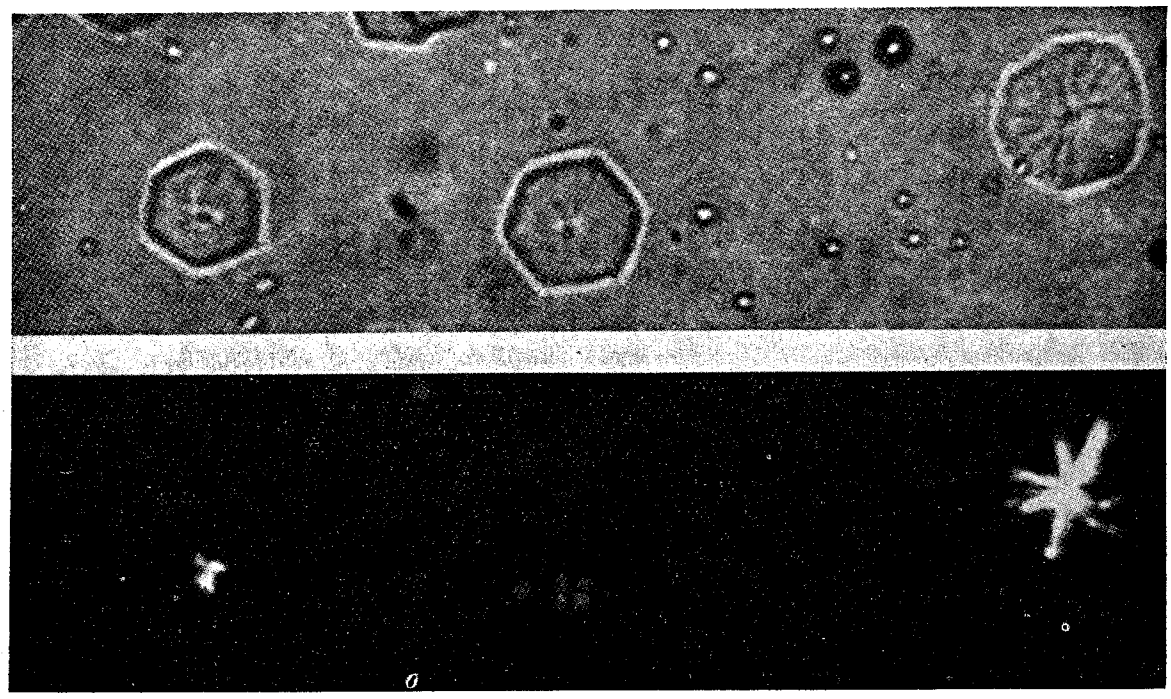


FIG. 1. Hexagonal polyhedrite (in the middle) and others partially formed (at the sides) observed by polarized light with paralell Nicols (top) and crossed Nicols (bottom) (×220).

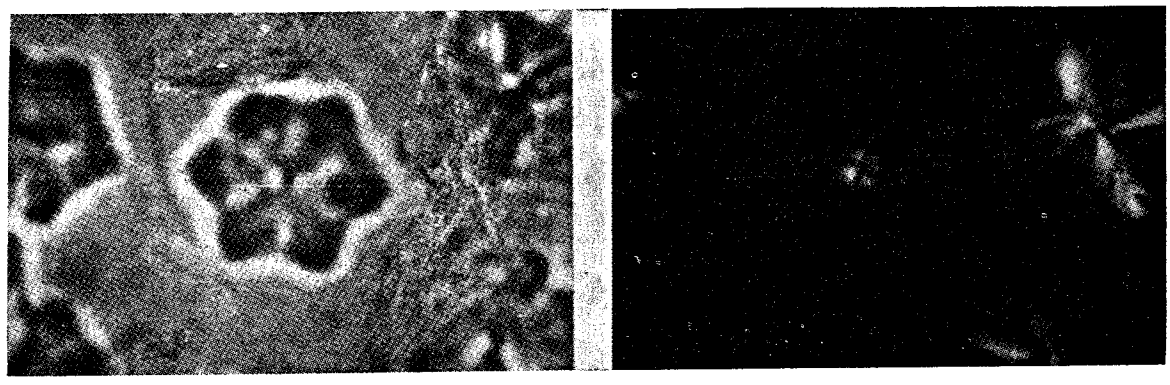


FIG. 2. Star-shaped dodecagonal polyhedrites observed with normal light (left), and with polarized light with crossed Nicols (right) (×600).

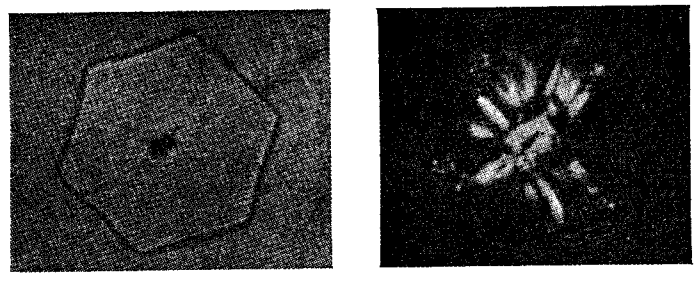


FIG. 3. Hexagonal polyhedrite with regular contour, observed with normal light with phase contrast (left) and intense polarized light with crossed Nicols (right) (×180).

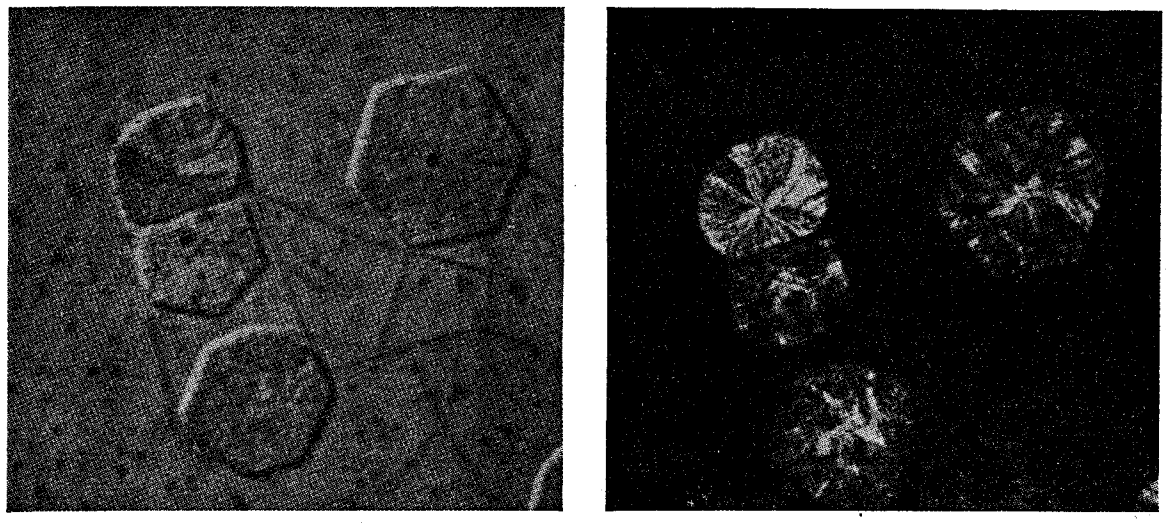


FIG. 4. Spherulites and polyhedrites having high thickness, observed with reflected light (left) and with intense polarized light with crossed Nicols (right) (×40).

the crystallographic unit cell. All this should demonstrate that polyhedrites are nothing but large regular crystallite aggregates, which are extraordinarily well-developed in the directions normal to the crystallographic *c* axis, by a parallel juxtaposition of the helicoidal macromolecular chains.

Figures 1–4 show some examples of polyhedrites observed both with normal light and with crossed Nicols.

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STEREOSPECIFIC POLYMERIZATION OF STYRENE. NOTE III: KINETICS WITH CATALYSTS FROM $Al(C_2H_5)_3$ AND $TiCl_4$

by F. Danusso, D. Sianesi and B. Calcagno

(June 1958)

[*Chimica e Industria* **40**, 628 (1958)]

ABSTRACT

A kinetic study of some principal aspects of the polymerization of styrene to isotactic polymer, with catalysts prepared by reacting $TiCl_4$ and $Al(C_2H_5)_3$, in constant molar ratio and in benzene solution, was made possible by carrying out experiments under uniform and selected conditions. The overall process is a complex one, with an apparent high order of reaction. However, it has been proved to consist of a polymerization reaction and of a parallel process, which modifies the activity of the catalyst. Polymerization as such is first order with respect to the amount of catalytic reagents introduced and to the monomer concentration. The process of aging of the catalyst during the polymerization can be interpreted as a decrease of its activity following a function of the time and not a function of the monomer concentration. In the conditions chosen in this work, for a series of experiments, this process was found to be of the first order with respect to the catalyst concentration.

Accurate measurements of initial reaction rate were performed by a suitable apparatus, by which the heterogeneous reaction mixture could be transferred directly in a capillary dilatometer in the same thermostatic bath (see fig. 2 of paper 52).

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PRESENT SITUATION AND PROSPECTS OF THE ITALIAN CHEMICAL INDUSTRY — HIGH POLYMER DEVELOPMENTS

by GIULIO NATTA

(June 1958)

[*The Canadian Journal of Chemical Engineering*, **114** (1958)]

The present and the future situation of the Italian chemical industry is the topic I am going to deal with especially from the point of view of its historical, economic and evolutionary bases. I shall neglect all statistical data concerning the various chemical productions, since they are reported in many other publications.

In this short paper I shall try to give an idea of how the Italian chemical industry started and progressed in the last decades, what is the present stage of evolution and especially the trends of its future developments.

I hope that this outline will be of interest: I will try to demonstrate how a spirit of enterprise, hard work and confidence has overcome the initial difficulties.

THE PRESENT SITUATION AND ITS ORIGIN

The Italian territory is neither rich in coal-fields (only very low grade lignites are available at very high cost) nor in petroleum and in important metallic ores, with the exception of bauxite and iron pyrites.

It is well known that the primary factors promoting the progress of the chemical industry are the availability of raw materials and the general technological level. In Italy, raw materials are very few. We can

say that the Italian chemical industry started using air, water, salt and pyrites as raw materials; plants were initially located where power was locally available or where it was possible to use seasonal surplus of hydroelectric power.

The availability of electric energy not only made it possible to start certain electrolytic productions, like those of chlorine, soda, aluminium, but also of synthetic ammonia (in 1924) from electrolytic hydrogen, and of methanol (in 1928) from synthesis gas. The latter was produced in the continuous low temperature coal gasification plants, which were the first in the world that used oxygen, obtained as a by-product of electrolytic hydrogen production or of nitrogen production by air fractionation. The local availabilities of power were taken up in more economically rewarding uses, as the civil consumption was growing, the country being in a development phase. Therefore, power became ever less available to the chemical industry.

In a densely populated country, like Italy, where tillable areas are limited, though extended to the most impervious and least fertile mountainous districts, it was obvious to focus research on the field of phosphatic fertilizers (needed in soils depleted by thousands of years of cultivation) and of nitrogen fertilizers. The latter field promoted the growth in the 1925's of the great chemical industry in Italy.

From this starting platform, the Italian chemical industry, in the period between the two World Wars, developed toward more complex productions, like dyestuffs and pharmaceuticals. At the same time, rayon was manufactured on a large scale; its production was favoured by the existing textile industry of natural fibres. Thus Italy became one of the leading exporters of this cellulose fiber.

In that period, Italy also made great strides in the production of ammonia, calcium carbide, inorganic and organic acids and calcium cyanamide.

Although the Italian chemical industry started later than in other European countries, it developed some original concepts and techniques, which, in some instances, contributed to the development of the world chemical industry. Such contribution is considerably greater than would have been predicted by the sole consideration of the limited Italian productions.

As an example, we quote the high pressure synthesis processes (ammonia, methanol) developed in Italy and the manufacturing units connected with them, which led to the construction of several plants in Europe, America and Asia.

In the years immediately before World War II the Italian chemical industry had tackled new advanced problems. Hydrocarbon hydrogenation plants were then built in Bari and Leghorn, where some very heavy Albanian crude oils were used. The main purpose of these industries was the production of fuels (thus they were not strictly petrochemical plants), but there was already a trend to utilize certain by-products to yield chemicals.

In the field of synthetic rubber, a plant was built in Ferrara in 1938 for the production of butadiene from alcohol and Buna S. This plant comprised a unit, the first in the world, that allowed the separation by extractive distillation of substances, like butadiene and butylene, having about the same boiling point. A plant for the manufacture of Buna S starting from calcium carbide was being built in Terni, when the war broke out and the work was interrupted.

The development of the Italian chemical industry was halted also in the first post-war period, when all efforts were directed to rebuild the productive structure of the whole country. Thus in 1945—46 the chemical production dropped to figures much below those of 1938.

In the last 10 years, the Italian people with great energy and capacity for work, have not only rebuilt their towns and industries, but have also increased production and welfare to a level exceeding considerably that reached before the war, as indicated by the monetary values shown in Table 1.

In the meantime, a deep change in the old conceptions on the raw materials suitable for the chemical industry took place in Italy, probably before that in other European countries.

Before the war, the European chemical industry was mostly based on coal, whereas petroleum was neglected. However, two new and important factors arose: the availability of new raw materials and the development of olefin chemistry.

TABLE 1.
ITALIAN CHEMICAL PRODUCTION

Year	*Value in billions of Lira (present value)*
1938	414
1948	414
1958	1160

After 1947, gas oil fields were found and exploited in Northern Italy. Table 2 shows the production from 1948 to 1957.

TABLE 2.
ITALIAN PRODUCTION OF NATURAL GAS

Year	*Millions of Normal cubic meters*	*Millions of Standard cubic feet*
1948	113	4,210
1949	240	8,950
1950	490	18,300
1951	930	34,700
1952	1,380	51,500
1953	2,200	82,000
1954	2,870	107,000
1955	3,490	130,000
1956	4,300	160,000
1957	4,820	180,000

In addition, the recent increase in oil production in the Middle East, the ever more efficient and economical transportation means and, last but not least, the geographical position of Italy, have allowed the development of a petroleum industry that now reaches an approximate capacity of 30 million tons of crude per year. This has opened up new possibilities for the chemical industry.

The technique of obtaining chemical products from gaseous or liquid hydrocarbons was mostly developed in the U. S. A. during the war, while it was almost unknown in Europe where, instead of using the petroleum hydrocarbons as raw material for chemical syntheses, years of work were spent to attain the opposite goal, namely synthetic gasoline. That conception and the rationalization of chemical engineering are rightly considered a major contribution by the U.S.A. to the development of the chemical industry.

After the war, chemical production from hydrocarbons was developed in Italy. Italian people again showed considerable energy and spirit of enterprise and further contributed to the progress of chemistry. Two main trends were followed: the study of chemical derivatives of natural gas, which, in Italy, is practically pure, sulphur-free methane, and of the derivatives of olefins obtained from petroleum.

The former is more important from a quantitative point of view; it was used to produce ammonia, then methanol, acetylene, hydrocyanic acid and some chlorinated solvents. By 1949 the problem of the chemical utilization of methane, as far as was possible, was reviewed. The products that might be obtained and the corresponding processes were re-examined. Not all known processes could be realized in Italy. It was therefore necessary to create suitable processes.

Pilot plants were built, and at the end of 1951 the design of two great factories was completed; they started working in 1953. Ever since, the ammonia production in Italy has been increasing, as shown in Table 3. Other plants, for an additional production of 180,000 metric tons per year, are now in an advanced stage of construction.

TABLE 3.
ITALIAN PRODUCTION OF AMMONIA

Year	*Metric Tons*
1952	237,000
1953	294,000
1954	361,000
1955	424,000
1956	484,000
1957	484,000

At the same time, the whole methanol production, which had been based on coke gasification, was shifted to methane as raw material: Table 4 shows the increase in methanol production from 1952 to 1957.

TABLE 4.
ITALIAN PRODUCTION OF METHANOL

Year	*Metric Tons*
1952	13,500
1953	14,700
1954	24,400
1955	31,600
1956	32,300
1957	38,600

The production was also started of hydrocyanic acid, acetylene, and chlorinated derivatives as well as of synthetic rubber based on butadiene and styrene: for this last, the construction of a plant, situated near a natural gas deposit, is nearing completion. Its output is expected to reach 35,000 metric tons per year. The process, developed by an industrial group sponsored by the Italian Government, was initially based on butadiene derived from acetylene obtained from natural gas by partial combustion.

The residual gas from acetylene production is then converted into ammonia. This process was later modified to use acetylene for production of vinyl compounds and, starting from petroleum refinery gases, to produce butadiene. It was courageous to build a GRS plant whose capacity exceeded the Italian consumption, especially at a time when some revolutionary changes were in view in the field of synthetic rubbers.

In Italy, acetylene from natural gas is converted into polyvinylchloride and into acetaldehyde. The production of these will certainly increase in the future.

Approximately 12 per cent of the Italian production of natural gas is now utilized for chemical purposes. No other country in the world reaches such a high percentage. In the United States, where the utilization of natural gas for chemical purposes dates back to almost 25 years ago, it is only 3:% it must be borne in mind that natural gas is not the only fuel existing in the U.S. (as it is in practice in Italy): the U.S.A. reach the highest world production of crude oil and have three quarters of the world coal reserves.

As already said, another branch of chemistry progressed considerably after the war, i.e. that of high polymers and particularly of olefins. Among them ethylene, obtained from suitable fractions of liquid hydrocarbons, held the supremacy. These processes, based on petroleum had already reached a high development in the United States, but in 1949 it was still unknown in Europe, where many and more basic problems had to be solved, such as food production, transportation, supplies, housing and the like.

Italy was one of the first countries in continental Europe that decided to build up a petrochemical industry in 1949.

The utilization of olefins preceded their production from petroleum sources. The raw materials were at that time obtained by emergency methods: the main raw material, ethylene, was obtained from ethanol. When the olefin production plants in turn were completed, plants were

ready to absorb their production. This was essential for the economy of such expensive plants and brought about a great advantage in the economy of the whole scheme.

Thus, in 1952 the first part of the program based on 10,000 tons per year of ethylene and of the same quantity of propylene was carried out. In this way the first post-war production of high pressure polyethylene started in continental Europe.

All this describes the situation of the Italian chemical industry and shows glimpses of the problems presented by its development. It includes also the bulk of traditional chemical plants which were rapidly rebuilt after the heavy damages of the war on the basis of their original design. This enterprise received great help from natural gas which, in the meantime, became available.

In this connection, the Italian ammonia and nitrogen fertilizer production methods deserve special mention, because now about a quarter of the world nitrogen production is obtained by the Italian processes by Fauser-Montecatini or Casale. The plants built all over the world according to these processes number several hundreds and the relevant investment is estimated to be around 1300 million dollars.

Many Italian processes show the characteristic tendency to economize on electrical and thermal energy consumptions.

Due to the fact that many important chemical reactions employed in the industry are exothermic, in many cases the heat of reaction has been employed for the production of steam; in the past, not only heat was wasted, but cooling water was required. It is common practice in Italy now to recover one ton of steam per ton of sulphuric acid produced or 0.85 ton of steam per ton of ammonia produced.

The same ideas were extended also to industrial processes of organic chemistry. To give an example I wish to mention the new plant (which came under my personal attention) for the production of formaldehyde by complete oxidation of methanol in a one step process and with a 90–92 per cent yield of theoretical.

In this plant, we not only eliminated the steam consumption needed in old plants, but we achieved a production of 0.4 tons of steam per ton of formaldehyde solution produced. Its capacity is of 70 tons/day. The principles of American industrial automation were applied to this plant so that it is run by one man only.

In 1952, the production of petrochemical derivatives and of polymers enhanced the existing basic situation already described. This new

production of organic chemicals was carried out with the methods and in the quantities characteristic of the so called heavy chemical industry.

The first PVC plant outside Germany was built in Italy in 1936. Its capacity was, initially, 1200 tons/year; now the total PVC capacity in Italy is of 50,000 tons/year; and the methods of production have been improved.

The factors favouring the rapid growth of the heavy organic chemical industry are, on one hand, the continuously improving experience in the production of olefins and derivatives, and on the other hand the development of new uses and of new end products.

The capacity of the ethylene production of the Ferrara plant is now being increased from the initial 10,000 to 40,000 tons/year. Other plants, which are now being built or are in the design stage will add a further 50,000 tons/year capacity in the near future.

THE FUTURE

Before examining the future prospect of the Italian chemical industry, I wish to give a rapid survey of the present situation of "man-made" fibres.

The production of these fibres is indicated in Table 5. The data reported for 1958 were obtained by multiplying the January production by twelve; therefore they cannot give an exact idea of the development of such industry. In fact many new plants are in an advanced stage of construction or have been recently put in operation.

A forecast of the far future can in general hardly be done; it has been called crystal-gazing. This is even truer in the chemical field, where new solutions of old problems, new approaches and new discoveries may revolutionize old beliefs and old programs. The evolution of the chemical industry is rapid: what was known yesterday by only a few, or is today pioneering work, will tomorrow become an established practice, if it is not even made obsolete by the rapid march of progress.

The contribution to progress of every country is different and framed in its own environment; it is pushed by the particular needs and depends on the evolution of the country itself.

The Italian chemical industry, which from its birth has been living under hard conditions, has nevertheless pioneered in some fields with new original conceptions. This is remarkable considering that any new chemical process developed in the laboratory requires noticeable efforts and a lot of money to be transformed to a commercial scale. Certainly

TABLE 5. ITALIAN PRODUCTION OF MAN MADE TEXTILE FIBRES

	1947	*1952*	*1957*	*Jan. 1958 × 12*
Cellulosic Artificial Fibres				
—Viscose	5,597	75,191	126,334	119,880
—Acetate	69	2,477	7,996	9,058
—Cuprammonia process	48	1,910	2,680	2,988
	5,714	79,578	137,010	131,926
—Casein Fibres	—	893	5,616	5,910
Synthetic Fibres				
—Polyamides	17	1,249	9,027	12,087
—Polyesters	—	—	480	1,090
—Polyvinyl	—	—	977	1,100
	17	1,249	10,484	14,277
Total of Man-Made Fibres	5,731	81,720	153,110	152,113

the future situation will depend on the progress that is now being made and progress is a consequence of fundamental research in Italy and abroad. The results of the research done today will determine the future aspects of industry.

These results however depend on many factors, some of which cannot be foreseen. At present, research centres have at their disposal modern and effective investigation methods and equipment: however, brilliant brains are still essential to open new fields of fundamental and practical importance.

While fundamental discoveries are made by naturally gifted men, helped by collaborators, the development of commercial plants is rather the result of team-work.

Besides, several years are required in the chemical field to move from the first laboratory conception to commercial production. This is due to the fact that chemical technology is not yet well defined and presents many variables, and that the theory of mechanical models is, in general, not valid for chemical equipment. As a consequence, two or even more stages of pilot plants are necessary before making the commercial production possible.

The increasing national and international competition, which will be speeded up in Europe by the creation of the Common Market, will

induce the chemical industry to take part in a competition for research and progress. The present expenses (ranging from 3 to 5 per cent of the total sales), incurred for research by the leading chemical industries, are bound to increase. At the same time, all possible ways to improve research well be tried. Profitable results in this field may or may not be achieved, but it is certain that the general effect is imposing. No other industry is moving forward as rapidly as the chemical industry.

Chemical progress, as already said, is based on research. However, research depends on another fundamental prerequisite: i.e. education.

In Italy, technical schools, such as the schools of engineering and, in particular, the chemical engineering department of the Polytechnic Institute of Milan differ, in certain respects, from analogous schools in other countries which, especially in North America, have a marked tendency toward specialization.

Our programs are very wide and we try to give our students a theoretical background as many-sided as possible. Of course this prevents a thorough specialization in given fields. At the end of our academic courses, chemical engineers have also a good knowledge in mathematics and in mechanical and civil engineering. In addition the possibility is given to our undergraduates to undertake some basic research.

This course seems the most suited to train people having a bent for research.

The department of chemical engineering of the Polytechnic Institute of Milan has been, for several decades, one of the main forges of the technicians employed in the Italian chemical industry and in chemical research laboratories. The research laboratories of the Milan Polytechnic have always had the help of the Italian chemical industry and in turn have made a good contribution to its development.

Studies made in the field of catalysis and of the kinetics of chemical reactions, taking into account the actual operating conditions of industrial plants, led to a better understanding of the mechanism of certain processes. Then fundamental contributions were made to achieve the best rational solutions in the design phase of process and operation units for industrial plants.

The kinetic study of the mechanism of catalysis and the study of catalyst structures done at the Milan Polytechnic led to original and rational solutions of the problems concerned with the methanol synthesis and oxosynthesis reactions and also with the economical production of formaldehyde in large scale units.

The studies on synthetic rubber made at our Polytechnic before World War II led to original processes, which were then developed in the first Italian factory in this field. Thus the first unit in the world was built to separate by physical methods, butadiene from butylene, by extractive distillation.

Finally, an important result obtained from the research carried out at our Polytechnic by scientific methods contributed greatly to the production of new macromolecules.

Such contributions were made by the X-ray Dept. (which developed high level research on the lattice structures of organic substances and of complex catalytic systems), by the departments specializing in organic synthesis, kinetics of chemical reactions, infrared spectrography and macromolecular physical chemistry.

The co-operation of specialists in the various fields led to results of a fundamental scientific character; thus the basic requisite for the subsequent commercial development has been the discovery of stereospecific polymers, such as the isotactic and syndiotactic ones, the determination of their structure, the preparation of highly stereospecific catalysts which allow us to obtain at will high yields of polymers with the desired steric structure, the synthesis of high purity isotactic polymers, of stereoblock polymers, of heteroblock copolymers; and of random copolymers; all this opened up enormous possibilities to the chemical industry.

What had exclusively been in the power of nature, namely to join the monomeric units in a giant macromolecule with a predetermined steric order and not at random, is now also possible for man. He has even created types of macromolecular structures that do not exist in nature.

Mankind, since prehistoric times, has been unconsciously using macromolecules having pre-ordered steric structure, such as clothing and building materials, food, etc. but only now can he synthesize them in laboratories and in industrial plants. Isotactic polymers with a high degree of crystallinity, obtained from alpha-olefins, which are very cheap raw materials derived from petroleum, will supply, in the future, building materials having, in the oriented state, the same tensile strength as steel, but one eight of its density.

Textile fibres having some mechanical properties better than those of nylon will be obtained at low cost.

The light weight will make it possible to obtain products with insulating properties like wool and soft to the touch. The low price will allow developments in the fields of classical building materials and the paper industry.

In the field of diolefins, U.S. industries produced *cis*—1,4 polyisoprene almost identical with natural rubber. We have been the first to produce *cis*—1,4 polybutadiene at a high degree of purity, which, like natural rubber, crystallizes when stretched.

The lower price of butadiene, its availability and the excellent properties of polybutadiene as sterically pure as the natural rubber, in my opinion, make polybutadiene more interesting than polyisoprene.

However, even more interesting in the field of synthetic rubbers are in my opinion, the essentially saturated C_2—C_3 (ethylene-propylene) copolymers because of their good elastic properties along with tensile strength and resistance to aging better than those of natural rubber.

Finally the application of stereospecific processes to non-hydrocarbon monomers completes the great revolution taking place in the field of macromolecules.

One of the most promising fields of application of macromolecules having a sterically regular structure will be that of textile fibres. Natural fibres (cellulose, silk) also have a sterically regular structure. The new processes of stereospecific polymerization allow us to obtain macromolecules by even starting from highly asymmetric monomers. It is therefore possible to make fibres with high tensile strength and a high melting point starting from olefinic monomers, some of which are available at low cost. The technique of obtaining thin yarns has now reached a high level of development, but owing to one reason or another the materials fit for spinning are still defective in quality or high in price and man-made fibres still cover only 10 per cent of total fibre consumption. Cotton remains the most widely used fibre. However, the stereospecific catalysis will supply raw materials suitable for the production of fibres at low price; and this may be considered a revolution.

Considering the entire Italian chemical production, its quantitative growth will more and more promote export especially toward the underdeveloped countries: actually export already covers one third of the whole production. It is to be foreseen that the production based on coal will remain stationary and will, in part, decline. The electrochemical industries have a tendency to limit their production to the most traditional fields like chloro-soda and aluminium.

Another indication of the progress of technology and of industrial organization is given by the continuous lowering (with some oscillation) of chemical prices, while the expenses for research, technical services, staff and tax load are increasing. This trend may be noticed all over the world, but is particularly marked in Italy. The sale prices of basic

products like synthetic fertilizers and home plastic materials are, in Italy, the lowest in the world. However this situation requires care and continuous updating of methods, especially in view of the fact that the amount of production in Italy is modest in comparison with that of other countries, and there cannot be the economical advantage of very large production units.

I have indicated some directions of the chemical progress in the next years; the Italian chemical industry will pioneer along these paths owing to the priority of its studies and inventions, and to the energy and spirit of enterprise demonstrated in difficult and serious situations.

Progress that may be achieved abroad will also be of help and taken into consideration; all considered, we shall witness much greater changes than those originated by violent upheavals and battles among nations.

The beneficial effect exerted by the increasing chemical industry on every aspect of human life all over the world will be the best reward for the labours and efforts of scientists and technicians working in this interesting field.

A revolution will be marked, as already said, by the development of processes that lead to the formation of macromolecules having a predetermined structure. They will render some branches of industry independent of agriculture (in the fields of textiles, of paper and of building materials) and increase the areas of land used for the production of food. In a few decades this will be a strict necessity dictated by the impressive growth of world population and by the increase of the standard of living which is the aim of all nations. Our peeping into outer space cannot distract us from our earthly problems.

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COPOLYMERIZATION OF ETHYLENE WITH ALIPHATIC α-OLEFINS. NOTE IV: ETHYLENE-PROPYLENE COPOLYMERIZATION WITH CATALYSTS OBTAINED FROM VANADIUM TRICHLORIDE

by G. NATTA, A. VALVASSORI, G. MAZZANTI and G. SARTORI

(4 July 1958)

[*Chimica e Industria* **40**, 717 (1958)]

ABSTRACT

By operating under suitable polymerization conditions and using catalysts made up of vanadium trichloride and trialkyl aluminum, we were able to prepare amorphous high-molecular-weight ethylene-propylene copolymers free from homopolymers.

Other factors being equal, the composition of the copolymers does not depend either on the concentration of the catalyst or on the time during which the solution of trialkyl aluminum is maintained in contact with vanadium trichloride; it does not depend either on the polymerization time, or on the molar ratio of the two reagents used in the preparation of the catalyst.

On the basis of a considerable number of runs, we have determined the dependence of the copolymer composition on that of the monomer mixture.

Finally we determined, in this copolymerization, reactivity ratios whose average values, referred to the concentrations of the two monomers in solution, are:

$$r_{C_2H_4} = 5.61 \qquad r_{C_3H_6} = 0.145$$

In order to compare the reactivity ratios of ethylene and of propylene we carried out their copolymerization at either 25° or 75°C with catalysts prepared from trihexyl aluminum and various vanadium halides. We first had to verify that the reactivity ratios did not vary appreciably in the range from 25° to 75°C.

A comparison was made between the values of the reactivity ratios, obtained at 25°C with catalysts prepared from $VOCl_3$, VCl_4 and trialkyl aluminums, and those obtained at 75°C with catalysts prepared from VCl_3 and trialkyl aluminums.

From this comparison one could assume that the difference between the reactivity of ethylene and that of propylene decreases with a decrease in the valence of the vanadium halide employed in the preparation of the catalyst.

TABLE 1. REACTIVITY RATIOS OF ETHYLENE AND PROPYLENE IN THE PRESENCE OF CATALYSTS PREPARED FROM $Al(C_6H_{13})_3$ AND VANADIUM HALIDE

Catalyst	$r_{C_2H_4}$	$r_{C_3H_6}$
$Al(C_6H_{13})_3+VOCl_3$	17·95	0·065
$Al(C_6H_{13})_3+VCl_4$	7·08	0·088
$Al(C_6H_{13})_3+VCl_3$	5·61	0·145

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THE REACTION BETWEEN STYRENE AND TRI-ISOBUTYLALUMINUM

by G. NATTA, P. PINO, G. MAZZANTI, P. LONGI and F. BERNARDINI

(7 July 1958)

[*J. Amer. Chem. Soc.* **81**, 2561 (1959)]

ABSTRACT

This is a study on the addition mechanism of tri-isobutyl-aluminum or of dialkyl aluminum monohydride to the styrene vinyl double bond.

It was found that aluminum dialkyl monohydride, in the presence or in the absence of solvents, and at temperatures of 20–100°C, adds to the styrene double bond, in such a way that the ratio, in the addition product obtained (tris(phenylethyl)aluminum), of the amount of aluminum bound to the α-carbon to the amount bound in the β-position ranges within a value of 0.3 (i.e. 22–24 per cent of aluminum bound in the α-position of the total addition product, tris-phenylethyl aluminum).

In the case in which aluminum tri-isobutyl is used, before its addition to styrene, the former undergoes a gradual dissociation, (catalyzed by the addition of nickelacetylacetonate), of $\rangle$Al—C to $\rangle$Al—H bonds, with the formation of stoichiometric amount of isobutene. For this reason the molar ratio between the two tris(phenylethyl) aluminum, in the final addition product to styrene, was very close to the above-mentioned value for the addition product of aluminum diethyl-monohydride to styrene.

The relative amount of the two isomers of tris(phenylethyl) aluminum was determined by subjecting the addition product to a

complete oxidation by means of air and oxygen followed by the hydrolysis and the determination of the amount of phenylethyl-1,2 types of alcohols (even the small amounts of acetophenone), by analytical methods and I.R. analysis.

The Authors have also noticed that the molar ratio found between the two isomers of tris-(phenylethyl)-aluminum is practically the same as that obtainable by isomerization, under the same experimental conditions adopted in the addition to styrene of the two single isomers prepared separately by synthesis (through the corresponding Grignard compound).

Therefore, one is led to believe that the 0.3 molar ratio value mentioned above represents the value for the equilibrium constant of the following equation:

$$R{-}CH_2{-}CH_2{-}AlR'_2 \overset{K}{\rightarrow} \begin{matrix} R \\ \diagdown \\ \quad CH \\ \diagup \\ CH_3 \end{matrix} \!\!> CHAlR'_2 ; \; K \simeq 0.33$$

under our adopted experimental conditions.

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THE COPOLYMERIZATION OF ETHYLENE WITH ALIPHATIC α-OLEFINS. NOTE V: ETHYLENE-PROPYLENE COPOLYMERIZATION WITH CATALYSTS OBTAINED FROM TITANIUM HALIDE

by G. NATTA, A. VALVASSORI, G. MAZZANTI and G. SARTORI

(4 July 1958)

[*Chimica e Industria* **40**, 896 (1958)]

ABSTRACT

The ethylene–propylene copolymerization carried out with catalysts prepared from aluminum trialkyl and various titanium chlorides, ($TiCl_4$, alpha-modification of $TiCl_3$, $TiCl_2$), is described here.

By operating under particular conditions and by carrying out the copolymerization runs with a continuous feeding of the monomer mixture at high speed, it was possible to prepare, also with these catalysts, at least within certain ranges of composition, amorphous linear ethylene–propylene copolymers free from homopolymers.

After having established that with our conditions an excellent reproducibility of the results could be achieved, we have verified that when using catalysts prepared from titanium tetra- or trichloride, the composition of the copolymers does not vary, the other conditions being equal, if the concentration of the catalyst, the time elapsed from the preparation of the catalyst to its use, and the molar ratios of alkyl aluminum to titanium halide employed (limited to ratios ranging from 1 to 4 for catalysts prepared from $TiCl_4$) are varied.

By carrying out runs with monomer mixtures having different compositions, we were able to establish the influence of the latter on the composition of the copolymers.

The composition of the copolymers prepared with the aid of $TiCl_4$ or $TiCl_3$ catalysts differs from that of the monomer mixture more than observed for the catalysts obtained from $VOCl_3$, VCl_4 or VCl_3, respectively.

Finally we determined the reactivity ratios of the two monomers for the various catalytic systems, whose average values, referred to the concentration of the two monomers in solution, are reported in Table 1.

From the data reported in Table 1, one can see that the greatest difference between the values of the reactivity ratios is observed for catalysts prepared from liquid halides having a high valency. This agrees with what was already observed by us for the vanadium halides.

TABLE 1. REACTIVITY RATIOS OF ETHYLENE AND PROPYLENE FOUND WHEN USING CATALYSTS PREPARED FROM $Al(C_6H_{13})_3$ AND TITANIUM CHLORIDES

Catalyst	$r_{C_2H_4}$	$r_{C_3H_6}$
$Al(C_6H_{13})_3+TiCl_4$	33·36	0·032
$Al(C_6H_{13})_3+TiCl_3$	15·72	0·110
$Al(C_6H_{13})_3+TiCl_2$	15·72	0·110

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ISOTACTIC POLYMERS OF VINYL MONOMERS CONTAINING SILICON

by G. NATTA, G. MAZZANTI, P. LONGI and F. BERNARDINI

(9 July 1958)

[*Chimica e Industria* **40**, 813 (1958)]

ABSTRACT

For the first time some linear, high molecular-weight, crystalline polymers of vinyl monomers containing an atom of silicon have been prepared. The polymerization of these monomers was carried out under analogous conditions as those commonly adopted for the stereospecific polymerization of alpha-olefins. In particular, such polymerizations were effected at temperatures of 70°–85°C with catalysts prepared from solutions of triethyl aluminum and titanium tetrachloride or trichloride (alpha-violet modification).

From the crude polymerizates, by extraction with solvents at their boiling point, fractions of amorphous, non-crystallizable polymers, fractions having a low crystallinity consisting of stereoblock macromolecules, and finally highly crystalline fractions consisting of isotactic macromolecules, have been isolated.

The comparison between the properties of the single fractions with those of the polymers obtained from the corresponding hydrocarbon monomers, revealed that the substitution of a carbon atom by a silicon atom in each monomeric unit does not significantly alter the properties of the macromolecules.

It can however be observed that the molecular weights (of the silicon-containing polymers) are generally lower and their melting temperatures slightly higher than those of the corresponding hydrocarbon polymers. On the other hand, certain interesting properties have been observed in the monoalkylsilane polymers.

Due to the high reactivity of the partially polarized Si–H bonds, the polymer can be easily crosslinked by heating in the presence both of oxygen, and of aqueous and alcoholic solutions. On the contrary, polybutene-1, its analogous hydrocarbon polymer, is completely stable under the same conditions because of the higher stability of the C–H bond.

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THE VOLUMETRIC DETERMINATION OF THE DEGREE OF CRYSTALLINITY OF ISOTACTIC POLYSTYRENE

by G. NATTA, F. DANUSSO and G. MORAGLIO

(18 July 1958)

[*Makromol. Chemie*, **28**, 166 (1958)]

ABSTRACT

The dilatomeric curve and some comparative volumetric data of an isotactic and an atactic polystyrene were determined. By extrapolating experimental data and by applying some empirical postulates, the theoretical dilatometric curve of a completely crystalline polystyrene was calculated.

From this curve and from experimental data, the following formula was derived to determine the approximate degree of crystallinity of samples of polystyrene, by a single specific volume measurement:

$$\chi = \frac{0{\cdot}943 + 2{\cdot}5 \times 10^{-4} t - v}{0{\cdot}053}$$

where v is the specific volume and t the temperature in °C ($t < 80$°C).

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NOMENCLATURE RELATING TO POLYMERS HAVING STERICALLY ORDERED STRUCTURE*

by G. NATTA and F. DANUSSO

(21 July 1958)

[*Chimica e Industria*, **40**, 743 (1958) *J. Polymer Sci.* **34**, 3 (1959)]

(A) POLYMERS HAVING ORDERED STRUCTURE

A1. A linear polymer is considered as having an ordered structure when it is formed by macromolecules whose monomeric units follow one another along the chain with dispositions and/or configurations ordered according to some rule.

The rule which characterizes a partially or completely ordered arrangement, can be simple or composed by a few simple rules (and therefore periodical); it must not possess, in general, a random or statistical character.

Thus, by way of example, one can consider as a polymer with ordered structure: (*a*) a linear vinyl polymer with a complete head-to-tail arrangement; or (*b*) a linear polymer, ordered head-to-tail, and with the monomeric units all arranged in the same steric configuration along the chain; or (*c*) a linear polymer whose macromolecules are composed by a succession of blocks or big, equal repeating units, each of them composed of a certain number of base structural units arranged according to a certain rule (which is periodical with respect to the whole macromolecule).

In the first example we have an arrangement in relation only to the

* Report presented at the Macromolecules Commission of I.U.P.A.C., during the International High-Polymer Conference, Nottingham, July 21–24, 1958. Subsequently, said Commission appointed a sub-committee (M. L. Huggins, V. Desreux, H. Mark, G. Natta) who published a definitive report in *J. Polymer Sci.* **56**, 153 (1962).

positional structure of the monomeric unit. In the second example we can think of two superimposed arrangements, one of positional structure, and the other of steric structure, or we can think of a unique arrangement of configuration.

Generally speaking, it is clear that an ordered arrangement can be composed by several arrangements which represent different steps of a partially or completely ordered arrangement.

The possibility of the existence of a plurality of arrangements finds its origin, first of all, in the possibility of existence of various isomeric structures, in the classical sense, of the monomeric units. In the case of monomeric units presenting some kind of asymmetry, the possibility also exists of different orientations of one monomeric unit with respect to an adjacent one or according to a selected direction along the chain (for instance head-to-tail arrangements or head-to-head—tail-to-tail arrangements).

This second possibility, however, can be considered in terms of positional isomerism (of the substituents) of monomeric units or of base units.

In general, therefore, ordered structures in the polymers find their origins in the possibility of isomerisms (positional, structural, geometric, steric, etc.) of the monomeric units or, in a more general way, of base units.

While in the past polymeric structures with arrangements related to positional or structural isomerisms of the units were considered and obtained, only recently, owing to the discovery of particular processes of stereospecific polymerization, has it been found advisable to classify new polymers whose macromolecules are ordered also with regard to the steric configuration of the constitutive units.

It is interesting to note that the obtaining of arrangements of steric character needs such a regularity of mechanism of polymerization that, as for the cases until now examined, the polymers ordered by steric isomerism of the units are found to be ordered also by positional and/or structural isomerism.

The present nomenclature will be related, therefore, to linear polymers which, unless explicitly mentioned, are to be considered as having in any case positional and structural arrangement of the units.

(B) TACTICITY AND EUTACTICITY(°)

B1. Linear tactic polymer* or simply *tactic polymer* is a polymer formed by macromolecules whose monomeric units (or base units) follow one another along the chain with steric configurations ordered according to some rule.

The rule, or *taxis*, which characterizes an arrangement partially or completely ordered, or *tacticity*, may be simple or composed by a few simple rules, but it must not have in any case random or statistic character.

More complex tacticities can be originated not only by steric configuration of a few units, but also by the possibilities, theoretically very numerous, of programmatic arrangements of monomeric units having different configuration along the macromolecular chain (*programmatic tacticities or taxis*).

*Eutactic polymer*** is a tactic polymer whose monomeric units (or base units) are ordered according to such a number and kind of tacticities that its macromolecules are completely ordered.

In other words, an eutactic polymer is a tactic polymer which is completely devoid of any element of structural disorder along the chains of its molecules.

It is advisable that the definition of eutactic polymer be restricted to those cases in which the overall arrangement (*eutacticity*) is relatively simple, that is to say, when the repeating unit assumes relatively small dimensions (with a maximum of some monomeric units).

By way of example, a butadiene polymer is eutactic when all the monomeric units have the same *trans*-1,4 configuration or all have the *cis*-1,4 configuration. A linear polyethylene is not to be called eutactic because, although it is formed by the ordered sequence of base units $-CH_2-$, these do not have any possibility of steric isomerism.

An optical antipode oxyacid leads, by polycondensation, to an eutactic polycondensate. A mixture of isomers of an amino acid, on the other hand, gives by normal polycondensation a polymer which, in respect to the arrangement of the monomeric units, can be considered as positionally ordered but is not eutactic, because of the statistical disorder deriving from the steric isomerism of the units.

Assuming the existence of a catalyst capable of polymerizing a

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(°) Eutacticity was later called "Olotacticity".

* From the Greek verb $\tau\alpha\tau\tau\omega$, I dispose, I order.

** From the Greek prefix $\varepsilon\upsilon$, well, and the verb $\tau\alpha\tau\tau\omega$, I dispose, I settle. Eutactic was later changed to "Olotactic".

mixture of stereoisomeric amino acids in such a way as to yield chains which were all formed by *l*-amino acid or by *d*-amino acid, the resulting polymer would be eutactic.

By radical polymerization of a vinyl monomer, one can obtain a polymer having some ordered chain, for instance, by head-to-tail arrangement; generally, however, the polymer will not be ordered from the point of view of the steric configuration (right or left in respect of one direction along the chain) of its units, and therefore it will not be an eutactic polymer. However, the same polymer can be obtained in an eutactic form through a polymerization method which is capable of disposing the monomeric units along the chain with the same steric configuration.

B2. It is likewise possible, as in the case of tactic polymers, to define *tactic macromolecules, tactic chains,* and *tactic blocks;* and in the case of eutactic polymers, to define *eutactic macromolecules, eutactic chains, eutactic blocks,* etc.

B3. Tactic polymerization is any polymerization producing a tactic polymer.

Eutactic polymerization is any polymerization producing an eutactic polymer. It is advisable, however, to restrict the significance of the term to the cases in which the formation of a tactic or eutactic polymer is the consequence of the particular polymerization mechanism and not simply of the structure of the monomer or of the monomeric unit.

(C) ATACTICITY

*C1. Atactic polymer** is a polymer whose macromolecules, although they have positional or structural arrangements, do not possess a steric order of the units or possess tacticities of such a complex character that cannot be understood without great difficulty.

Therefore, *atacticity* must be considered as a structural state having

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* From the Greek prefix α, non-, and the verb ταττω, I order, I dispose. The term "atactic" was first introduced by G. Natta during the meeting of the Gesellschaft Deutscher Chemiker at Bad Nauheim (Germany), on April 25, 1956 [*Angew. Chem.* **68**, 393 (1956); *Chimica e Industria* (*Milan*), **38**, 751 1956)]. It has a more general significance with respect to the original "anisotactic", proposed in the meeting of Accademia Nazionale dei Lincei in Rome (Italy) on December 11, 1954 [G. Natta and P. Corradini, *Atti Accad. Naz. Lincei Mem.* **4**, (8), 73 (1955)]

steric character, but devoid of specific tacticities and, of course, also of eutacticities.

A vinyl polymer, for instance, obtained by conventional radical processes, is generally an atactic polymer; it may possess a head-to-tail arrangement, but it is disordered with regard to the steric configurations of the tertiary carbon atoms which follow each other along the main chains of the macromolecules.

C2. In a manner quite similar to atactic polymers, one can define *atactic macromolecules, atactic chains, atactic blocks,* etc.

C3. Atactic polymerization is any polymerization which leads to an atactic polymer.

(D) PARTICULAR TACTICITIES

In the chemistry of substances having low molecular weight, different kinds of steric isomerism are known, owing to differences of molecular configuration which are comprehensible only by spatial observation.

Steric isomerisms often considered are, for instance, the isomerism due to the presence of asymmetric carbon atoms (isomerism usually indicated as optical); the ethylene isomerism, due to the *cis* and *trans* configurations of two substituents, with respect to the double bond; *cis* and *trans* isomerisms of more complex structures (sometimes also called geometric), etc.

Since steric isomerisms are usually classified into different types, the classification of tactic polymers in various classes or categories may be justified.

In the present report we will define three types of tacticities relating to macromolecular structures which have been practically obtained and identified up to now. For these, some terms have already entered in current use, and we will specify them in three separate sections.

(a) Isotacticity

Da1. In the case of polymers whose monomeric units (or base units) may exist in two enantiomorphous configurations (the one being the mirror image of the other), either intrinsically or because of their position in the chain, tacticities due to configurations of asymmetrically

substituted carbon atoms may occur. We will regard the units of such a kind of polymers as *asymmetric units*.

*Isotactic** is a polymer whose monomeric units (or base units) are asymmetric units, ordered in such a way that when passing along a single chain from one monomeric unit (or base unit) to the subsequent one, one finds repetition of the unit configuration. In geometric terms, when considering two successive monomeric units (or two base units), by translation and rotation of one of them one can obtain the superimposition of the two units (this can take place also by rotation of single groups around internal bonds).

An isotactic polymer is usually eutactic. The corresponding arrangement, or *isotacticity*, can be resumed in a simple rule (*isotaxis*), which is the *repetition* of the configuration of the monomeric units along a single chain.

It follows that all the arrangements which may compose the isotacticity must be only repetitive arrangements.

Thus, for instance, a polymer of a vinyl monomer or of a vinylidenic asymmetrically substituted monomer is isotactic when it is both positionally ordered by a head-to-tail arrangement and tactic, having all its monomeric units with the same steric configuration along the chain.

A hypothetical polyisoprene having 1–2 arrangement, and therefore a structural order, could be isotactic only if it also had a positional head-to-tail arrangement and a steric arrangement, with repetition of the spatial configuration of the quaternary carbon atom.

The polymer obtained by polycondensation from a *d*-amino acid is, according to the above definition, an isotactic polymer. Isotactic is the crystalline polymer obtainable by a particular polymerization method from racemic propylene oxide.** It is to be noted that the different steric configurations of a monomeric unit may also derive from more than one site or center of asymmetry. Thus, from a vinyl monomer, the substituent of which contains one asymmetric

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* From the Greek term ισος, the same, equally, and ταττω, I put in order. The term "isotactic" was first introduced by Giulio Natta during a meeting of the "Accademia Nazionale dei Lincei" in Rome (Italy) on December 11, 1954. G. Natta, *Atti Accad. Naz. Lincei, Mem.* 8 [4], 61 (1955). G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, and G. Moraglio, *J. Am. Chem. Soc.* **77**, 1708 (1955). G. Natta, *J. Polymer Sci.* **16**, 143 (1955). See also: G. Natta, P. Pino, and G. Mazzanti, *Gazz. chim. ital.* **87**, 528 (1957).

** C. C. Price, M. Osgan, R. E. Hughes, and C. Shamberlan, *J. Am. Chem. Soc.* **78**, 690 (1956); G. Natta, P. Corradini, and G. Dall'Asta, *Atti. Accad. Naz. Lincei*, **8**, 20, 408 (1956).

carbon atom, one can obtain a truly isotactic polymer only if the following repetition arrangements are realized: (*a*) positional (head-to-tail), (*b*) steric along the main chain, and (*c*) steric because of the configuration of the substituents.

Leaving out tacticity (*c*), one could have isotacticity limited to the main chain, and the tacticities of the side chains could be considered separately. Thus one could perhaps distinguish, using different words, between *main chain isotacticity* and *side chain* (or *substituent group*) *isotacticity*.

Unless otherwise stated, we will refer only to isotacticities of the main chain.

Note. Originally the definition of "isotactic polymer" had been introduced to indicate briefly (avoiding the use of long explanatory phrases) those polymers, of monomers of the CH_2=CHR type, in the macromolecules of which all the tertiary carbon atoms have, at least for long chain portions, the same steric configuration.

To make things simpler, an isotactic macromolecule deriving from a CH_2=CHR monomer was defined as the one in which, supposing the main chain fully stretched in a plane, all the R substituents find themselves on one side of the plane, while the hydrogen atoms linked to the tertiary carbon atoms are on the other side of the plane. Each tertiary carbon atom of the main chain is comprised in these polymers between two —CH_2—groups.

Therefore, for each tertiary carbon atom the possibility of existence of two steric configurations is determined by a difference in the end groups and/or by a different length and different configuration of the two main chain segments linked to it.

The first examples of these polymers were the isotactic polymers of propylene, of butene, of several other α-olefins, and of styrene, i.e. of substances which, at the state of monomer, do not contain asymmetric carbon atoms.

Subsequently a strong tendency was shown by many authors to extend the definition to other cases. Thus, for instance, polymers derived from monomers formerly containing asymmetric carbon atoms were also called "isotactic" (e.g. Price *et al.*, loc. cit.). In this Report we intend to favor this tendency which, under certain aspects, simplifies the terminology and which, on the other hand, follows the etymological significance.

The broader definition may, however, lead to some discussions. Thus, for instance, the polymer obtained by polycondensation from a

d-amino acid is, according to the extended definition, an isotactic polymer. This is, however, one of the cases in which the term "isotactic" is not strictly necessary since the polymer can be clearly identified, in its eutactic character, by the term "poly(*d*-aminoacid)".

The crystalline polymers, which are now obtainable from propylene oxide, can similarly be defined in their structure as "poly(*l*-propylene oxide)" or as "poly(*d*-propylene oxide)" when obtained from an optically active monomer, and as "racemic poly(propylene oxide)" when obtained from a racemic monomer.

A *non*-crystalline polymer obtained by conventional polymerization of racemic propylene oxide can be defined by the term "poly($d + l$)-propylene oxide" or, more simply, "polypropylene oxide."

Similar considerations can be made for the syndiotactic polymers, for which a broader or more restricted definition can be given, while as for the atactic polymers, the definition given in the present Report corresponds to the original one.

Da2. In a similar way one can define *isotactic macromolecules, isotactic chains, isotactic blocks,* etc.

Da3. Isotactic polymerization is any polymerization which, owing to a particular mechanism, produces an isotactic polymer.

This term is of significance either when one starts from a monomer which does not admit steric isomers (such as, for example α-olefins) or when one starts from a monomer which does admit them. For the sake of clarity one should distinguish between the two cases of isotactic polymerization which can be defined by the following two more general types of polymerization having a steric effect:

(*a*) *Stereotactic* (*or stereospecific*) *polymerization* occurs when from a single monomer, which can be the origin of two stereoisomeric monomeric units, one obtains a tactic polymer.

(*b*) *Stereolectic** (*or stereoelective*) *polymerization* occurs when from a mixture of stereoisomeric monomers, each of which can be the origin of a unique type of monomeric unit, one obtains a tactic polymer.

In the case of the formation of isotactic polymers, one may thus distinguish between *stereoisotactic polymerization* (e.g. the one of α-olefins) and *stereoisolectic polymerization* (e.g. the one of random propylene oxide). It is interesting to note that in the case of stereoisolectic polymerization, the macromolecules formed by one of the monomeric

* From the Greek verb λεγω, I pick up, I choose.

stereoisomers are optically active, but the total polymer may be inactive because there can be present, in equal number, enantiomorphous molecules formed by the second monomeric stereoisomer. On the other hand, in the case of stereoisotactic polymerization, the macromolecules (e.g. in vinyl polymers) formed by monomeric units of one type (e.g. left) may be practically identical with those formed by monomeric units of the other type (e.g. right), because for polymers of high molecular weight the asymmetry due to end groups can be neglected.

(b) Syndiotacticity

Db1. A *syndiotactic** polymer is a polymer formed by macromolecules whose monomeric units (or base units) are asymmetric and ordered in such a way that, when passing along the chain from one unit to the subsequent one, one finds a repetition of position (of the substituents) and of structure, but inversion of the steric configuration.

In geometric terms, this occurs when considering two successive monomeric units (or two base units) by translation and rotation of one of them (and, if necessary, by rotation around single internal bonds) one cannot obtain the superimposition of the two units, but each of them may only become the mirror image of the other.

Syndiotacticity is the corresponding arrangement. We can think of it as composed of positional and structural arrangements identical with those of isotacticity (repetition arrangements) and of a tacticity opposite to that of isotacticity (inversion tacticity).

For example, a butadiene polymer formed through 1–2, head-to-tail arrangement, the successive monomeric units of which have alternatively right and left configuration along the chain in respect of a selected direction, is a syndiotactic polymer.

In a similar way a polymer derived from a vinyl monomer or from a vinylidene asymmetrically substituted monomer can also be syndiotactic.

Db2. In a similar way one can define *syndiotactic macromolecules, syndiotactic chains, syndiotactic blocks,* etc.

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* From the Greek terms $\sigma\upsilon\nu$, together; $\delta\upsilon o$, two; $\tau\alpha\tau\tau\omega$, I put in order. The term "syndiotactic" was first introduced by Giulio Natta during a meeting of the Accademia Nazionale dei Lincei in Rome (Italy) on November 12, 1955. G. Natta and P. Corradini, *Atti Accad. Naz. Lincei,* 8, 19, 229 (1955); *J. Polymer Sci.* **20**, 251 (1956).

Db3. Syndiotactic polymerization is any polymerization producing a syndiotactic polymer. As in the case of isotactic polymerization, one could, in addition to *stereosyndiotactic polymerization,* expect a *stereosyndiolectic polymerization,* depending on whether the polymerization is stereotactic or stereolectic.

It is interesting to note that the syndiotactic macromolecules, obtainable through the second type of polymerization, are always identical with each other in their structure and are not formed by a mixture of enantiomorphous macromolecules as is the case with isotactic polymers.

(c) cis-Tacticity and trans-Tacticity

Dc1. When a polymer contains a double bond or a bond or group with equivalent structural effects in its monomeric unit, two tacticities may occur which regulate the *cis* and *trans* configuration of the involved groups.

cis-Tactic polymer or trans-tactic polymer is any polymer whose macromolecules are formed by monomeric units (or base units) susceptible to *cis* and *trans* isomery, and which follow each other all with the same *cis* or *trans* configuration along the chains. Typical examples of these polymers have been obtained from diolefins (*cis* and *trans* polybutadienes or polyisoprenes).

The following terms can be defined in a similar way:

Dc2. cis-Tactic and *trans-tactic macromolecules, chains, blocks,* etc.

Dc3. cis-Tactic and *trans-tactic polymerization.*

(E) STEREOCOPOLYMERS

E1. Stereocopolymers are polymers with macromolecules which are formed by monomeric units (or base units) which are chemically identical (homopolymers), and which are ordered through positional and structural arrangements (possibly also through tacticities), but which do not have a unitary steric structure.

An atactic polymer is, for instance, a stereocopolymer.

E2. A stereocopolymer is eutactic only when the sterically differentiated units are ordered according to taxes. A simple case of eutactic stereocopolymer is the syndiotactic polymer.

More generally, a stereocopolymer is eutactic whenever the realization of a programmatic tacticity is achieved (for instance, the alterna-

tion of blocks having uniform dimensions and presenting two different eutacticities).

E3. Stereoblock-polymers (or *stereoblock-homopolymers*) are stereocopolymers with molecules which are formed either by tactic blocks of at least two types, or by tactic and atactic blocks.

It is preferable to limit this denomination to the cases in which the blocks have a relatively large average size (for instance, a size not smaller than the one necessary to impart a crystallinity detectable by X-rays or infrared rays).

Otherwise a stereocopolymer will be an atactic polymer, which could be considered as an atactic stereocopolymer.

NOTE

The first draft of this text, presented at the Macromolecules Commission of IUPAC, attributed to the term "tacticity" the broadest significance of "arrangement" in general. Following the opinion expressed by some members of the same Commission, we thought it advisable to modify the significance of tacticity, as expressed in the present report, by limiting it to the only case of arrangement of steric configurations.

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KINETIC STUDIES OF α-OLEFIN POLYMERIZATION*

by G. NATTA

(22 July 1958)

[*J. Polymer Sci.* **84**, 21 (1959)]

SYNOPSIS

The kinetics of chain growth and chain transfer processes in the stereospecific polymerization of propylene, using catalytic systems such as $TiCl_3$—$Al(C_2H_5)_3$ and $TiCl_3$—$AlCl(C_2H_5)_2$, has been examined. The number of active centers present on the catalyst surface has been determined radiochemically by kinetic and adsorption measurements, using ^{14}C labelled aluminum alkyls. The mean life of macromolecules was determined by radiochemical determination of terminal groups, and the relationships between intrinsic viscosity and number-average molecular weight were found. Kinetic research into ethylene-propylene copolymerization enabled us to determine the different reactivity ratios of the monomers.

I. INTRODUCTION

The kinetic study of some organic syntheses has been, for over 15 years, one of the major research interests of the Industrial Chemistry Institute of the Milan Polytechnic. Kinetic work on catalytic hydrogenation, methanol synthesis and oxo-synthesis has been particularly fruitful in explaining apparent anomalies observed in the industrial development of these processes, and in clarifying their catalytic mechanism.[1]

In the polymerization field, we undertook a basic kinetic study on the products of n concurrent successive reactions, which, by 1945, had led to the solution of the resulting n differential equations.[2] Our application of this method to the anionic stepwise addition of ethylene oxide to

* Lecture held at the International High Polymer Conference, Nottingham, July 21—24, 1958

alcohols showed that the reaction rate of each successive reaction step is higher than that of each initial step, owing to an activation attributable to the preceding highly exothermic reaction step.[3]

In 1952 we started research work on the stepwise polymerization of ethylene by organometallic compounds, as described by Ziegler[4], and began a kinetic study to determine the mechanism of growth and termination reactions.[5] At first our main aim was to gain a sufficient understanding of these reactions, which would enable us to control and increase the molecular weight in the production of the polymers.

At the beginning of 1954 we succeeded in obtaining the first regular, linear, head-to-tail polymers of α-olefins. We attributed the heterogeneity of the raw polymers to the presence of macromolecules having different steric configurations; we also devised methods for the separation of isotactic and atactic polymers.[6] After establishing both the structure of the isotactic polymers and the conditions suitable to control stereospecificity of the catalytic systems, our experimental work turned to a thorough investigation on the nature of the catalysts and on the polymerization kinetics. This new field of research has proved to be so wide that in the last four years the work has been divided at least in two different groups.

One group is connected with the chemical problems of the polymerization processes, e.g. the nature of the catalytic complexes and the improvement of their stereospecificity. By selecting particular catalytic systems, we have succeeded in synthesizing directly highly crystalline crude polymers (for instance, practically pure isotactic polymers) or alternatively, with other systems, completely amorphous linear polymers of very high molecular weight.[7]

In the field of di-olefins, we have found processes with different kinds of stereospecificity, and have discovered classes of polymers previously unknown, e.g. polymers with 1-2 arrangements and isotactic or syndiotactic structure.[8] In the case of butadiene, we have succeeded in preparing all four possible types of crystalline polymers that differ chemically and sterically, and in determining their crystalline structure. The *cis*-1,4 and *trans*-1,4 polymers were obtained with a very high degree of steric purity and with very interesting properties, having close analogies with the corresponding isoprene polymers.[9]

In the course of our work on structure of catalysts, we have been able to isolate crystallizable complexes containing organometallic bonds and at least two different metal atoms, one of which is a transition metal.[10] Their crystalline structure has been accurately

determined, and their catalytic behavior toward different monomers investigated.[11]

In an attempt to extend coordination catalysis to vinyl monomers other than hydrocarbons, we have succeeded in obtaining isotactic polymers of aliphatic monomers containing oxygen,[12] silicon, tin,[13] and also of aromatic monomers containing halogen atoms.[14]

A second group of studies consists of investigations on the structure of crystalline polymers, their physical properties, and the kinetics of the polymerization reaction. The kinetic study was extended to the stereospecific polymerization of α-olefin and conjugated di-olefin heterogeneous systems, or in systems which are, at least initially, homogeneous.

In this paper I will refer in detail to a system we have studied most thoroughly, viz. the polymerization and copolymerization of propylene.

II. STEREOSPECIFICITY AND ACTIVITY OF POLYMERIZATION CATALYSTS

The heterogeneous nature of the catalysis in the stereospecific polymerization of α-olefins we first suggested in 1954,[15] has been confirmed in our subsequent work.

The production of highly isotactic polymers (crude polymers containing over 85–95 per cent of the weight not extractable by boiling heptane) was found to depend on the presence both of a catalyst and of a highly crystalline substrate (having a layer lattice).[16] Catalytic complexes containing transition metals and metal-organic bonds, which alone do not polymerize α-olefins, are non stereospecific catalysts when adsorbed on the surface of amorphous substances, but become highly stereospecific when adsorbed on highly crystalline supports.[17] Furthermore, there are some insoluble crystalline compounds (having a layer lattice) which alone, or even in the presence of aluminum alkyls, cause virtually no polymerization; but when they are added to soluble complexes (which also are inactive alone) yield stereospecific polymerization catalytic systems.[18] For example, certain crystalline compounds of metals of the eighth group of the Periodic System show this behaviour (Table 1).

The structure of the crystalline support is of great importance. $TiCl_3$ was believed to be dimorphous, but we found that it can exist in three crystalline forms we have called α, β, and γ. Figure 1 shows

TABLE 1. STEREOSPECIFICITY OF PROPYLENE POLYMERIZATIONS WITH TRIETHYL ALUMINUM AND DIFFERENT TITANIUM COMPOUNDS AT 70-80°C, USING *n*-HEPTANE AS SOLVENT

Titanium compound	*% polypropylene not extractable with boiling n-heptane*
Violet $TiCl_3$	80–90
Brown $TiCl_3$	40–50
$Ti(OC_3H_7)_4$	Only traces
$Ti(OC_3H_7)_4$ on SiO_2—Al_2O_3	0–10
$Ti(OC_3H_7)_4$ on $CoCl_2$	35–45

the structures of the α (violet)[19] and pure β (brown)[20] modifications. In the case of diolefins, the formation of polymers with predominantly *cis*-1,4 structure occurs only with the β-modification, while the α-modification gives the *trans*-1,4 polymer. The γ-modification also gives mainly *trans*-1,4 polymer.[21] In the case of α-olefins, the α-modification leads to sterically purer polymers than the other forms do.

Stereospecificity also depends on the ionic radius of the metal of the organometallic compounds. Organometallic compounds of highly

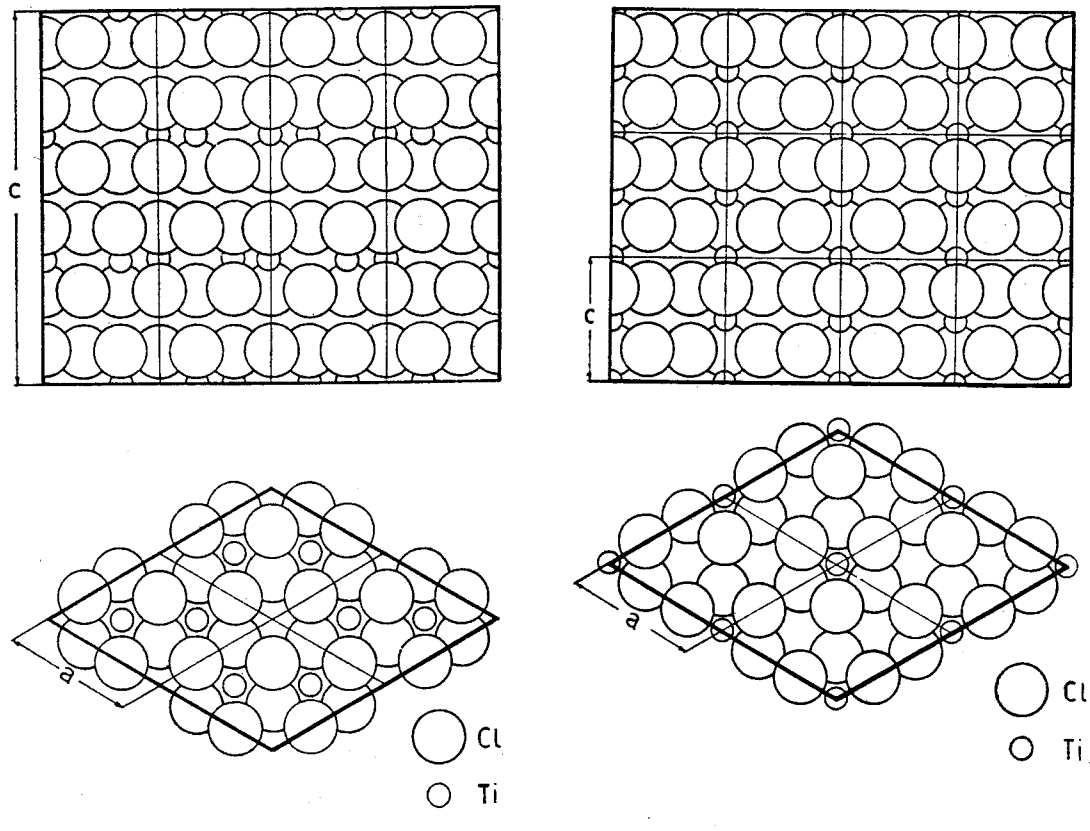


FIG. 1. Crystalline structure of α (violet)- and β (brown)- $TiCl_3$

electropositive metals with a very small ionic radius give complexes with transition metal compounds which are more stable than the corresponding complexes containing either less electropositive or more electropositive metal atoms with a larger ionic radius (Table 2).[16, 22]

TABLE 2. STEREOSPECIFICITY OF CATALYST PREPARED FROM A SAMPLE OF VIOLET $TiCl_3$ AND $Me(C_2H_5)_n$

(Temp. = 75°C. pC_3H_6 = 2.4 atm.)

Me	*Ionic radii of Me*, Å	*% polypropylene not extractable with boiling n-heptane*
Be	0·35	94–97
Al	0·51	80–90
Mg	0·66	78–85
Zn	0·74	30–40

In our research on the kinetics of α-olefin polymerization, the catalysts used were prepared form the α-modification of $TiCl_3$ and of $Al(C_2H_5)_3$.

III. STEREOSPECIFIC POLYMERIZATION OF PROPYLENE

(a) *Overall Rate of Polymerization*

Our kinetic studies on the polymerization of propylene with highly stereospecific catalysts prepared from crystalline α-$TiCl_3$ (violet) and aluminum alkyls have shown that the addition of propylene to the organometallic complex is catalyzed, in the proper meaning of the word, by the α-$TiCl_3$.[23] The polymerization of α-olefins, under suitable conditions (low temperature), may be considered as mainly a stepwise addition to an organometallic compound. At high temperature the reaction can also become catalytic with respect to the organometallic compound, since the polymeric alkyl dissociates and transfers to the catalytic complex a hydride ion capable of starting a new polymer chain.

$$[Cat]^{(+)(-)}CH_2CHCH_3(CH_2CHCH_3)_nH \longrightarrow [Cat]^{(+)}H^{(-)} + CH_2=CCH_3(CH_2CHCH_3)_nH$$

$$[Cat]^{(+)}H^{(-)} + CH_2=CHCH_3 \longrightarrow [Cat]^{(+)(-)}CH_2CH_2CH_3$$

$$[Cat]^{(+)(-)}CH_2CH_2CH_3 + (n+1)CH_2=CHCH_3 \longrightarrow [Cat]^{(+)(-)}CH_2CHC_3(CH_2CHCH_3)_nCH_2CH_2CH_3$$

When operating under hydrogen pressure, the hydrogenation process is followed by the stepwise addition reaction.[24]

$$[Cat]^{(+)(-)}CH_2CHCH_3(CH_2CHCH_3)_nR + H_2 \longrightarrow [Cat]^{(+)}H^{(-)} + CH_3CHCH_3(CH_2CHCH_3)_nR$$

$$[Cat]^{(+)}H^{(-)} + (n+2)CH_2=CHCH_3 \longrightarrow [Cat]^{(+)(-)}CH_2CHCH_3(CH_2CHCH_3)_nCH_2CH_2CH_3$$

The whole process of polymerization turns out to be catalytic.

At constant temperature and pressure, the rate of polymerization, after an initial settling period, becomes independent of time (Fig. 2).

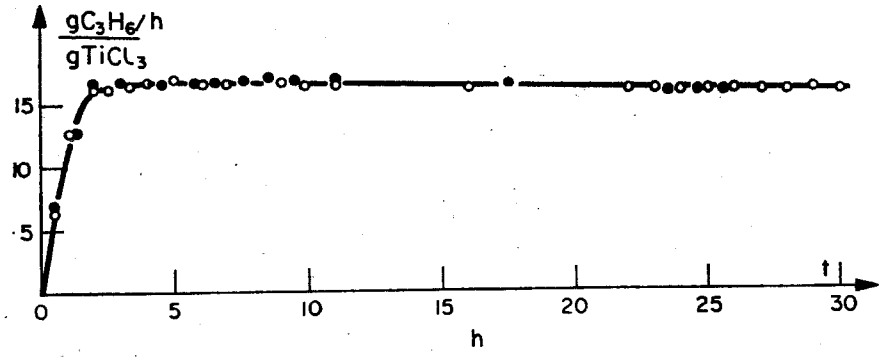


FIG. 2. Kinetic curve of the polymerization of propylene at constant temperature and pressure:

α-$TiCl_3$, g/l.	$Al(C_2H_5)_3$, mole/l.	T °C	$p\,C_3H_6$ mm Hg
0·80	$4{\cdot}45\times10^{-2}$	70	1450
1·00	$2{\cdot}94\times10^{-2}$	70	1450

(Solvent = 250 ml n-heptane)

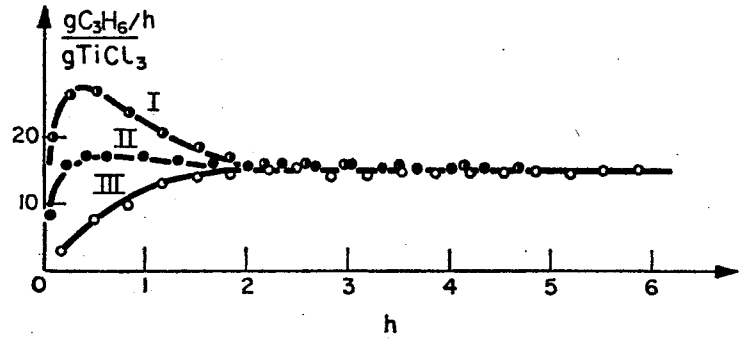


FIG. 3. Effect on the polymerization rate of previous physical treatments on a sample of α-$TiCl_3$. (I) $TiCl_3$ powdered and washed with anhydrous n-heptane. (II) $TiCl_3$ powdered, washed with anhydrous n-heptane, and dried. (III) TiCl not powdered. T = 70°C. $p_{C_3H_6}$ = 1450 mm Hg.

If $TiCl_3$ consists of relatively large crystals (e.g. size $\sim$ 10 μ), the activity increases during the settling period, and this fact is related to the phenomenon of cleavage of the large crystals. On the other hand, with finely dispersed $TiCl_3$ the opposite effect occurs, and the small crystals tend to coalesce. Using finely dispersed $TiCl_3$ subsequently stabilized by heating, the rate of polymerization reaches a constant value in a few minutes (Fig. 3).[25]

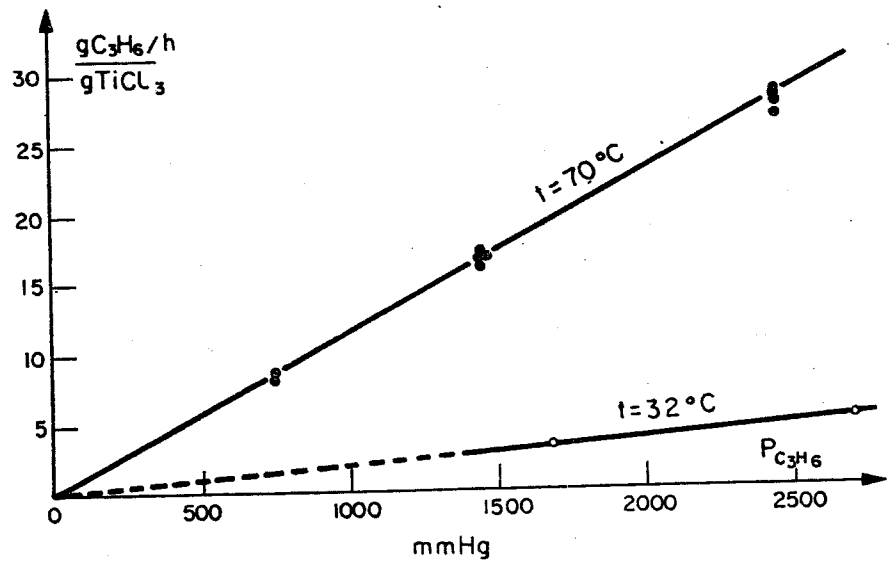


FIG. 4. Polymerization rate, in steady conditions, plotted vs. partial pressure of propylene. Quantities of α-$TiCl_3$ vary from test to test from 0·8 to 20 g/l., and of $Al(C_2H_5)_3$ from $1{\cdot}5\times10^{-2}$ to 20×10^{-2} mole/l. Solvent = 250 ml n-heptane.

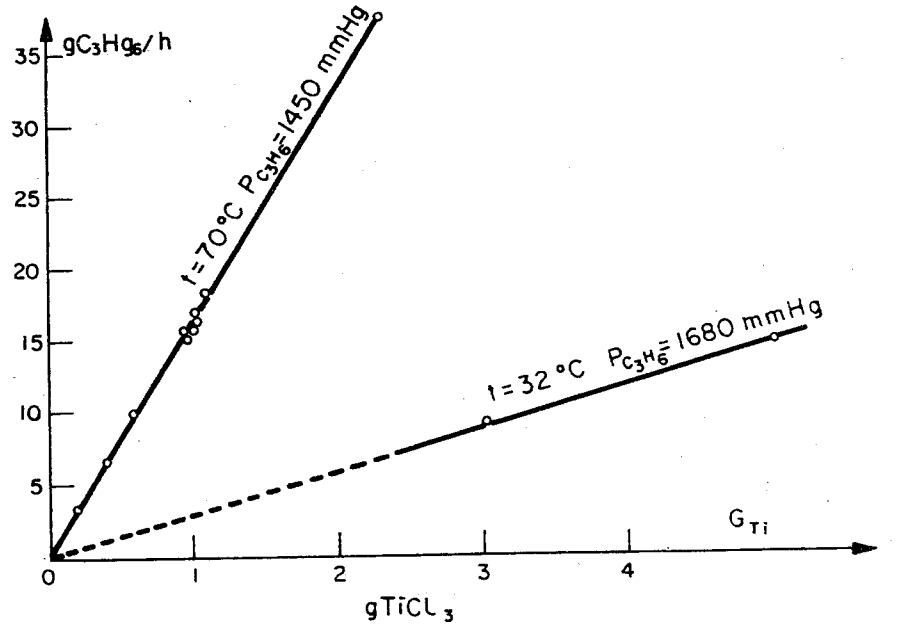


FIG. 5. Polymerization rate, in steady conditions, plotted vs. the quantity of α-$TiCl_3$. $Al(C_2H_5)_3$ concentration varies from test to test from $1{\cdot}5\times10^{-2}$ to 20×10^{-2} mole/l. Solvent = 250 ml n-heptane.

Under steady-state conditions, the rate of polymerization of propylene with α-$TiCl_3$ and $Al(C_2H_5)_3$ is independent of the $Al(C_2H_5)_3$ concentration, and is given by the following equation, deduced from the data summarized in Figs. 4, 5, and 6:

$$r = A\, e^{-E/RT} p_{C_3H_6} G_{Ti} \qquad (1)$$

where

r = rate of polymerization (g C_3H_6 polymerized/hr)
$A = 10^{7.3}$
$E = 10{,}000$ cal/mole
T = °K
$p_{C_3H_6}$ = partial pressure of propylene (atm)
G_{Ti} = g of $TiCl_3$ in the catalytic system.

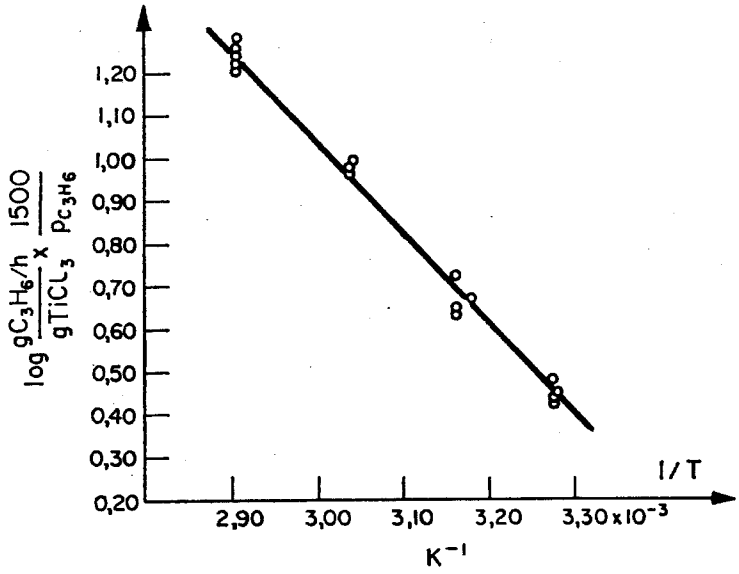


FIG. 6. Logarithm of the polymerization rate in steady conditions, plotted vs. $1/T$. The rate values were referred, with a proportionality relation, to a partial pressure of propylene of 1500 mm Hg.

This equation was verified with $TiCl_3$ used in the temperature range 20–70°C with reaction rates up to 80–100 g polymer/hr per liter of solvent.[23, 25]

(b) Mechanism of Chain Termination

An analysis of the factors affecting the intrinsic viscosity of the mainly isotactic polypropylene fractions, and also the use of a radioactive ^{14}C labelled aluminum alkyl, (together with α-$TiCl_3$ in

n-heptane), followed by a radioactive analysis of the polymer, shows that the inverse degree of polymerization is given by the equation:

$$\frac{1}{x} = \frac{k_1 + k_2 p_{C_3H_6} + k_3\sqrt{C_{Al}} + k_4 p_{C_3H_6}\sqrt{G_{Ti}}}{k_p p_{C_3H_6}} \qquad (2)$$

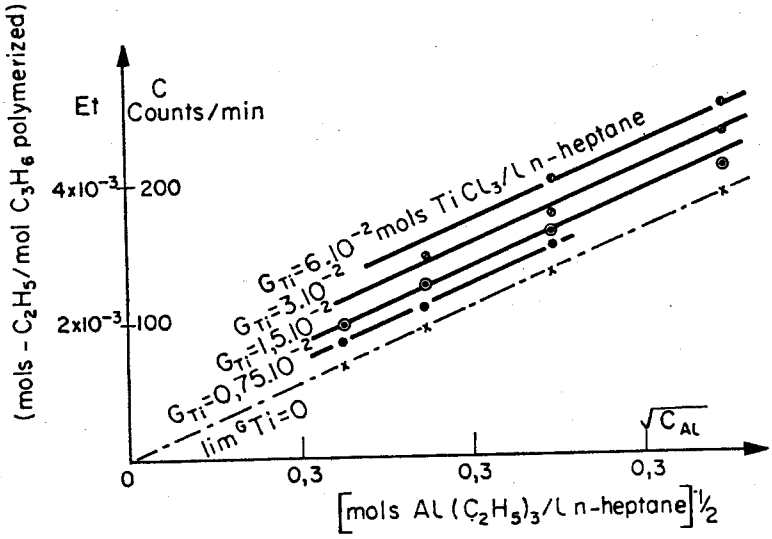


FIG. 7. Specific radioactivity (and corresponding value of $-C_2H_5$ moles per mole of polymerized C_3H_6) of the mainly isotactic polypropylene fraction, obtained with the reported quantities of α-$TiCl_3$ and radioactive $Al(C_2H_5)_3$, plotted vs. the square root of the aluminum alkyl concentration. T = 70°C. $p_{C_3H_6}$ = 450 mm Hg. Solvent = 100 ml n-heptane.

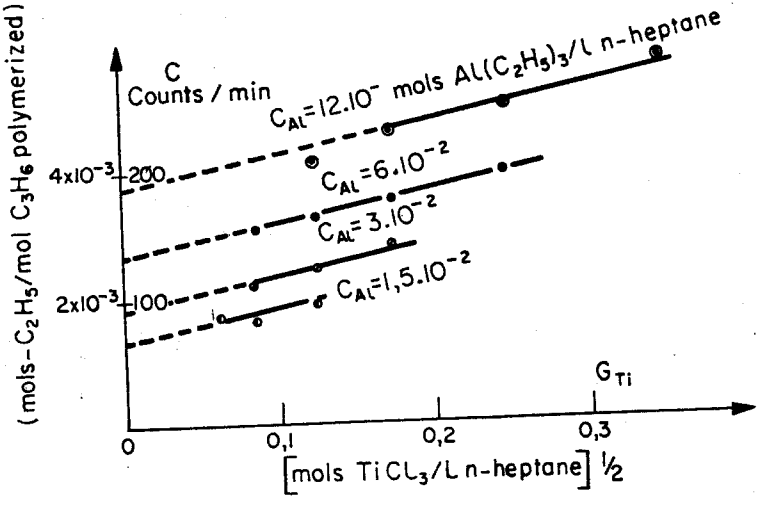


FIG. 8. Specific radioactivity (and corresponding value of $-C_2H_5$ moles per mole of polymerized C_3H_6) of the mainly isotactic polypropylene fraction, obtained with the reported concentration of radioactive $Al(C_2H_5)_3$ and with α-$TiCl_3$, plotted vs. the square root of $TiCl_3$ concentration in n-heptane. T = 70°C. $p_{C_3H_6}$ = 450 mm Hg. Solvent = 100 ml n-heptane.

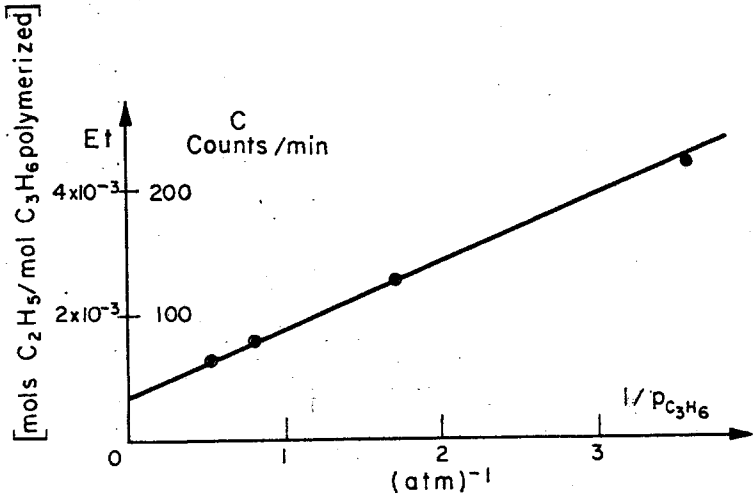


FIG. 9. Specific radioactivity (and corresponding value of $-C_2H_5$ moles per mole of polymerized C_3H_6) of the mainly isotactic polypropylene fraction, obtained with α-$TiCl_3$ and radioactive $Al(C_2H_5)_3$, plotted vs. $1/p_{C_3H_6}$. T = 70°C. $TiCl_3 = 1{\cdot}5 \times 10^{-3}$ mole. $Al(C_2H_5)_3 = 3 \times 10^{-3}$ mole. Solvent = 100 ml n-heptane.

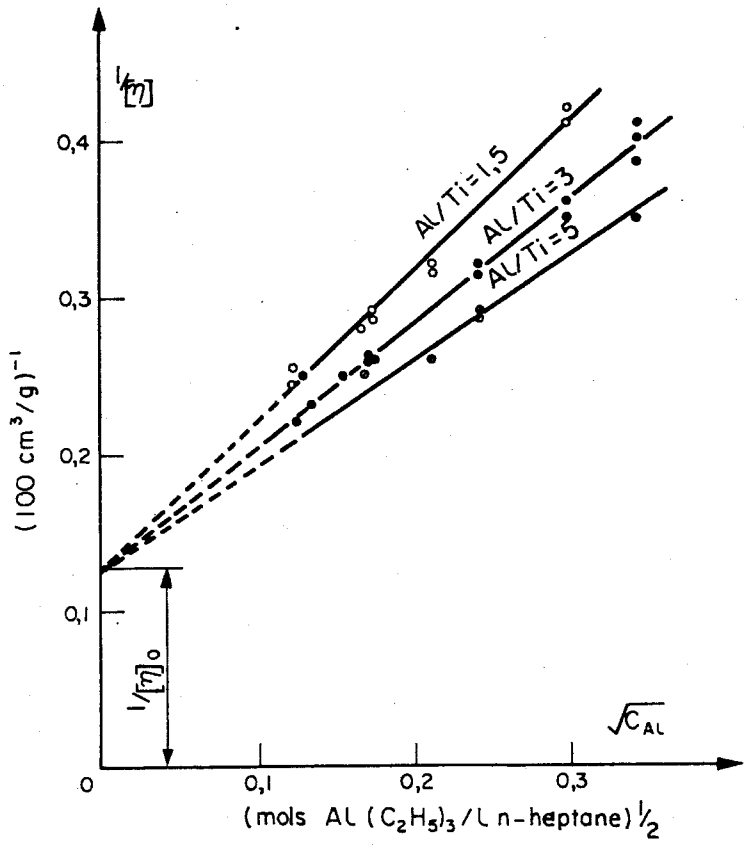


FIG. 10. Reciprocal of the intrinsic viscosity of the mainly isotactic polypropylene fraction, obtained with the reported pressure and $Al(C_2H_5)_3$/α-$TiCl_3$ ratios, plotted vs. the square root of the aluminum alkyl concentration. T = 70°C. $p_{C_3H_6}$ = 950 mm Hg. Solvent = 250 ml n-heptane.

where k_1, k_2, k_3, and k_4 are the rate constants of the different chain-termination processes, k_p is the propagation rate constant, and C_{Al} is the aluminum alkyl concentration. Equation (2) is easily deduced from the graphs shown in Figs. 7–11.[26, 27]

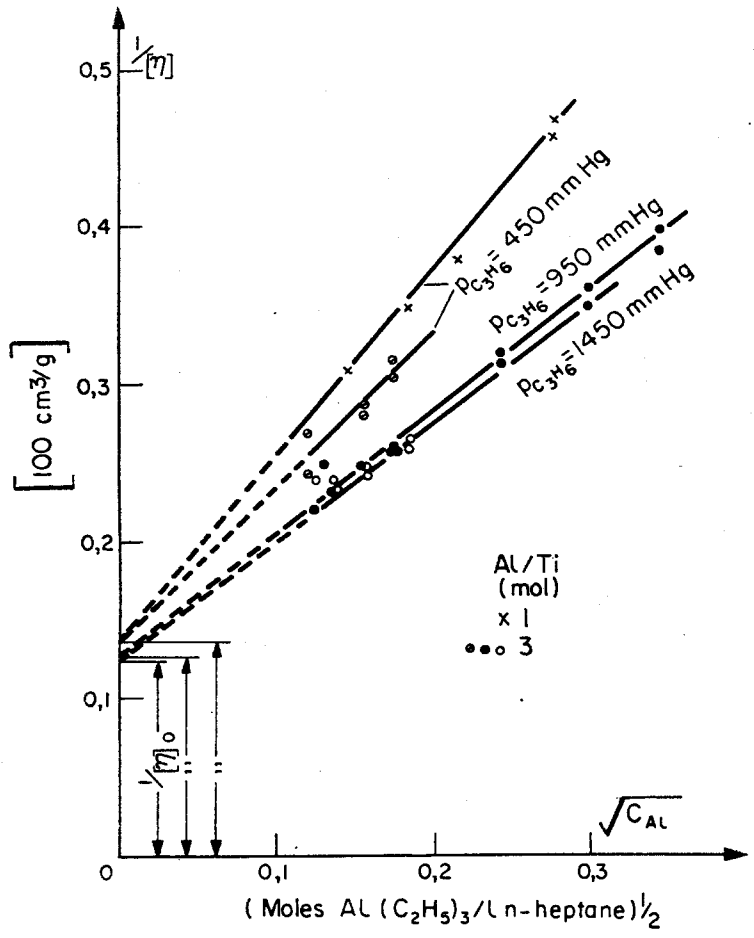


FIG. 11. Reciprocal of the intrinsic viscosity of the mainly isotactic polypropylene fraction, obtained at 70°C, at the reported pressure and $Al(C_2H_5)_3$/α-$TiCl_3$ ratios, plotted vs. the square root of the aluminum alkyl concentration.

Using aluminum tri-ethyl labelled with ^{14}C, we have been able to detect termination reactions which depend on the aluminum alkyl concentration, and on the quantity of $TiCl_3$ present.[27] Both processes involve the incorporation of ethyl groups derived from the aluminum alkyl into the polymer chain. The quantity of ethyl groups (Et) introduced per weight unit of polymer is given by the following equation, which is derived directly from the graphs shown in Figs. 7–9:

$$\mathrm{Et} = \frac{k_3\sqrt{C_{Al}} + k_4 p_{C_3H_6}\sqrt{G_{Ti}}}{k_p p_{C_3H_6}} \qquad (3)$$

The terms appearing in the numerator of eq. (3) are, theoretically, equal to the corresponding terms in eq. (2). The relation between reactions introducing ethyl groups and chain termination is shown by the increase of the inverse molecular weight with the increase of the aluminum alkyl concentration and of the quantity of $TiCl_3$ in the system (Fig. 10).

As C_{Al} and G_{Ti} tend to a limiting value of zero, $1/[\eta]$ tends to a limiting value different from zero (Fig. 10). This limiting value $1/[\eta]_0$ decreases slowly to an asymptotic value when the pressure is increased (Fig. 11).

Below 70°C the temperature has only a minor effect on the molecular weight (Fig. 12). It would therefore appear that the activation

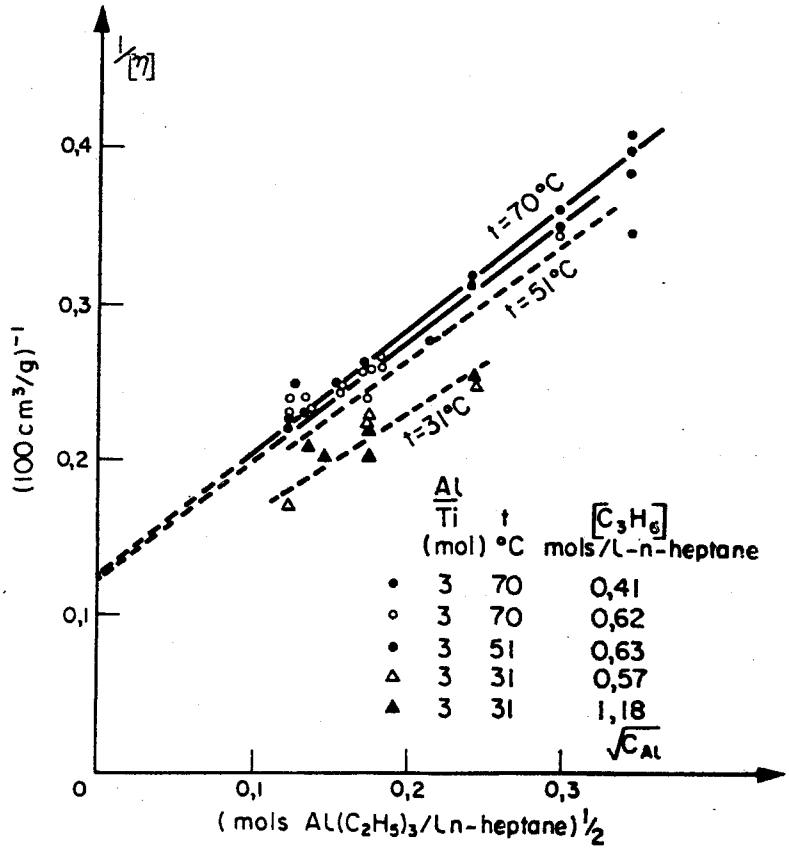


FIG. 12. Reciprocal of the intrinsic viscosity of the mainly isotactic polypropylene fraction, obtained at the reported temperature and olefin concentrations, plotted vs. the square root of the aluminum alkyl concentration.

energies of the important termination reactions do not differ greatly from that of the propagation process. Under the conditions of our experiments, none of the chain termination reactions seems to lower the overall rate of polymerization.

The mechanism which we have proposed for the complete polymerization reaction is shown in Table 3.

The termination reaction, which is first order with respect to monomer concentration, may be considered as a chain transfer to the monomer, but an alternative mechanism with many stages cannot be excluded. One possibility is a monomolecular dissociation of the

TABLE 3. REACTION SCHEMES FOR THE PROPYLENE POLYMERIZATION PROCESS WITH STEREOSPECIFIC CATALYSTS

(a) Initiation and propagation

$$[Cat]^{(+)}__^{(-)}R + CH_2=CHCH_3 \longrightarrow [Cat]^{(+)}__^{(-)}CH_2CHCH_3R$$

$$[Cat]^{(+)}__^{(-)}CH_2CHCH_3(CH_2CHCH_3)_{n-1}R + CH_2=CHCH_3 \longrightarrow [Cat]^{(+)}__^{(-)}CH_2CHCH_3(CH_2CHCH_3)_nR$$

where R = H, C_2H_5, C_3H_7 or other polymeric alkyl groups

(b) Termination

1. Monomolecular process:

$$[Cat]^{(+)}__^{(-)}CH_2CHCH_3(CH_2CHCH_3)_nR \longrightarrow [Cat]^{(+)}__^{(-)}H + CH_2=CCH_3(CH_2CHCH_3)_nR$$

2. First-order process with respect to the monomer:

$$[Cat]^{(+)}__^{(-)}CH_2CHCH_3(CH_2CHCH_3)_nR + CH_2=CHCH_3 \longrightarrow [Cat]^{(+)}__^{(-)}CH_2CH_2CH_3 + CH_2=CCH_3(CH_2CHCH_3)_nR$$

3. Process depending on aluminum alkyl concentration:

$$[Cat]^{(+)}__^{(-)}CH_2CHCH_3(CH_2CHCH_3)_nR = R_1AlR_2 \longrightarrow [Cat]^{(+)}__^{(-)}R_1 + R_2AlCH_2CHCH_3(CH_2CHCH_3)_nR$$

or:

$$TiCl_nAlY_2P + AlR_3 \longrightarrow TiCl_nAlR_3 + AlY_2P$$

where Y = alkyl and P = polymeric chain.

growing polymer chain, with transfer of a hydride ion to the catalytic complex. Such a hydride, reacting with the monomer, should give an alkyl group and initiate a new chain.

The termination reaction of the order ½ with respect to the aluminum alkyl concentration has been interpreted as an exchange of alkyl groups between the growing polymer chain and the aluminum alkyl in solution.

The nature of the termination reaction which involves the quantity of $TiCl_3$ present is not yet completely clear, but it is connected with an exchange of alkyl groups between the growing polymer chain and alkyl compounds in solution containing ethyl groups derived from the triethyl aluminum.

A comparison of the inverse intrinsic viscosity ($[\eta]$) which varies with the degree of polymerization, [eq. (2)] with the number of ethyl groups (Et) found in the polymer [eq. (3)] supports our hypothesis concerning the termination mechanism. At a given pressure, the result should be as follows:

$$1/x = B + \mathrm{Et} \tag{4}$$

where B = constant, or $1/x$ is a unique and monotonic function of Et. In Fig. 13, $1/[\eta]$ is shown as a function of Et.

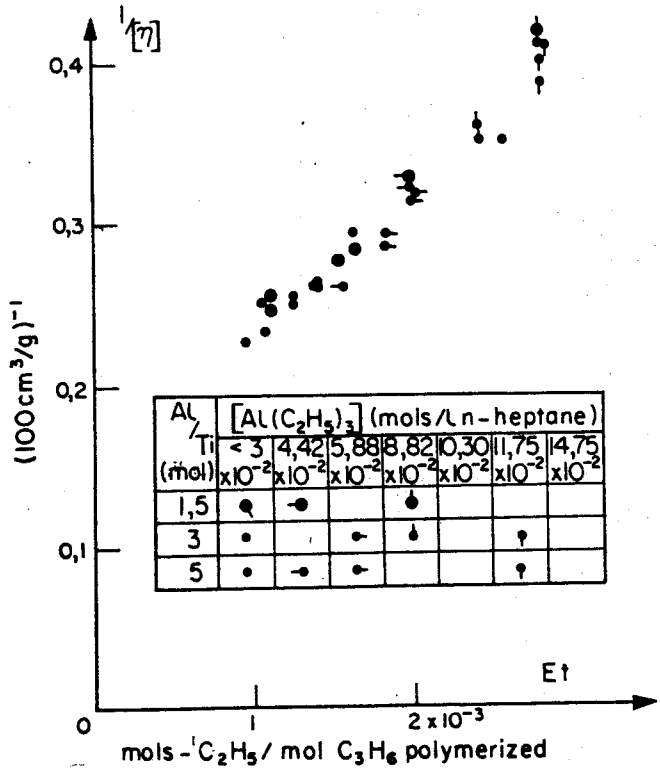


FIG. 13. Reciprocal of the intrinsic viscosity of the mainly isotactic polypropylene fraction, obtained with α-$TiCl_3$ and $Al(C_2H_5)_3$, as a function of the moles $-C_2H_5$ bound to the polymer.

(c) Determination of the Active Centers by Radiochemical Methods

The number of active centers in the various catalytic systems α-$TiCl_3$/$Al(C_2H_5)_3$ and α-$TiCl_3$/$Al(C_2H_5)_2Cl$, used in the polymerization of propylene, was determined by using a sample of powdered α-$TiCl_3$ and aluminum alkyls labelled with ^{14}C. Two methods were used for this evaluation: (*1*) Direct measurement of the adsorption of radioactive aluminum alkyl on $TiCl_3$, and (*2*) determination of the active centers by kinetic methods.

In order to determine the number of active centers resulting from the adsorption of aluminum alkyls on α-$TiCl_3$, the following procedure was adopted[28]: treatment of crystalline $TiCl_3$ at a given temperature with a solution of aluminum alkyl, and filtration followed by repeated washing of the solid at a given temperature with anhydrous benzene, until the filtrate was no longer radioactive.

By treating the $TiCl_3$ thus obtained with acid, free C_2H_4 and C_2H_6 are produced. This shows that during the treatment of the $TiCl_3$ with aluminum alkyls, formation of complexes which is at least partially irreversible occurs on the surface of the crystalline substrate.

In another series of experiments, $TiCl_3$ which had been treated with labelled aluminum alkyl and subsequently washed with anhydrous hydrocarbon, was used to polymerize propylene (and also ethylene) after the further addition of nonradioactive aluminum alkyl. This last addition is not strictly necessary for the formation of the catalyst and the initiation of polymerization. The polymer obtained is radioactive, and the total number of—C_2H_5 groups found in the polymer does not depend on either the duration of the polymerization or on the amount

TABLE 4. DETERMINATION OF THE NUMBER OF ACTIVE CENTERS ON A POWDERED SAMPLE OF α–$TiCl_3$ FROM ADSORPTION DATA OF ^{14}C LABELLED ALUMINUM ALKYL COMPOUNDS, FOLLOWED BY POLYMERIZATION OF PROPYLENE

($TiCl_3$ = 0.5 g. Aluminum alkyl compound = 0.5 ml. Solvent = 30 ml n-heptane)

Aluminum compound	*Adsorption temperature, °C*	*Time of adsorption, hr*	*Solvent*	*Washing temperature with anhydrous solvent, °C*	*Moles of C_2H_5 adsorbed per mole of $TiCl_3$*	
					Total alkyl groups remaining on $TiCl_3$ after washing	*Number of alkyl groups on active centres pre-adsorbed alkyl groups found in the polymer*
$Al(C_2H_5)_3$	—18	½	n-Heptane	—18	$17{\cdot}0\times10^{-3}$	n.d.
$Al(C_2H_5)_3$	—18	3	n-Heptane	—18	$45{\cdot}0\times10^{-3}$	$9{\cdot}3\times10^{-3}$
$Al(C_2H_5)_3$	20	½	Benzene	20	48.2×10^{-3}	$10{\cdot}1\times10^{-3}$
$Al(C_2H_5)_3$	46	½	Benzene	46	$17{\cdot}7\times10^{-3}$	$10{\cdot}5\times10^{-3}$
$Al(C_2H_5)_3$	46	½	Benzene	20	$10{\cdot}5\times10^{-3}$	$10{\cdot}8\times10^{-3}$
$Al(C_2H_5)_3$	70	½	Benzene	70	$6{\cdot}2\times10^{-3}$	$6{\cdot}7\times10^{-3}$
$Al(C_2H_5)_3$	100	½	Toluene	100	$3{\cdot}0\times10^{-3}$	$3{\cdot}0\times10^{-3}$
$Al(C_2H_5)_2Cl$	70	½	n-Heptane	20	$3{\cdot}0\times10^{-3}$	$3{\cdot}1\times10^{-3}$

of nonradioactive aluminum alkyl added. This confirms our previous hypothesis as to the nature of the catalyst.[29]

Below 60°C the number of ethyl groups found in the polymer is lower than the total number of ethyl groups adsorbed on the $TiCl_3$ as measured by gas evolution. This can be attributed to two different types of adsorption. At a temperature of 70°C the number of ethyl groups found in the polymer corresponds to the total amount adsorbed on the $TiCl_3$ (Table 4), and we may therefore assume that at this temperature the ethyl groups found in the polymer correspond to the number of active centers initially present on the $TiCl_3$ surface. The results obtained for both systems are shown in Table 4. The same value for the number of active centers was found over the entire range of temperatures investigated (about 1 mole per 100 moles of $TiCl_3$ in the $Al(C_2H_5)_3/\alpha$-$TiCl_3$ system). The number of active centers found in the α-$TiCl_3/Al(C_2H_5)_2Cl$ system at 70°C is less than the number found in the system α-$TiCl_3/Al(C_2H_5)_3$. This can be correlated with the different activities observed in the two systems.

TABLE 5. RADIOACTIVE CONTAMINATION, IN THE TREATMENT OF A POWDERED SAMPLE OF α-$TiCl_3$ WITH ^{14}C LABELLED $Al(C_2H_5)_3$, INDEPENDENT OF ADSORBED ALKYL GROUPS

($TiCl_3$ = 0.5 g. $Al(C_2H_5)_3$ = 0.5 ml. Solvent = 30 ml n-heptane)

Treatment temperature °C	*Radioactive contamination, as—C_2H_5 moles per $TiCl_3$ mole*	*Ratio between the radioactivity of contamination and the radioactivity of alkyls adsorbed on active center from the data of Table 4, %*
—18	$1{\cdot}8\times10^{-3}$	19·5
20	$1{\cdot}3\times10^{-3}$	13
46	$1{\cdot}2\times10^{-3}$	11·5
70	$1{\cdot}6\times10^{-3}$	15

(d) Determination of the Active Centers by Kinetic Methods

The method of determining active centers described in the preceding section only applies to those centers present on the $TiCl_3$ surface after treatment with aluminum triethyl and repeated washing with the solvent before polymerization. These centers do not necessarily cor-

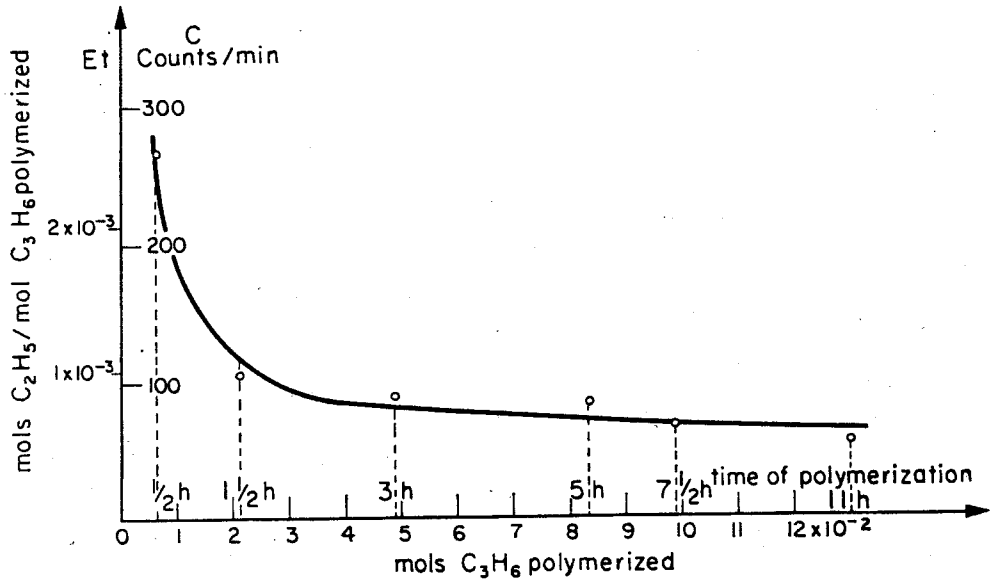


FIG. 14. Specific radioactivity (with the corresponding value of $-C_2H_5$ moles per mole of polypropylene) plotted vs. the quantity of polypropylene obtained at different times of polymerization. $t = 70°C$. $p_{C_3H_6} = 450$ mm Hg. $Al(C_2H_5)_2Cl = 0{\cdot}6$ ml. $TiCl_3 = 0{\cdot}3$ g. Solvent = 100 ml n-heptane.

respond to the centers present during steady-state polymerization. In fact, depending on the size of the $TiCl_3$ crystals, the polymerization may show an initial settling period, lasting for some minutes, during which there is a variation in the surface area of the $TiCl_3$, and consequently in the number of accessible active centers.

We have been able to calculate the total number of active centers taking part in the polymerization by a kinetic method, which can be summarized as follows: each catalytic complex initiating polymerization can be written as [Cat]·R, where [Cat] is the catalytic complex bound to the crystalline substrate of $TiCl_3$, and R is the alkyl group derived from the organometallic compound initially added as part of the catalytic system.

The monomer molecules enter in the [Cat]—R bond, thus separating from the active center the R group, which remains as the terminal group of the first molecule of polymer produced by this active center. If R is present in the catalytic complex at the start of the polymerization, the total number of R groups found in the polymer should be the same as the number of active centers. However, in the polymerization of propylene by the system $Al(C_2H_5)_3/\alpha$-$TiCl_3$/n-heptane, we have observed that R also enters, at a constant rate, into macromolecules formed under steady-state conditions, presumably as a result of some chain-termination reaction. Thus, in steady conditions, some of the growing chains will have an R group at one end,

while others have a $-C_3H_7$ end group, introduced by the various termination or transfer processes which involve the linkage of a monomeric molecule to the active center. Because of this, in some of our experiments with radioactive aluminum alkyl, a variation of the ratio: R groups found in the polymer/total number of polymer molecules was observed as the polymerization time increased. This enabled us to evaluate the number of active centers taking part in the polymerization process.

It has been shown[30] that in the systems which we have examined, the number of ethyl groups found in the polymer per mole of propylene polymerized is given by the following equation:

$$\mathrm{Et} = \frac{C^* + \Sigma r_1 t}{r_p t} \tag{5}$$

where

Et = "moles" of ethyl groups found in the polymer for each mole of propylene polymerized.

Σr_1 = rates of the termination reactions which introduce ethyl groups derived from the aluminum alkyl as terminal groups in the polymer chains.

r_p = rate of propagation of the growing polymer chain.

C^* = number of active centers.

t = polymerization time.

This equation can only be used to determine the number of active centers when Σr_1 is sufficiently low in comparison with C^*. This condition has been shown to hold in the system α-$TiCl_3$/$Al(C_2H_5)_2Cl$/n-heptane.[33] On the other hand, systems containing triethyl aluminum gave excessively high values of Σr_1.

Specific radioactivities, corrected for radioactive contamination, together with the corresponding values of Et found in polymerizations using the α-$TiCl_3$/$Al(C_2H_5)_2Cl$/n-heptane system, are shown in Fig. 14. These experimental values tend toward an asymptotic value corresponding to the ratio $\Sigma r_1/r_p$. They agree with the curve shown, which was calculated assuming that:

$$C^* = 6{\cdot}3 \times 10^{-3} \text{ moles } -C_2H_5/\text{mole } TiCl_3$$

Using the same catalytic system at the same temperature, the two methods used to determine the number of active centers, *viz.* radiochemical adsorption and kinetic measurements, lead to values of the

same order of magnitude. A comparison of the highest value obtained by the kinetic method (about 0·6 per cent expressed as moles $-C_2H_5$ per mole of $TiCl_3$) with that obtained by the adsorption method (about 0·3 per cent) indicates that not all the active centers taking part in the polymerization are initially present on the surface of the catalyst used [i.e. α-$TiCl_3$ treated with $Al(C_2H_5)_3$ and washed repeatedly].

(e) Variation in the Molecular Weight of the Polymer as a Function of Reaction Time

In any polymerization process, the number-average degree of polymerization of the total polymer produced after a time t is given by the equation:

$$x = \frac{\int_0^t r_p \, dt}{C^* + \int_0^t \Sigma r_r \, t} \tag{6}$$

where Σr_r is the termination rate of growing chains. If all rates are independent of time, then:

$$x = r_p t/(C^* + \Sigma r_r t) \tag{7}$$

Under conditions where Σr_r is sufficiently small, and consequently C^* not negligible in comparison with $\Sigma r_r t$, a variation of x with reaction time is detectable. Figure 15 shows the results of some preliminary experiments on the polymerization of propylene with the system α-$TiCl_3$/$Al(C_2H_5)_3$/n-heptane, operating at a temperature of 15°C and a partial pressure of propylene of 200 mm Hg.

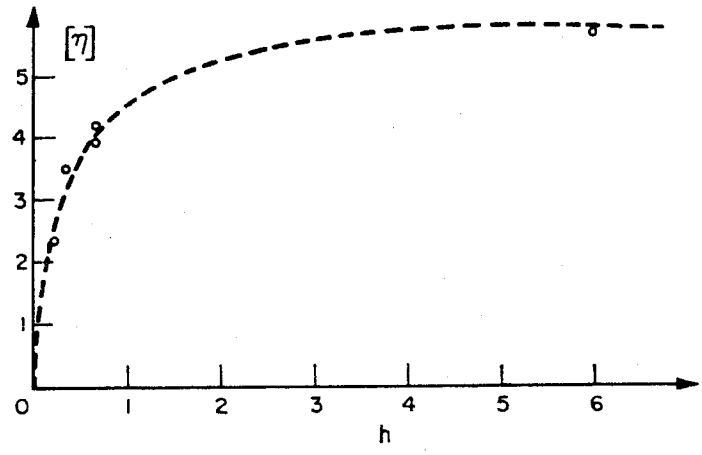


FIG. 15. Intrinsic viscosity of the mainly isotactic polypropylene fraction, plotted vs. the polymerization time. T = 15°C. $p_{C_3H_6}$ = 200 mm Hg. α-$TiCl_3$ = 1 g. $Al(C_2H_5)_3$ = 0·8 ml. Solvent: 250 ml n-heptane.

Knowing x as a function of time it is possible to calculate C^*. In order to obtain the x values from viscosity data, we must have a relation between the intrinsic viscosity of the polymer and its number-average degree of polymerization.

(f) Attempt to Determine a Relation between the Intrinsic Viscosity and the Number-Average Degree of Polymerization by a Radiochemical Method

A combination of eqs. (2) and (3) gives:

$$\frac{1}{x} = \frac{1}{x_0} + \mathrm{Et} \tag{8}$$

On the basis of the results shown in Fig. 13, we can assume that, over the range in question, the following relationship holds approximately:

$$\frac{1}{[\eta]} = \frac{1}{[\eta]_0} + K\mathrm{Et} \tag{9}$$

Eliminating Et between eqs. (8) and (9), we have:

$$\frac{1}{x} - \frac{1}{x_0} = \frac{1}{K}\left[\frac{1}{[\eta]} - \frac{1}{[\eta]_0}\right] \tag{10}$$

where x_0 and $[\eta]_0$ are, respectively, the number-average degree of polymerization and the intrinsic viscosity of the polymer, obtained by extrapolating the experimental values to the limiting conditions $C_{\mathrm{Al}} = 0$, and $G_{\mathrm{Ti}} = 0$. Since

$$1/x_0 = 1/K[\eta]_0 \tag{11}$$

it follows from eq. (10) that:

$$x = K[\eta] \tag{12}$$

From the results shown in Fig. 13, which refer to the mainly isotactic polypropylene fraction (representing about 90 per cent by weight of the total polymer) obtained with the system α-$TiCl_3$/$Al(C_2H_5)_3$/n-heptane, the following approximate results are obtained:

$$x = 90[\eta]$$

or

$$M_n = 3800[\eta]$$

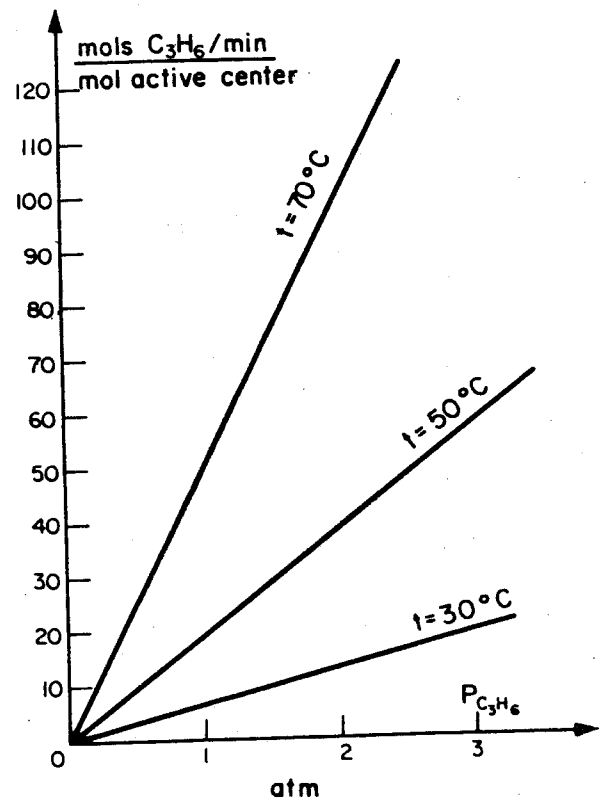


FIG. 16. Mean growth rate of the chains of polypropylene with a catalytic system: α-$TiCl_3$-$Al(C_2H_5)_3$.

The number-average molecular weight, determined in this way, is much lower than the viscometric molecular weight (determined on the assumption that the known relations for polyethylene are also valid for polypropylene). The very low value (<0.1) found for the ratio between the number-average and the viscometric molecular weights shows that the polymer has a wide molecular weight distribution.

(g) Average Life-Time of the Growing Chains

Knowing the number of active centers and the overall rate of polymerization, we can calculate the mean growth rate of the chains on each active center. We have assumed that in the system α-$TiCl_3$/$Al(C_2H_5)_3$/n-heptane, the number of active centers is independent of the temperature in the range 30–70°C, and is equal to 1 mole per 100 moles $TiCl_3$. The resulting average growth rates are shown in Fig. 16.

It is also possible to determine the average life-time of each macromolecule if the rates of the different termination processes are known. The rate at which the alkyl complexes undergo chain separation can be deduced directly from eq. (3), in which all the factors are known.

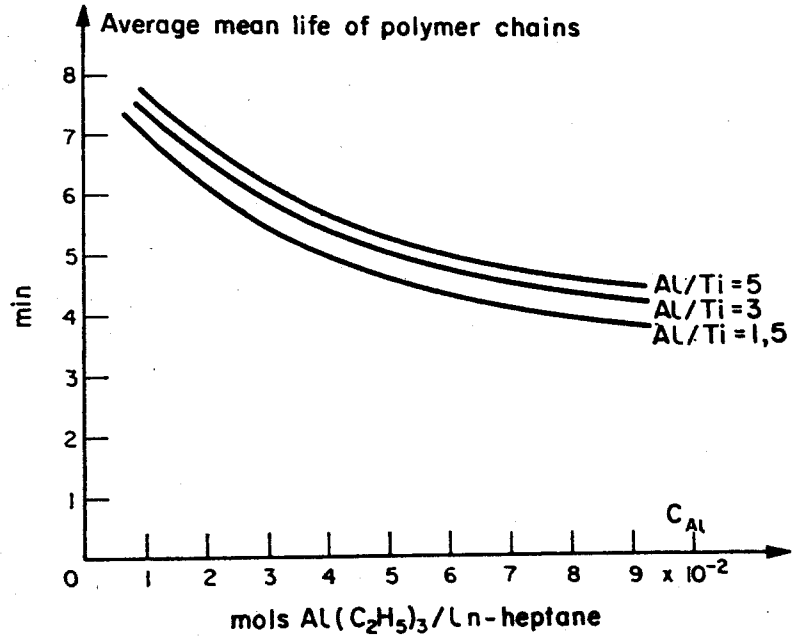


FIG. 17. Average mean life-time of the polypropylene chains growing on the active centers of a catalytic system: α-$TiCl_3$-$Al(C_2H_5)_3$. T = 70°C. $p_{C_3H_6}$ = 950 mm Hg.

The rate of the other termination reaction can be determined from the graph shown in Fig. 10, with the aid of eq. (3). The average life-time of the growing chains, determined in this way, under various polymerization conditions, is given in Fig. 17.[31]

We have also tried to calculate the number of active centers from the variation of the intrinsic viscosity with reaction time.[31] The results obtained using this method are of the same order of magnitude, but the values are lower than those obtained by the method previously described (0.2 per cent—C_2H_5 per mole $TiCl_3$ instead of 1 per cent). Calculation of the number of active centers from the variation of intrinsic viscosity with reaction time is necessarily indirect, since the determining factor is the rate of propagation of the polymer chains; only if all the growing chains had the same propagation rate would it be possible to obtain the same value as that resulting from direct measurements.

The propagation rate of the mainly isotactic crystalline fraction, and of isotactic chains with a high molecular weight, appears to be higher than the propagation rate of the amorphous chains, which always have a lower molecular weight. We can therefore assume that not all the active centers have the same polymerization rate: the centers with higher rates should produce polymer chains of higher molecular weight. Since the intrinsic viscosity of a polymer is mainly determined by the higher molecular weight fractions, the number of active centers deduced from the variation of the intrinsic viscosity

with reaction time is, to a large extent, controlled by the propagation rate of the high molecular weight chains. In this case, the number of active centers obtained from viscosity measurements is lower than the real value.

IV. COMPARISON OF THE REACTIVITIES OF α-OLEFINS AND ETHYLENE BY A KINETIC STUDY OF THEIR COPOLYMERIZATION

Kinetic investigations on the polymerization and copolymerization of α-olefins can be useful in clarifying the influence of the structure of different monomers on their response to this type of coordination catalysis, and in forecasting their behaviour in copolymerization. In this section, we wish to summarize very briefly the results we have obtained for the copolymerization of ethylene and propylene.

The problems involved were by no means simple, since in addition to known difficulties arising from the ionic character of the polymerization, there were others due to the differing activities of the different parts of the typical heterogeneous Ziegler catalyst. We have concentrated our research on the preparation of catalysts having a composition and physical structure as much homogeneous as possible, to avoid the presence of active centers having different reactivity ratios with respect to the two monomers to be copolymerized. One class of catalysts which has proved to have these requirements is that of highly dispersed catalysts, which, with α-olefins, produce a mainly atactic, noncrystallizable polymer.[32] It should be said, however, that under suitable experimental conditions we have also succeeded in preparing homogeneous copolymers using other classes of catalysts; for instance, those obtained starting from solid crystalline halides of transition metals, virtually containing only one type of active center, which is effective in polymerizing both α-olefins and ethylene.

Another difficulty was the much higher reactivity of ethylene compared with that of α-olefins in anionic copolymerization. This has been overcome by using a continuous-flow method, with a high rate of flow of a gaseous mixture of monomers, in very different proportions from those desired in the copolymer. Only under these conditions has it been possible to prepare true copolymers, free from homopolymers.

The composition of the copolymers has been established within a very close approximation by using ethylene labelled with ^{14}C. Another method of analysis which we have used for ethylene-propylene copoly-

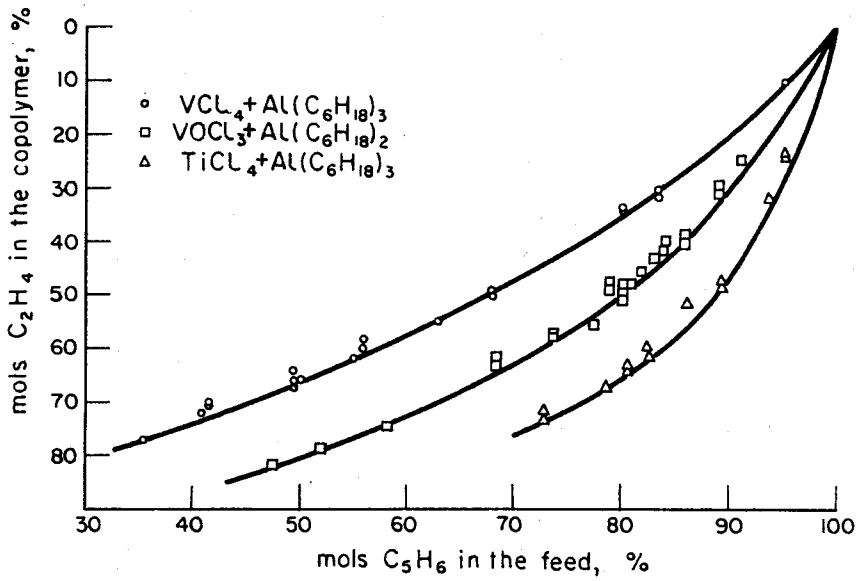


FIG. 18. Composition of ethylene-propylene copolymers obtained with different catalysts, corresponding to different compositions of the feed.

mers is based on measuring the intensity of the absorption band at 7·25 μ, working in carbon tetrachloride solution. Using these methods, we have been able to show that the composition of ethylene–propylene copolymers prepared using highly dispersed catalysts does not depend on the concentration of the catalyst, the aging time of the catalyst, the duration of the polymerization, or on the ratio: moles aluminum trialkyl/moles halide used in the preparation of the catalyst.[32]

As an example of our results, Fig. 18 shows the variation in composition of the ethylene–propylene copolymers with varying composition of the gaseous feed mixture, using catalysts prepared respectively from $VOCl_3$, VCl_4, and $TiCl_4$. At high rates of flow, the copolymer composition is independent of the feed rate, and we have been able to determine the variation of copolymer composition with variation of the ratio between moles of propylene in solution and total moles of both monomers in solution.[33,34] The results are shown in Fig. 19.

We have applied the copolymerization equation proposed by Alfrey and Goldfinger to these results, which, in the case of ethylene–propylene copolymerization can be written as follows:

$$\frac{m_{C_3H_6}}{m_{C_2H_4}} = \frac{M_{C_3H_6}}{M_{C_2H_4}} \frac{r_{C_3H_6} M_{C_3H_6} + M_{C_2H_4}}{r_{C_2H_4} M_{C_2H_4} + M_{C_3H_6}}$$

The reactivity ratios $r_{C_2H_4}$ and $r_{C_3H_6}$ were determined using the experimental data of Figs. 18 and 19, which give the mole percentages $m_{C_2H_4}$ and $m_{C_3H_6}$ of the two monomers present in the copolymer,

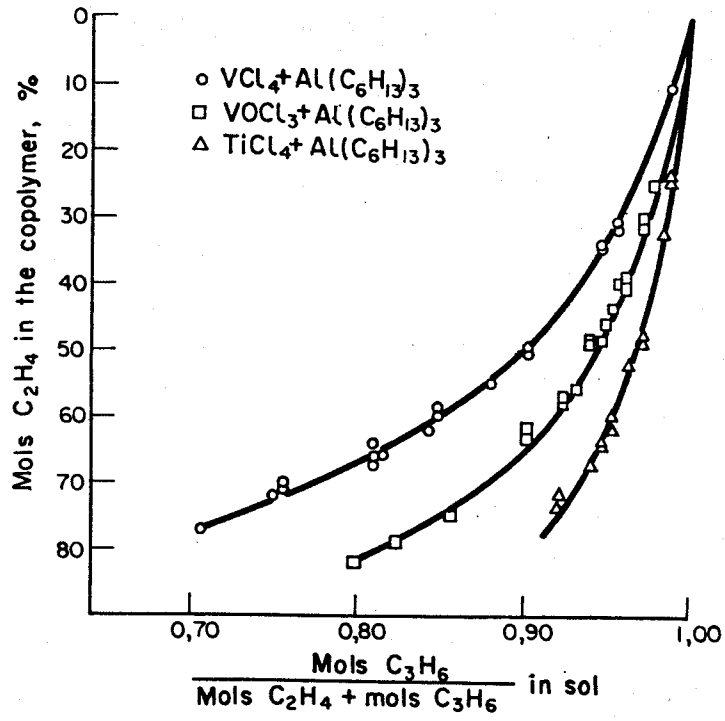


FIG. 19. Composition of ethylene-propylene copolymers obtained with different catalysts, referred to the ratio between the moles of dissolved propylene and the total moles of the two monomers in solution.

and the corresponding molar concentrations $M_{C_2H_4}$ and $M_{C_3H_6}$ of the monomers in solution. The calculation has been carried out both by the method of Lewis and Mayo,[35] and by that of Fineman and Ross.[36] Values of the reactivity ratios found for different catalytic systems are given in Table 6.

TABLE 6. REACTIVITY RATIOS IN ETHYLENE–PROPYLENE COPOLYMERIZATION IN THE PRESENCE OF DIFFERENT CATALYSTS

(Temperature = 25°C. Solvent = *n*-heptane[a])

Catalyst	$r_{C_2H_4}$	$r_{C_3H_6}$	$r_{C_2H_4} \times r_{C_3H_6}$
$Al(C_6H_{13})_3+TiCl_4$	37.36 ± 1.31	0.032 ± 0.001	1.20
$Al(C_6H_{13})_3+VOCl_3$	17·95 ± 0·27	0·065 ± 0·002	1·15
$Al(C_6H_{13})_3+CVl_4$	7·08 ± 0·20	0·088 ± 0·003	0·63

[a] Monomer reactivity ratios are referred to molar fraction of the monomer in solution.

The reactivity ratios of the two monomers differ considerably, and their product is remarkably close to unity, in agreement with the general results found for ionic copolymerization. The reactivity of propylene is

much lower than that of ethylene, as might be expected in an anionic copolymerization, owing to the presence of an electron-releasing methyl group in the propylene molecule. The fact that the reactivity ratios depend on the type of catalyst used is a further proof of the ionic mechanism of these polymerizations.

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PROPERTIES OF ISOTACTIC, ATACTIC, AND STEREOBLOCK HOMOPOLYMERS, RANDOM AND BLOCK COPOLYMERS OF α-OLEFINS*

by G. NATTA

(24 July 1958)

[*J. Polymer Sci.* **34,** 531 (1959)]

SYNOPSIS

The study of several methods of controlling the molecular weight in the stereospecific polymerization of α-olefins leads to a better understanding of the nature of coordinated ionic catalysis. Some physical and chemical factors that influence the steric composition of polymers have been examined and a kinetic interpretation of stereoblock polymers is proposed. A continuous variation of physical properties, particularly of crystallinity, melting point, and densities, and mechanical properties is observed as a function of the length of the sterically homogeneous section in stereoblock polymers. This length is related to the number of steric irregularities of the chain. A new method to prepare block copolymers of different monomers is described; these copolymers show evidence of crystallinity due to long sequences of the same monomeric units, but properties different from those of physical mixtures of homopolymers and from those of random copolymers. The production of random copolymers has been examined, particularly of amorphous ethylene-propylene copolymers having interesting elastomeric properties.

1. INTRODUCTION

In the paper submitted to the general section of this Symposium**, I discussed the stereospecific polymerization of α-olefins. In particular, I examined the kinetics of the different chain-growth, chain-termination

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* Lecture held at the International High Polymer Conference, Nottingham, July 21-24, 1958.

** Paper 92.

and chain-transfer processes which determine the molecular weight of the polymers obtained in the presence of stereospecific catalysts. Such catalysts act through a mechanism which we have defined as coordinated anionic, and are more or less stereospecific according to their chemical composition, their physical state, and the different polymerization conditions.[1]

Our investigations on the nature of the catalysts and on the polymerization kinetics enabled us to produce a great variety of linear polymers, the properties of which differ among themselves to a remarkable extent, according to the type of the steric structure prevailing in the polymer. In the present paper I refer only to the different types of polymers obtainable by α-olefin polymerization and copolymerization.

The examination of polymers and copolymers of propylene is sufficient, by itself, to demonstrate the great variety of new products now available to the macromolecular chemists, which include for instance, isotactic, atactic, and stereoblock homopolymers, random copolymers, block copolymers, and graft copolymers, which can all be obtained using the same monomers. I wish to emphasize that, until four years ago, no high polymer of propylene was known having any practical interest.

2. MOLECULAR WEIGHT REGULATION IN THE ANIONIC COORDINATED POLYMERIZATION PROCESSES

The problem of the regulation of the average molecular weight in polymerization, without altering the stereoisomeric composition, is one of the most important problems, from the commercial point of view, in the polymerization of the α-olefins. In the case of isotactic polymers, excessively high molecular weights corresponding to values of many hundreds of thousands, reduce the processability in the melted state and, in particular, hinder a high spinning speed in the production of textile fibers.

On the other hand, in the case of atactic polymers and of amorphous copolymers, high molecular weights (over 100,000–200,000) are necessary for the production of elastic rubbers having high tensile strengths and low creep. The synthesis of crystalline, not-too-high molecular weight polymers and of amorphous high polymers requires particular working conditions. As a rule, the isotactic, sterically purer fractions,

have relatively higher molecular weights, while the atactic fractions, obtained under similar polymerization conditions, show low molecular weights. We have thus been forced to elaborate stereospecific processes capable of producing isotactic polymers with the desired not-too-high average molecular weight. Other processes have been developed to obtain atactic polymers having the highest possible average molecular weight. No data have been published until now on the different processes which have been used for this purpose in pilot plants as well as in commercial plants. In this paper I shall refer only to some processes of theoretical interest, since they lead to a better understanding of the nature of coordinated ionic catalysis.

Compounds containing bonds between carbon atoms and a different metallic or non-metallic atom, having a partial ionic character, are generally effective in lowering the molecular weight of the polymers, if they are able to transfer negative groups to the catalytic complex. The molecular weight, in particular, is lowered by increasing the concentration of a particular metal-alkyl in the polymerization medium. In the first paper I delivered at this Symposium I discussed the influence of increasing aluminum alkyl concentration on molecular weight.

TABLE 1. LOWERING OF THE MOLECULAR WEIGHT OF ISOTACTIC POLYPROPYLENE IN THE PRESENCE OF TERMINATION AGENTS

Reaction conditions: $T = 70°C$; $p = 1450$ mm Hg; α-$TiCl_3$ (containing traces of $TiCl_4$), 0.5 g; $Al(C_2H_5)_3$, 1 ml; polymerization time. $2^1/_2$ hr; solvent, 250 ml *n*-heptane

Transfer agent		*Polymer Produced, g*	*Intrinsic viscosity of the ether insoluble polymer fraction (II+III) (100 ml/g)*	*Polymer fraction*		
Type	*g*			*I, extracted with boiling ether, %*	*II, extracted with boiling n-heptane, %*	*III, residue, %*
—	—	15·7	3·05	14·8	5·5	79·7
HCl	0·12	12·5	1·68	20·5	10·0	69·5
$CH(C_6H_5)_3$	0·187	15·8	2·30	19·6	6·7	71·8
C_2H_5Br	0·10	8·8	2·15	22·8	6·7	70·5
$Zn(C_2H_5)_2$	0·12	16·5	1·43	12·4	8·8	79·0
$Zn(C_2H_5)_2$	0·38	17·0	1·15	15·0	8·3	75·8
$Zn(C_2H_5)_2$	0·9	16·2	0·69	12·5	11·5	76·0
$Zn(C_2H_5)_2$	1·40	16·8	0·59	12·6	11·2	76·5

The addition of other metal (e.g. zinc) alkyls to the $Al(C_2H_5)_3$–$TiCl_3$ system does not influence the stereospecificity, but can exert an influence on the molecular weight by acting as an alkyl transfer agent (Table 1).[2]

It has been possible to demonstrate that the decrease of the molecular weight is not due to a $TiCl_3$–$Zn(C_2H_5)_2$ catalytic system. In fact, the catalytic complexes containing zinc alkyls are less stable than those containing aluminum and show a very low stereospecificity. As is shown in Table 1, the large decrease in the molecular weight is not accompanied by a corresponding decrease in the stereospecificity of the polymerization. Chain stopping and molecular weight reduction are shown by other compounds having a partial ionic character, such as the alkyl halides.

If, on the contrary, one adds traces of onium complexes to the normal catalytic system, there is no decrease but a slight increase in molecular weight (Table 2). This fact can be explained by considering that in the dissociation of the onium complexes no carbon ions are involved. The very high molecular weight of the amorphous α-olefin polymers obtained in the presence of oxygen-containing catalysts can be attributed to the formation of more stable complexes containing oxygen atoms chemisorbed on the surface of the solid support.[3]

According to the patent literature, a decrease of the molecular weight can be achieved by carrying out polymerization in the presence of

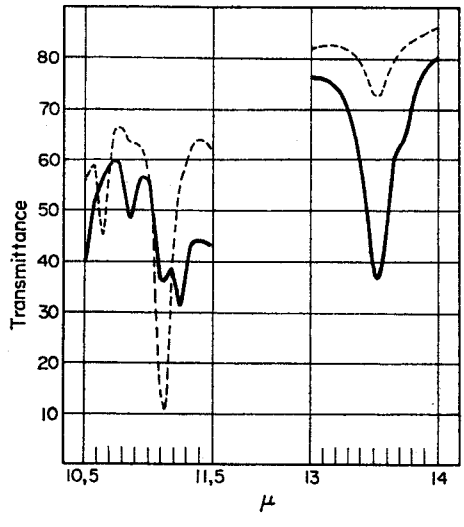


FIG. 1. Infrared spectra between 10·5 and 11·5 μ, and between 13 and 14 μ showing the vinylidene (11·27), isopropyl (10·88), and propyl (13·54) terminal groups of a low molecular weight amorphous (continuous line) and isotactic (dotted line) polypropylene (m.p. 146°, viscosity MW <2000, crystallinity 70 per cent obtained in the presence of high hydrogen pressures).

TABLE 2. EFFECT OF SOME HYDROCARBON SOLUBLE COMPOUNDS ON THE ACTIVITY AND STEREOSPECIFICITY OF α-$TiCl_3$ (CONTAINING TRACES OF $TiCl_4$) IN THE POLYMERIZATION OF PROPYLENE. REACTION CONDITIONS: 70°C.; $p_{C_3H_6}$ = 1450 mm Hg

$TiCl_3$, g	*Al $(C_2H_5)_3$, ml*	*Polymerization time min*	*Solvent*	*Soluble compounds*		*Wt. of polymer, g*	*Polymer fractions*			*Intrinsic viscosity of the polymer fractions (II+III) (100 ml g)*
				Type	*g*		*I, extracted with boiling ether, %*	*II, extracted with boiling n-heptane, %*	*III, residue, %*	
0·5	1	150	n-Heptane	—	—	15·7	14·8	5·5	79·7	3·05
0·5	1	150	n-Heptane	$(C_4H_9)_4.NI$	0·051	29·8	8·60	3·1	88·6	3·51
0·5	1	150	n-Heptane	$Ti[O.CH(CH_3)_2]_4$	0·095	21·0	10·85	5·8	83·0	3·20
0·5	1	150	Benzene	$TiCl_2(C_5H_5)_2$	0·039	70·6	12·26	1·84	84·6	4·06
1·19	2	225	Toluene	—	—	8·0	13·8	4·5	81	3·38
1·19	2	225	Toluene	$TiCl_2(C_5H_7O_2)_2$	0·31	10·8	13·0	5·2	82	3·75

hydrogen, the decrease being dependent on the hydrogen partial pressure used. These processes are always accompanied by a certain decrease in the steric purity. We have attributed such a decrease of molecular weight to a process involving a heterolytic split of the hydrogen molecule, which is influenced by the nature of the metal alkyl, according to which a proton saturates the end of the growing polymeric chain and a hydride ion is attached to the catalyst, thus replacing the alkyl chain. Such a hydride ion, linked to the catalyst, reacts with propylene to form an alkyl group which can start a new polymeric chain. It follows that the polymers obtained are mainly saturated, and have n-propyl terminal groups at one end (corresponding to the beginning of the chain), and isopropyl groups at the other end (corresponding to the termination of the chain). Such groups can be easily detected by infrared analysis (Fig. 1).

Under these conditions, the normal polymerization process is accompanied by a catalytic stepwise addition of α-olefin followed by an hydrogenation step:

$$m\mathrm{C}_n\mathrm{H}_{2n} + H_2 \xrightarrow{[\mathrm{cat}]^+\mathrm{H}^-} \mathrm{C}_{mn}\mathrm{H}_{2mn+2}$$

which causes the production of saturated hydrocarbons.

By using different regulating factors it is now possible to obtain, at will, molecular weights within wide limits; for instance, it is possible, at very high H_2 pressure (50–150 atm), to obtain highly crystalline low-melting isotactic polymers soluble in ether and having an average molecular weight of about 1000. High melting (175–176°C) crystalline polymers, having a viscometric molecular weight between 30,000 and more than 500,000, can be obtained with different regulating agents.

3. INFLUENCE OF THE POLYMERIZATION CONDITIONS ON THE STERIC COMPOSITION OF THE POLYMERS

The properties of vinyl polymers depend, to a remarkable extent, on their stereoisomeric composition. The first α-olefin polymers we obtained by coordinated anionic heterogeneous catalysis were complex mixtures of head-to-tail, linear polymers, containing isotactic and atactic molecules, as well as molecules which we found to be made up of stereoblocks, having intermediate properties between those of the

TABLE 3. FRACTIONATION BY BOILING SOLVENT EXTRACTION OF POLYPROPYLENES OBTAINED IN THE PRESENCE OF DIFFERENT CATALYSTS AT 70–80°C. AND WITH A CONSTANT PRESSURE OF 2.4 ATM.

Catalyst	*Acetone extractable fraction*, %	*Ether extractable fraction*		*Hexane extractable fraction*				*Heptane extractable fraction*			
		%	$[\eta]$	%	$[\eta]$	*Crystallinity*, %	*Melting point*, °C.	%	$[\eta]$	*Crystallinity* %	*Melting point*, °C.
$TiCl_4+Al(C_2H_5)_3$	6·6	38·7	0·70	9·3	1·1	25	115	10·2	0·92	41	159
$TiCl_3+Al(C_2H_5)_3$	1·50	6·5	0·42	4·0	0·52	32	125	3·3	0·65	52	159
$TiCl_3+Be(C_2H_5)_3$	0·8	2·7	0·31	1·6	0·35	32	120	0·8	0·29	53	161

Catalyst	*2-Ethyl hexane extractable fraction*				n-*Octane extractable fraction*				*Residue*			
	%	$[\eta]$	*Crystallinity*, %	*Melting point*, °C.	%	$[\eta]$	*Crystallinity*, %	*Melting point*, °C	%	$[\eta]$	*Crystallinity*, %	*Melting point*, °C.
$TiCl_4+Al(C_2H_5)_3$	17·4	1·01	52	168	17·8	3·1	60	174	—	—	—	—
$TiCl_3+Al(C_2H_5)_3$	18·0	0·90	62	170	16·20	1·3	64	175	50·5	3·0	66	175
$TiCl_3+Be(C_2H_5)_3$	14·2	0·6	62	170	15·5	1·5	65	174	65	2·3	70	175

isotactic and the atactic ones.[4] In Fig. 2 the mechanical characteristics of isotactic, atactic, and stereoblock polymers of propylene are indicated.

Using well crystallized α-$TiCl_3$ (violet) and alkyl derivatives of highly electropositive metals having a very small radius, such as aluminum and beryllium, highly isotactic crude polymers have been produced.[3] The crude polymers contain more than 85 per cent, and in some cases more than 95 per cent, of polymer insoluble in boiling heptane, most of which is insoluble in boiling octane and has a melting temperature of 175°C (Table 3).

Polymers having a high steric purity, even if of comparatively low molecular weight, do not show viscous creep under loads at room temperature, being thus different from the crude polymers containing larger proportions of atactic and stereoblock molecules.

The most important factors influencing the formation of stereoblock polymers are the nature of the transition metal compound, its crystallinity, its ability to yield complexes with organometallic compounds, and the stability of the complexes produced. For instance, some vanadium compounds with a valence higher than 3 are

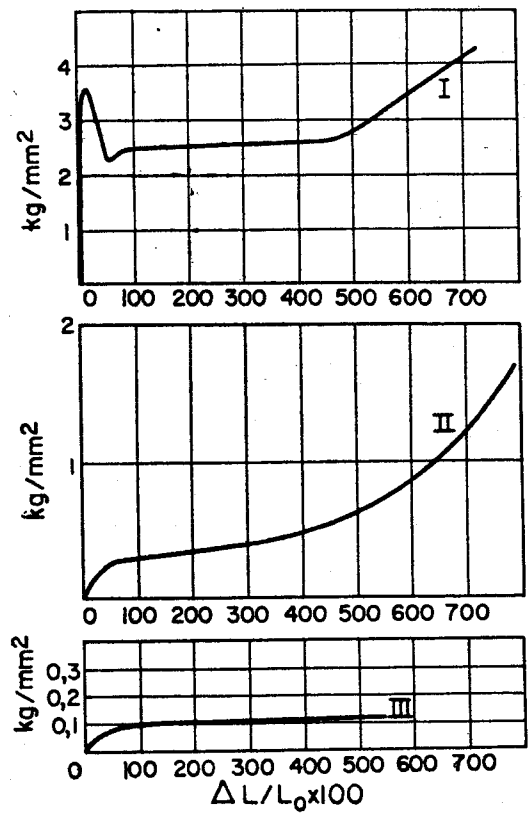


FIG. 2. Stress-strain curves of a highly isotactic (I), stereoblock (II), and atactic (III) propylene polymers.

more suitable than the titanium compounds to prepare poorly stereospecific catalysts. They give high yields of stereoblock polymers having very high molecular weight.

For each compound of a transition metal, the stereospecificity in polymerizing α-olefins depends on many factors, and particularly on the stability of the chemisorbed catalytic complexes. The stereospecificity is reduced by every factor which makes such complexes more easily desorbable or dissociable. The most important factors are: (*1*) an increase in the ionic radius of the metal linked to the organometallic compound;[5] (*2*) an increase in the length of the alkyls, having at least two carbon atoms linked to the complex;[6] (3) an increase in temperature;[7] and (*4*) irregularities and low cohesion force in the crystal lattice, which acts as a support to the chemisorbed catalytic complex.

Other factors reducing stereospecificity are connected with the exchange between compounds containing metal alkyls or components of non-chemisorbed complexes, also containing metal alkyls, with the corresponding components of the catalytically active chemisorbed complexes. Furthermore, it has been observed that many conditions which directly or indirectly influence the molecular weight (e.g. ionic or ionizable compounds in solution, temperature) also have some influence on stereospecificity.

In general, increase of polymerization temperature reduces stereospecificity. The effect is reversible if the catalyst is used at a temperature much lower than that of its preparation. At higher temperatures the effect is generally not reversible, because an irreversible change of the chemical structure of the catalyst, containing transition metals, takes place. This effect depends on the chemical nature and in particular on the reducibility nature of the compound of the transition metal used, on the nature of the organometallic compound, and on the ratio between the different components used to prepare the catalysts. For instance an increase in the preparation temperature of the catalyst causes an increase in stereospecificity for catalysts prepared from $TiCl_4$ and a decrease for those prepared from $TiCl_3$. In the first case, an increase in temperature causes the formation of a more highly crystalline precipitate (increase of stereospecificity). On the other hand, in the second case ($TiCl_3$), if the temperature is raised above 100°C., surface corrosion of the previously existing crystals occurs with a decrease of stereospecificity. In both cases the catalytic activity of the stereospecificity must be attributed to the formation

of complexes containing transition metals and organometallic compounds which are chemisorbed on more or less crystalline solid phase.[6]

In some catalysts prepared at high temperature and thermally stabilized, one observes a behaviour which depends reversibly on the temperature, and a good reproducibility in experiments carried out at a temperature not to exceeding that at which the catalyst was stabilized. With such catalysts the stereoisomeric composition shows a regular variation which is almost linear with the temperature. This can be ascribed to the predominance of a single factor regulating both molecular weight and stereospecificity, most probably the dissociability of a chemisorbed complex.

A kinetic interpretation of the processes which control the stereoisomeric composition, carried out with thermally stabilized catalysts, allowed us to determine a very low activation energy corresponding to a process which causes an inversion in the steric configuration of the monomeric units in the growing chain.[7] The formation of stereoblock polymers depends on the ratio between the growth rate and the rate of steric configuration inversion. The inversion rate is probably related to processes involving the dissociation and the reassociation processes in different active centers of the growing chains or of groups containing

TABLE 4. FRACTIONATION OF RAW POLYMERS OBTAINED WITH DIFFERENT CATALYSTS PREPARED FROM TITANIUM CHLORIDES AND TRIETHYL ALUMINUM AT TEMPERATURES FROM 35 TO 90°C.

Fraction	*Soluble in*	*Insoluble in*	*Crystallinity, %*	*Melting temperature, °C.*	*Irregularity, %*[a]
I	—	Trichloroethylene	75–85	176	0
II	—	n-Octane	64–68	174–175	0·4–0·8
III	n-Octane	2-Ethyl hexane	60–66	174–175	0·4–0·8
IV	2-Ethyl hexane	n-Heptane	52–64	168–170	2·5–3·4
V	n-Heptane	n-Hexane	41–54	147–159	7·2–12·2
VI	n-Hexane	n-Pentane	25–37	110–135	17·3–27·8
VII	n-Pentane	Ethyl ether	15–27	106–114	26·1–29·5

[a] Supposing that ideal sterically pure crystalline polymer melts at 176°C.

them. The rate of such dissociation processes also influences the molecular weight of the polymers, because other processes hindering the growth of the polymeric chains take place before the reassociation processes. To this cause can be attributed the different molecular weights of the various fractions of stereoblock polymers, simultaneously obtained and separated from the same crude polymer. The shorter the stereospecific blocks, the lower are crystallinity, melting temperature, and also molecular weight. On the same basis it is possible to explain the even lower molecular weight of the amorphous fractions. These latter are produced by a different type of active center with a lower propagation rate and must be considered as very short

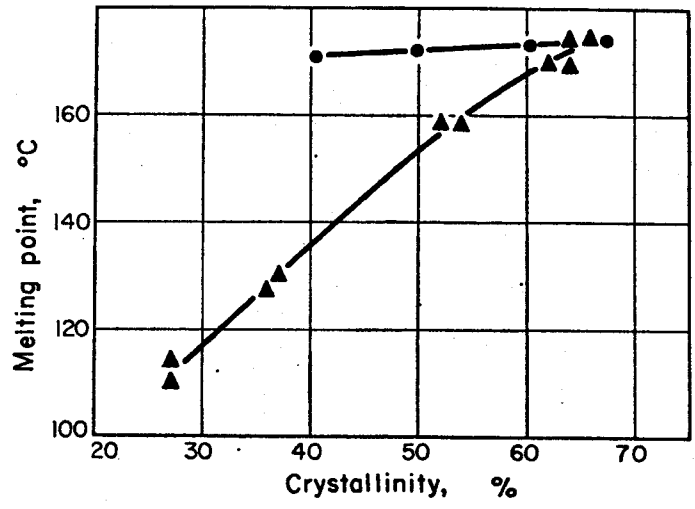


FIG. 3. Melting temperature of mixtures of isotactic and atactic polypropylenes (●) and of stereoblock polypropylenes (▲) having different crystallinity.

stereoblock polymers, the formation of which is characterized by a low ratio between the propagation rate and the inversion rate.

Stereoblock polymers of propylene show a melting temperature and a crystallinity depending on the average lengths of the isotactic sections of the chain. The theoretical decrease of the melting point was determined according to Flory's theory for copolymers, assuming that the steric irregularities act like the irregularities due to the presence of different monomeric units (Table 4). In Fig. 3 the lowering of crystallinity as a function of the melting temperature is shown for stereoblock polymers and for mechanical mixtures of isotactic and atactic high molecular weight polypropylenes.

Figure 4 shows the X-ray spectra of stereoblock polymers, having increasing melting point, and of isotactic polymers.

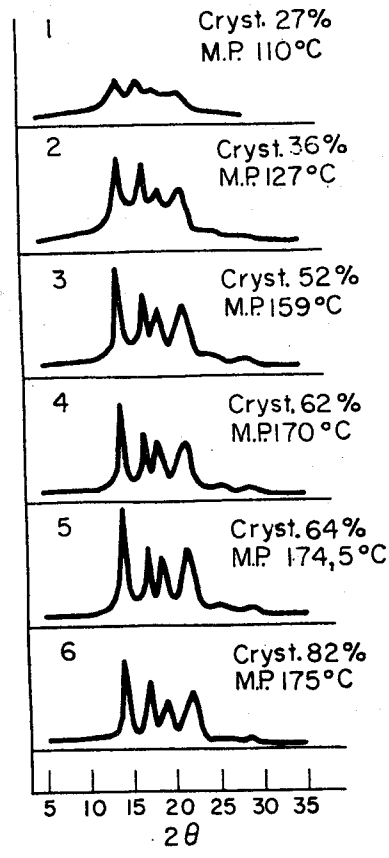


FIG. 4. Geiger counter X-ray spectra of stereoblock polypropylenes having different melting temperatures

4. PHYSICAL PROPERTIES OF STEREOBLOCK POLYMERS

The mechanical properties of stereoblock homopolymers confirm their characteristic structure. Very significant properties are observed on examining, in particular, block copolymers having 15–30 per cent crystallinity (determined by X-rays). The stress-strain diagrams show that the initial elastic moduli are very low in comparison with those of highly isotactic polypropylene. The modulus increases with stretching. On the contrary, mixtures of amorphous and isotactic polymers, having the same crystallinity, show very rapid creep, even under a very low constant load.

The most interesting property of the block polymers is their high elasticity in the oriented state. The reversible elongation by stretching of oriented block polymers, having a crystallinity of about 25 per cent, reaches values between about 100 and 200 per cent (for stereoblock having intrinsic viscosities between about 1 and 1·5).[4] From this point of view, certain oriented propylene stereoblock polymers may be considered true elastomers, as they fall within the definition normally

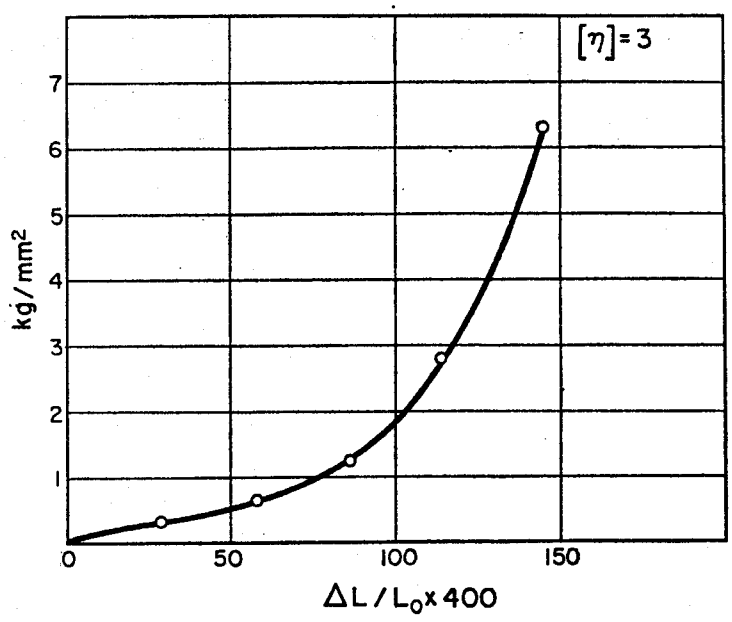


FIG. 5. Stress-strain curve of a stereoblock polypropylene (intrinsic viscosity 3) pre-stretched to 700 per cent.

accepted for such materials. Their elastomeric behaviour becomes evident if one examines the stress-strain diagram of a stereoblock polymer previously oriented by 700 per cent stretching (Fig. 5). The diagram shows that such polymers have initial low elastic modulus, reversible elongation, and relatively high tensile strength. The creep at constant load diagram is very similar to that of a vulcanized elastomer (Fig. 6). The creep is very small for products of very high molecular weight. This behaviour can be attributed to the fact that in the oriented products the chains tend to dispose themselves parallel to the stretching direction, their isotactic sections are associated into crystals and the lattice energy hinders the flow of the chains. Crystallinity exerts an action similar to that observed in natural rubber when it is rapidly stretched. Its effect is similar to that of a thermo-labile vulcanization.

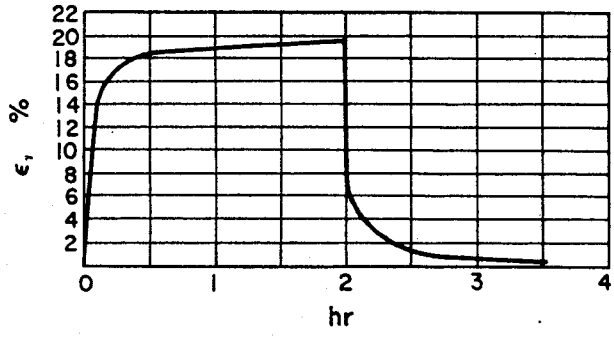


FIG. 6. Creep curve at constant load (10 kg/cm²) prolonged for 2 hr and successive recovery curve of a stereoblock polypropylene.

The stereoblock polymers having a higher crystallinity (40–50 per cent) show higher initial elastic modulus, higher tensile strength, and in general, rather lower elastic elongation (of the order of 10–20 per cent).

5. BLOCK COPOLYMERS: HETEROBLOCK POLYMERS OF α-OLEFINS

By alternating introduction of different monomers in the reaction medium we succeeded in lengthening a growing polymeric chain with long successive homogeneous sections of monomeric units in the same macromolecule, obtaining block polymers of the type:

...AAAAAAABBBBBBBAAAAAAABBBBBBB...

In order to achieve this result, we operated with catalysts containing catalytic centers active for both monomers and at temperatures at which the average life of each macromolecule was sufficiently long.[8]

When operating at room temperature with highly stereospecific catalysts based on α-$TiCl_3$, we employed the following polymerization steps: (*1*) Polymerization of monomer A for a short time (τ'); (*2*) complete elimination of the unreacted monomer A from the system (e.g., by evacuating or stripping with an inert gas); (*3*) introduction of monomer B and polymerization for a time τ''; and (*4*) complete elimination of unreacted monomer B.

These four steps can be repeated at will with the same or with different monomers. The average length of each block of monomeric units A (or B) depends on the time τ' (or τ'') and on the polymerization rate r' (or r''). Equal length blocks can be obtained by adjusting the concentration of the monomers and the time in order to obtain $r'/r'' = \tau''/\tau'$.

The crude polymers obtained by successive polymerization of ethylene and propylene show, by X-ray examination, the presence of crystals, some of them having the structure of polyethylene, others having the structure of polypropylene. Fractionation enables us to separate the crude polymers into many fractions which possess different total crystallinity but about the same ratio of crystalline polyethylene content to crystalline polypropylene content.

In Table 5 the results of the extraction of a crude block copolymer (propylene-ethylene) are compared with those of the extraction of crude polyethylene or crude polypropylene obtained under similar con-

TABLE 5 COMPARISON BETWEEN THE FRACTIONATIONS OF AN ETHYLENE–PROPYLENE HETEROBLOCK COPOLYMER, ETHYLENE AND PROPYLENE HOMOPOLYMERS OBTAINED WITH THE SAME CATALYTIC SYSTEM [α-$TiCl_3$+$Al(C_2H_5)_3$], AND A RANDOM COPOLYMER

Polymer	*% by weight of fraction extractable with different boiling solvents*			
	Ether	n-*Heptane*	n-*Octane*	*Residue*
Heteroblock copolymer, C_2:C_3 = 1:1 mole	0·9	17	30·5	51·6
Random copolymer, 1:1 mole	48·9	51·1	—	—
Polyethylene	Traces	4·6	65·0	30·4
Polypropylene	14·4	6·5	22·8	56·6

ditions (alternating polymerization and evacuation steps but operating with only one monomer). The melting temperatures of the polyethylene crystals and of the isotactic polypropylene crystals present in the heteroblock polymers are lower than those of the pure homopolymers.

The study of block copolymers of α-olefins with more or less long sections of homopolymers with a regular structure is a new field of research showing interesting aspects from theoretical and in particular from stereochemical viewpoints.

6. RANDOM COPOLYMERS OF α-OLEFINS

The properties of the random copolymers of α-olefins show some analogies with those of stereoblock homopolymers. Small quantities of a different monomer introduced into an isotactic polymer reduce its crystallinity and lower the melting point, as does the presence of sterically different units in stereoblock homopolymers. Larger quantities (e.g. more than 20 per cent) make the copolymers amorphous.

Although the physical properties of the α-olefin amorphous copolymers should be practically independent of the relative configurations of the monomeric units when the sequences of each monomeric unit are very short, the production of random copolymers is made easier by using highly dispersed catalysts which, in the homopolymerization of α-olefins, yield mainly atactic homopolymers. While, as a rule, by using certain Ziegler-type catalysts one obtains products containing mixtures of macromolecules including homopolymers and copolymers having a very large range of composition, the products obtained continuously, either with certain catalysts containing only one type

of highly stereospecific active centers, or with non stereospecific catalysts (for instance, obtained from VCl_4 and triethyl aluminum), consist entirely of copolymers and are free from homopolymers.

The above mentioned findings have been demonstrated by us by carrying out some accurate fractionations of the copolymerization products and examining the properties of different fractions.[9,10]

The amorphous copolymers of ethylene with propylene [obtained with VCl_4 and $Al(C_2H_5)_3$] are completely soluble in boiling n-heptane. On the contrary, polyethylene obtained using the same catalyst is almost completely insoluble, and also polypropylene is partially insoluble in boiling n-heptane.

The infrared spectra of the copolymer fractions isolated by solvent extraction differ remarkably from the spectra of the corresponding fractions obtained from propylene homopolymers, from the spectrum of pure polyethylene, and from the spectra of their mechanical mixtures (Fig. 2 of paper 79). The infrared spectra of all the copolymer fractions show absorption bands between 13·4 and 13·8 μ. These can be attributed to the presence of sequences of methylene groups having different lengths.

X-ray examination also confirms the nature of the copolymers prepared by us. The fractions which can be isolated by ether extraction are amorphous, and the maximum diffraction intensity appears in the spectra at an angle which is different from the angles corresponding to the maximum of amorphous linear polypropylene and from the maxima which can be expected for an amorphous polyethylene and for the mixture of both the amorphous polymers. Also the fractions successively extractable by hexane and by boiling heptane prove, in general, to be amorphous to X-rays, contrary to the analogous fractions obtainable from the propylene homopolymers which show remarkable crystallinity (between 30 and 50 per cent). As an example, we have reported in Fig. 3 of paper 79 a comparison between the X-ray examination of a linear polyethylene, an ethylene–propylene copolymer fraction insoluble in ether but extractable by hexane, and a corresponding fraction obtained from pure polypropylene.

The mechanical properties of the copolymers prepared by us are different from those of the homopolymers and of their physical mixtures, and can be used as raw materials for the production of good elastomers.[9] Ethylene–propylene copolymers are made up of long linear hydrocarbon chains containing short sequences of methylene groups, having no tendency to crystallize when unstretched. The

amorphous sequences of methylene groups confer a great mobility on the chain due to the low energy barrier contrasting small rotations of chain segments around the CH_2—CH_2 bond. The non-vulcanized polymers show, in fact, a visco-elastic behaviour which is very similar to that of the polyhydrocarbon rubber having a low second order transition temperature. They show low initial elastic moduli, high ultimate elongations, and low hardness. The temperature at which the resilience passes through a minimum is near to the one shown by natural rubber (Fig. 4 of paper 79).

The crosslinking of the ethylene–propylene copolymers can be suitably achieved by different methods and leads to vulcanized products having excellent chemical resistance, high tensile strength, and good elastic properties[11] (Fig. 5 of paper 79). They can be reinforced with active fillers, such as carbon-black or silica, and mixed with conventional plasticizers (Fig. 6 of paper 79). A 50 per cent propylene–50 per cent ethylene copolymer having an intrinsic viscosity of about 4, reinforced with 45 parts of carbon-black shows, after vulcanization, a tensile strength of 300–400 kg/cm^2, an ultimate elongation of 500–600 per cent, a hardness of 60–70 degrees shore A, and a resilience, at room temperature, of 60–70 per cent. In comparison with other elastomers, the ethylene–propylene copolymers, being substantially saturated, have a high resistance to oxidation and aging; furthermore, they resist quite well the attack of many chemical reagents such as sulfuric acid and nitric acid.

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THE PRODUCTION OF GRAFT COPOLYMERS FROM POLY-α-OLEFIN PEROXIDES*

by G. NATTA, E. BEATI and F. SEVERINI

(24 July 1958)

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SYNOPSIS

The catalytic and autocatalytic peroxidations of the surface of filaments and laminae of isotactic and stereoblock poly-α-olefins have been studied. The peroxidation of atactic and stereoblock polymers in solution has also been examined. Peroxidized polymers have been used as radical initiators in the polymerization of vinyl monomers to achieve their grafting on poly-α-olefin chains. Some properties of these graft polymers, e.g., anti-shock properties of polystyrenes grafted on poly-α-butene, have been reported.

Linear polymers and copolymers of the α-olefins have the interesting characteristic that one-half of the carbon atoms belonging to the main chain are tertiary carbon atoms to which an electron-releasing alkyl group is linked. Tertiary carbon atoms of the same type are contained, although to a lesser extent, in the copolymers of α-olefins with ethylene. The hydrogen atom linked to such tertiary carbon atoms shows a greater reactivity than the hydrogen of a CH_3 or CH_2 group. Such reactivity of the hydrogen can be considered as an inconvenience with regard to the aging stability at high temperature of the unstabilized polymers; however, it can be utilized to modify the properties of poly-α-olefins, particularly the surface properties, and to prepare a very large series of grafted or crosslinked derivatives. In 1954, shortly after the first preparations of isotactic polypropylene

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and polybutene, we started to study the thermal and catalytic peroxidation of such polymers, taking advantage of the experience previously acquired in studying the low temperature peroxidation of cumene.[1]

It has been proved that the autoperoxidation of poly-α-olefins can be interpreted according to the kinetic schemes described by Bolland and Gee[2] and that this shows, in certain aspects, some analogies with the peroxidation of other saturated hydrocarbons containing tertiary carbon atoms, such as 1,4-dimethyl-cyclohexane, studied by Stannett, Woodward, and Mesrobian.[3] Such analogies hold more accurately for polymer solutions, and in such cases, we have observed a zero-order reaction with respect to the oxygen pressure. By peroxidation of non-dissolved polymers, in particular highly crystalline polymers in the solid state, it has been possible to observe an influence of the oxygen pressure, probably due to the influence of the pressure on the diffusion rate of oxygen inside the samples.

The bimolecular mechanism of hydroperoxide decomposition, which, in the case of dimethylcyclohexane, prevails at low temperatures, would seem to be less probable in the case of crystalline poly-α-olefins, for which the association of the hydroperoxidic groups is hindered by the low mobility of those molecules which are part of crystals. This can be one of the reasons for the limited degradation and for the consequent slight change with aging of the mechanical properties of the crystalline high molecular weight polymers slightly peroxidized at low temperature.

Monomolecular dissociation of the hydroperoxide does not take place or occurs reversibly at low temperature in the absence of free radical capturing substances. However, grafting takes place rapidly in the presence of monomers which can be polymerized by free radicals, even at relatively low temperature.

In the study of peroxidation with air or oxygen, we have observed that peroxidation can be carried out, without substantial degradation by operating at a temperature lower than 70–80°C. In such conditions, the peroxidation of the crystalline isotactic polymers takes place only on the surface of the crystals or in the intercrystalline amorphous regions next to the external surface. On the contrary, in the crude polymers containing stereoblock and atactic polymers, the peroxidation takes place more deeply, depending on the stereoisomeric composition. This is related to the solubility and the diffusion rate of oxygen.

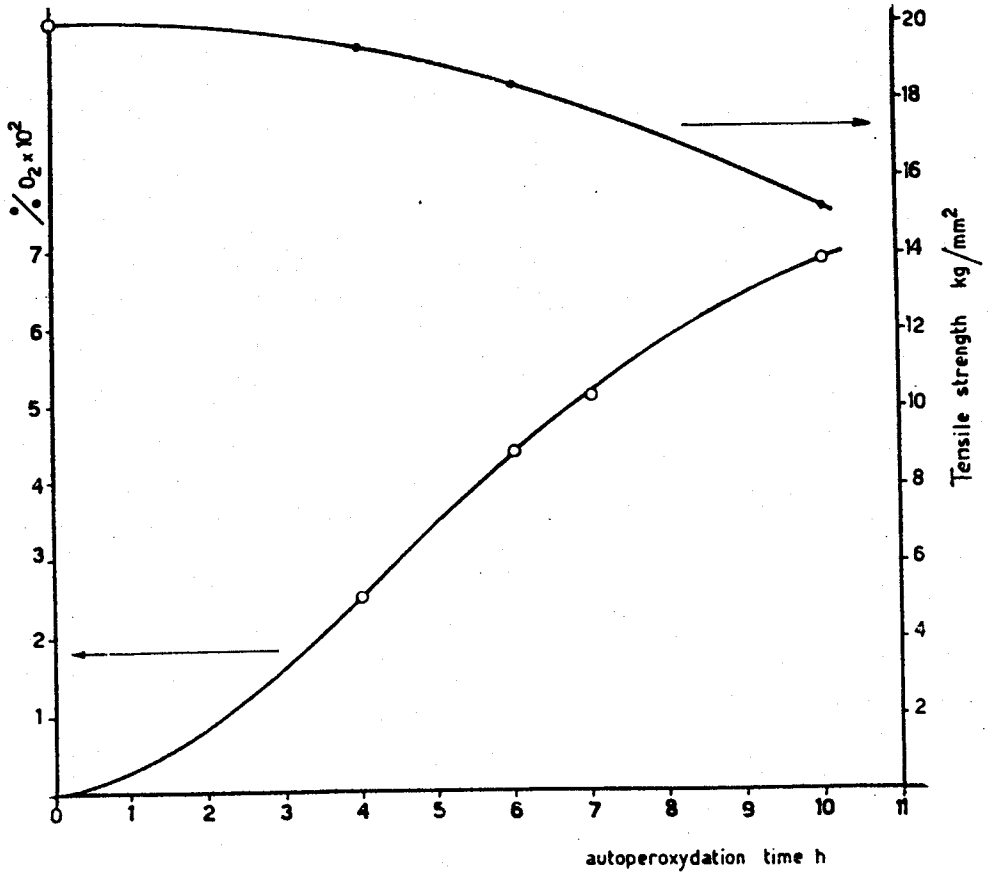


FIG. 1. Surface autoperoxidation at 70°C and 3 atm air pressure on oriented 0·016 cm-thick sheets of crystalline polypropylene (85 per cent insoluble in boiling n-heptane).

Figure. 1 shows the results of mainly superficial peroxidation on laminae of crystalline polypropylene (85 per cent insoluble in boiling heptane) oriented by stretching and having a maximum tensile strength of 20 kg mm^2 and an elongation of 27 per cent in the direction of stretching. The peroxidation was carried out at a temperature of 70°C and an air pressure of 3 atm. The mechanical characteristics remained practically unchanged (the decrease was no more than 10 per cent) for oxygen contents up to 0·035 wt. % of oxygen present as peroxide plus hydroperoxide groups. A decrease of more than 20 per cent in the tensile strength of the initial product takes place if the oxygen content, as defined above, exceeds 0·05 per cent.

The peroxidation in such products does not take place homogeneously and, most probably, mainly concerns the surface regions to a depth of the order of 0·001 mm. This is also proved by the fact that, in the peroxidation of a filament having a diameter of 0·025 mm it is possible to reach oxygen contents about 10 times higher, without

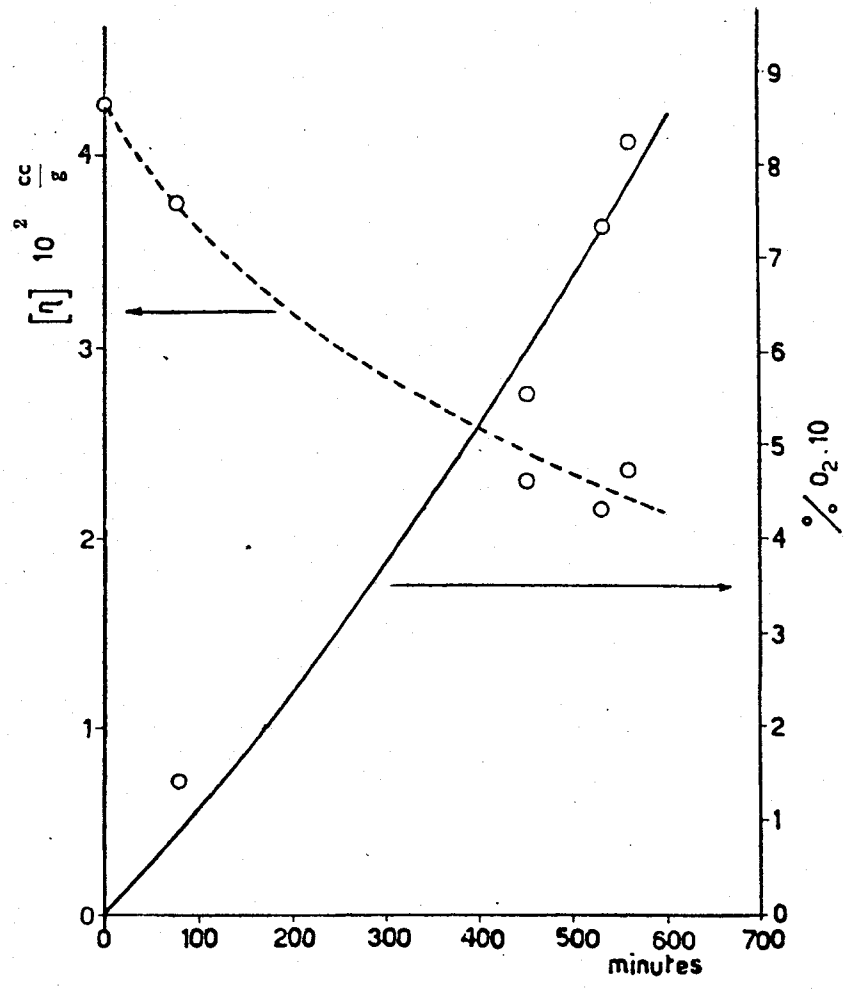


FIG. 2. Peroxidation of atactic polypropylene dissolved in isopropylbenzene (concentration 15·5 per cent containing 4 per cent methanol) at 70°C in stainless steel vessel under air pressure

any remarkable change in the mechanical characteristics. This behaviour can be explained by considering the difference in the surface area/weight ratio existing in the tested filaments and laminae. In fact, the oxygen content referred to the external surface reaches about the same values in both cases. In the course of tests carried out at a temperature of 75—85°C on a polypropylene filament having a resistance of 5.9 g/den, one observes that at oxygen contents up to 0.4 wt.%, the resistance remains almost unchanged (the decrease is not higher than 10 per cent). The influence of pressure on the peroxidation rate is less important in samples having a high surface-volume ratio, such as filaments.

Although the filaments under examination contained almost 85 per cent of crystallizable isotactic polymer (insoluble in boiling heptane) peroxidation took place chiefly on the amorphous part. In fact, almost one-half of the fixed oxygen is linked to the atactic poly-

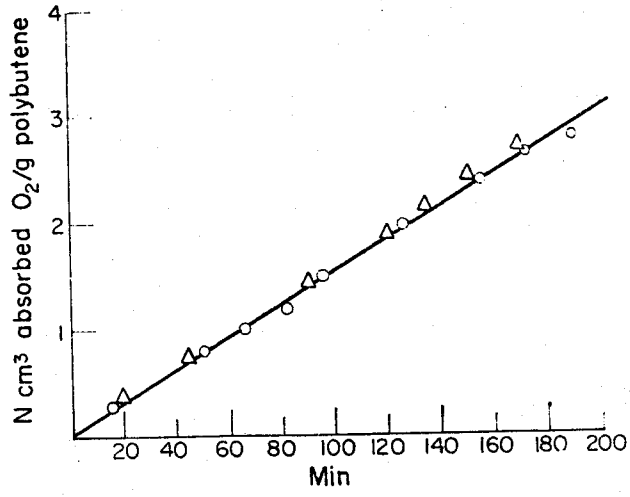


FIG. 3. Peroxidation of poly-α-butene (residue after extraction with ethylether) $[\eta]^{\text{toluene}}_{75\,^\circ\text{C}} = 4{\cdot}5\times10^2$ cc/g; X-ray crystallinity = 45 per cent; initiator: Bz_2O_2: (o) temperature 83°C after induction period of 10 min; (△) temperature 83°C, after induction period of 20 min.

mers (extractable by ether) present in the sample in very small amounts (about 5–6 per cent).

Peroxidation can be achieved in a more homogeneous way, if it is carried out in solution, in the presence of initiators. A suitable method for rapid peroxidation of α-olefin polymers on a laboratory scale consists in operating in cumene solution (and also in the presence of small quantities of preformed cumene hydroperoxide). The presence of a small percentage of methanol (3–5 per cent with respect to cumene) hinders side reactions.[1] Under such conditions, by bubbling air at atmospheric pressure into a 15–20 per cent solution of the polymer, peroxidation occurs rapidly at a temperature of 65–70°C (Fig. 2). It is interesting to point out that cumene hydroperoxide and the poly-α-olefin peroxides act mutually as catalysts, since the cumene hydroperoxide catalyzes the poly-α-olefin peroxidation, while the peroxidized poly-α-olefins catalyze the cumene peroxidation.

The suitability of such a laboratory method is evidenced by the fact that, under the same conditions, it is also possible to peroxidize polystyrene. In tests carried out on 30 per cent solutions of an atactic polystyrene with a low average viscometric molecular weight (10,000) in cumene with oxygen contents of 2–4 wt.% (corresponding to 6–12 peroxidic groups/100 styrene monomeric units) can be obtained easily without significant degradation (Table 1). In the literature, less highly peroxidized derivatives of polystyrene, containing 1·6 peroxidic groups/100 styrene units, have been previously described.[4]

TABLE 1. AIR PRESSURE PEROXIDATION OF 34 PER CENT POLYSTYRENE SOLUTIONS IN ISOPROPYLBENZENE CONTAINING 4 PER CENT METHANOL AT 70 °C IN STAINLESS STEEL VESSELS

Temperature °C	*Time, min.*	*Peroxidic oxygen wt. %*	$[\eta]$ *initial*[a]	$[\eta]$, *final*[a]
70	240	1·98	0·095	0·095
70	460	4·03	0·095	0·0875
80	600	1·03	1·07	0·575

[a] Intrinsic viscosities have been determined in benzene at 34°C and expressed in 100 cc/g.

The sharing of oxygen between polymer and cumene takes place at different rates for the different polymers. Under the above-mentioned conditions, the oxidizability of polystyrene, referred to the monomeric unit, seems to be higher than that of polypropylene.

In case of such polymers as partially crystalline polybutene, which are easily swollen or soaked by initiator solutions, a rather homogeneous peroxidation can be achieved with air. Figure 3 shows the oxidation data of two samples of polybutene (the residue after ether extraction having 45 per cent X-ray crystallinity), in the presence of benzoyl peroxide at 83°C and 3 atm oxygen. The peroxidized samples, after elimination of undecomposed benzoyl peroxide, show an oxygen content of 0·4 per cent, which is very close to the quantity of oxygen absorbed.

The peroxidized polymers can be used as initiators for peroxidation reactions and can supply a variety of products by grafting. It is convenient, in order to describe the different types of products, to consider the peroxidized α-olefin polymers separately according to their stereoisomeric structures: (a) crystalline isotactic polymers and (b) atactic polymers and stereoblock polymers.

GRAFTING ON ISOTACTIC α-OLEFIN POLYMERS

The surface peroxidation of manufactured articles from isotactic polymers makes it possible to modify the surface properties by grafting, to produce for instance hydrophilic fiber or films, dyeable fibers, etc. A concentration of 0·01–0·02 g oxygen/m² of surface is, generally, sufficient to obtain a thickness of grafted polymers on the surface

TABLE 2. GRAFTING OF METHYL METHACRYLATE AT 70°C ON SURFACE PEROXIDIZED POLYPROPYLENE SHEETS

Peroxidized poly-α-olefin			*Grafting time, hr*	*Initial thickness, mm*	*Final thickness, mm*	*Mechanical properties of the grafted product*		
Peroxidic oxygen, wt. %	*Ultimate tensile strength, kg/mm²*	*Elongation at break, %*				*Weight increase, %*	*Ultimate tensile strength, kg/mm²*	*Elongation at break %*
—	20·0	27	—	0·16	—	—	—	—
0·0235	19·3	46·5	2	0·16	0·20	44·6	14·1	44·5
0·0268	17·1	41·2	2	0·16	0·23	48	12·45	58·9
0·0542	15·3	41	2	0·17	0·23	50	11	47
0·0156	20·8	29·5	3	0·16	0·45	149	7·4	50
0·0204	18·4	35·2	3	0·16	0·40	150	8·8	59
0·0345	18·4	27·0	3	0·15	0·42	162	6·13	68·8

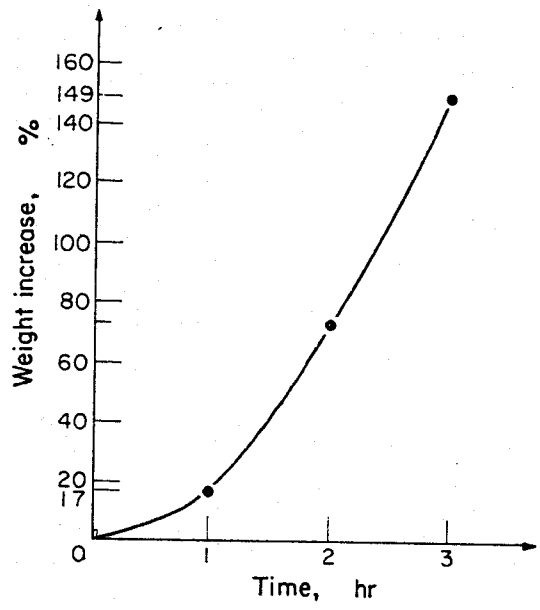


FIG. 4. Weight increase of peroxidized polypropylene sheets, (thickness 0·16 mm; oxygen content 0·038 g/m²) by methyl methacrylate grafting at 70°C.

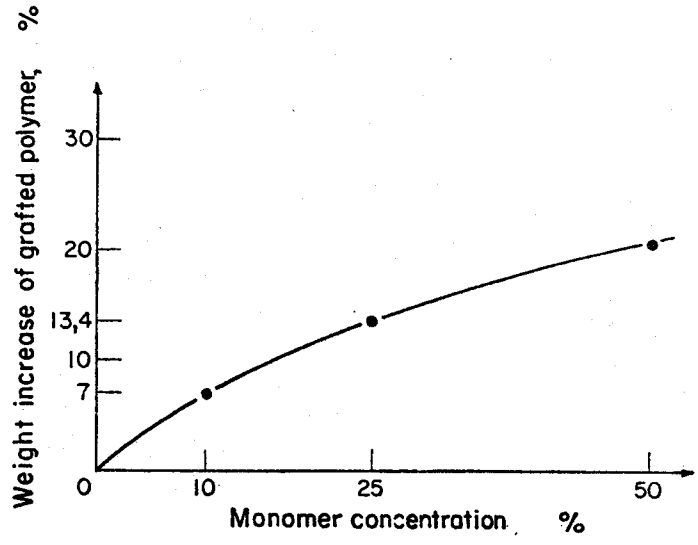


FIG. 5. Grafting of methyl methacrylate in toluene on polypropylene autoperoxidized fiber. Oxygen content: 0·0159 g/m², grafting temperature: 75°C; time 20 hr

which, according to the conditions and to the type of monomer used, can vary from 0·01 to 0·1 mm.

Some data of grafting on laminae, achieved by immersing the surface of the peroxidized polymer in solutions of the monomer to be grafted, are shown in Table 2 and Fig. 4. The grafted products were washed with solvents to remove the monomer and, in some cases, the homopolymer of the monomer used for the grafting.

Moderate grafting, unless followed by thermal treatment, does not greatly modify the ultimate tensile strength and elongation of a filament. The increase in section due to the grafting does not contribute

appreciably, therefore, to the mechanical resistance of the filament.

The increase of the peroxide content from 0·01–0·02 g/m² to values of 0·3–0·5 g/m² causes only a slight increase in the grafting rate. A variation of the weight of grafted polymer can be obtained by varying either monomer concentration or time (Fig. 5).

GRAFTING ON ATACTIC α-OLEFIN POLYMERS

The high linearity of α-olefin atactic polymers and copolymers obtained by the coordinated anionic catalysis processes and the ease with which they can be peroxidized, both in solution and in the dry or slightly swollen state, make them suitable for the production of very interesting grafted copolymers. The simplest method for preparing these polymers is to dissolve the peroxidized poly-α-olefin containing 0·2–0·4 per cent of peroxidic oxygen in the monomer and to operate under the normal polymerization conditions (e.g. emulsion, suspension, or block polymerization).

The peroxidic and hydroperoxidic groups present in the poly-α-olefin polymers act as polymerization initiators. Comparative tests of styrene polymerization with or without peroxidized poly-α-olefin show the following to be true.

(1) In the presence of unperoxidized poly-α-olefin, styrene does not polymerize at a temperature of 80–90°C if no initiator is present. The addition of conventional initiators mainly causes the formation of homopolymers of styrene. In fact, the mechanical properties (e.g. impact strength) of the polymers thus obtained are not improved, in comparison with conventional polystyrenes.

(2) In the presence of peroxidized poly-α-olefins (10–12 wt.%) and under nitrogen at a temperature 80–90°C there is formation of grafted polystyrenes having high impact strengths.

It is interesting to note that, while the high impact strength polystyrenes obtained by copolymerization with or by grafting of styrene on unsaturated rubbers show, in general, a low stability to aging, as shown by the variation of the physical properties with time (i.e. of the sound velocity), the polystyrenes grafted on α-olefins show mechanical properties that do not vary with aging.

Table 3 reports some properties of grafted polystyrenes. The use of α-olefin polymers with intrinsic viscosity >1 appears to be useful for obtaining grafted polystyrenes having high resilience. The use of low crystalline poly-α-olefins leads to a greater increase in resilience;

TABLE 3. GRAFTING OF STYRENE ON PEROXIDIZED POLY-α-OLEFINS

Peroxidized poly-α-olefin used for grafting				*Poly-α-olefin, %*	*Grafted polystyrene on poly-α-olefins*			*Impact strength, kg. cm/cm²*
Polymer	*Crystallinity (X-ray), %*	*Peroxidic oxygen wt. %*	*[η]*		*Grafting temperature, °C*	*Time, hr*	*Rockwell hardness*	
—	—	—	—	—	—	—	70–80M	10[g]
Polypropylene[c]	0	0·288	0·36[d]	12	80	44	n.d.	30
C_2–C_3 co-polymer	10	0·206	1·04[d]	12	80	50	n.d.	30
Polybutene[c]	0	0·402	0·36[d]	12	80	48	42 M	34
Polybutene[a]	25	0·515	0·64[d]	12	90	50	51 M	40
Polybutene[a]	25	0·412	0·65[d]	12	90	50	48 M	55
Polybutene[a]	25	0·412	0·77[d]	12	90	50	41 M	40
Polybutene[a]	25	0·382	0·82[d]	8	80	52	49 M	29
Polybutene[a]	25	0·382	0·82[d]	11·5	80	52	22 M	>100
Polybutene[a]	25	0·247	1·18[d]	12	80	48	17 M	>100
Polybutene[b]	44	0·247	1·38[e]	12	90	50	77 L	40

[a] Residue after extraction with acetone (mixture of atactic and isotactic polymers).
[b] Residue after extraction with ethyl ether (isotactic and stereoblock).
[c] Atactic polymer.
[d] Intrinsic viscosities determined in tetralin at 135°C and expressed in 100 cc/g.
[e] Intrinsic viscosities determined in toluene at 75°C and expressed in 100 cc/g.
[f] Impact strength measured on 3 × 12·75 × 125 mm unnotched specimens with a Charpy pendulum.
[g] Ungrafted polystyrene.

TABLE 4. GRAFTING OF VINYL CHLORIDE ON PEROXIDIZED POLY-α-OLEFINS

Peroxidized poly-α-olefin used for grafting				*Vinyl chloride, g*	*Reaction conditions*		*Grafted polymer residue after extraction with ethyl ether*					
Polymer	*Peroxidic oxygen weight-%*	$[\eta]^a$	*Weight of polymer, g*		*Polyamine, g*	*Grafting temperature, °C*	*Time hr*	*Chlorine in polymer, %*	*PVC content in polymer, %*	*Polymerized monomer, %*	*Grafted poly-α-olefin, %*	$K_{Fikentscher}$[b]
Polypropylene	0.41	0.24	15	180	0.4 TEP[c]	46	30	54	95	66	42	84.5
Polybutene	0.206	0.71	12	180	0.24 TEP[c]	37—46	24	52	91.5	60	83.5	84
Polybutene	0.206	0.57	12	135	0.25 TEP[c]	53	24	47.6	83.5	29.3	65	79
Polybutene	0.206	0.60	7.5	180	0.15 TET[d]	46	24	54.2	95	79	100	79
Polybutene	0.206	0.60	7.5	180	0	75	24	54.5	96	13.4	13.4	56

[a] Intrinsic viscosities measured in toluene at 75°C.
[b] Intrinsic viscosities of polyvinyl chlorides measured in cyclohexanone at 30°C and expressed in 100 cc/g.
[c] TEP = Tetraethylene pentamine (Delta chemical).
[d] TET = Triethylene tetramine (Eastman Organic Chemicals.)

the grafted polystyrenes thus obtained show a smaller loss in hardness than the conventional graft copolymers.

It is particularly interesting to examine the products obtained by grafting vinyl chloride on poly-α-olefin, because of the difference in solubility as compared to the homopolymers. Such grafting proves to be rather difficult, and it is necessary to adopt particular conditions to avoid the formation of vinyl chloride homopolymers to the exclusion of grafting. The high solubility of amorphous poly-α-olefins in aliphatic hydrocarbons allows an easy separation of the non-grafted poly-α-olefins from the homopolymers and from the grafted copolymer of vinyl chloride. A separation, at least in part, of the last can be carried out, although less easily, by dissolution or by fractional precipitation of solutions in ketonic solvents. If the polymerization is carried out in an aqueous emulsion in the presence of polyethylene amines, grafting of the poly-α-olefin present is favoured (Table 4).

The plasticizing action of the poly-α-olefins bound to the grafted polyviny lchloride (PVC) is quite different from that of the conventional PVC plasticizers. The latter contain polar groups which tend to form association complexes with the polar groups of the polyvinyl chloride, thus behaving as good solvents. On the contrary, poly-α-olefins do not show any affinity with polyvinyl chloride and would separate out if they were not grafted. Grafting prevents the separation of poly-α-olefins; these in turn, do not prevent the association of the polyvinyl chloride chains among themselves. An increase in resilience and ultimate elongation, and a relatively small reduction of the ultimate tensile strength are observed.

Due to the great number of problems dealt with at this Institute in the last few years, we have been compelled to limit our investigations on grafting to only a preliminary orientative survey. Nevertheless, the methods adopted by us seem more interesting than those using high energy radiations or initiators with a low molecular weight. Also, the results of studies on crosslinking of α-olefin polymers by chemical methods appear more interesting than those involving high energy radiation. The high number of tertiary carbon atoms very clearly differentiates poly-α-olefins from polyethylene, especially if highly crystalline, and makes poly-α-olefin more sensitive to chemical crosslinking and grafting processes, which are milder and more easily controlled than high energy radiation processes.

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STEREOSPECIFIC POLYMERIZATION OF STYRENE. NOTE IV: THE INFLUENCE OF THE CATALYTIC RATIO $Al(C_2H_5)_3/TiCl_4$

by F. DANUSSO and D. SIANESI

(22 Sept. 1958)

[*Chimica e Industria* **40**, 909 (1958)]

ABSTRACT

The influence of the ratio ϱ between the amounts of the two catalytic reagents, used to prepare $Al(C_2H_5)_3/TiCl_4$ catalysts, on styrene polymerization was studied by following the overall polymerization process in the time. With low ϱ values, a cationic and a stereospecific anionic process occur simultaneously and independently. With increasing ϱ values, above a certain limit the quantity of stereospecific catalyst, which is practically the only one formed, becomes independent of the amount of $Al(C_2H_5)_3$ introduced, whose excess, however, causes aging of the catalyst during the time of polymerization, to an extent increasing with increasing ϱ. In the first range of ϱ values, the same catalyst is formed in smaller quantities, but it is stable during the polymerization time. Kinetic equations are eventually established, embracing all the experimental results.

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ON THE BEHAVIOUR OF ISOTACTIC AND ATACTIC POLYPROPYLENE IN SOLUTION

by FERDINANDO DANUSSO and GIOVANNI MORAGLIO

(30 Sept. 1958)

[*Makromol. Chemie* **28**, 251 (1958)]

Considerable interest is displayed today in the comparison between the behaviour in solution of isotactic and atactic polymers of the same monomer. It clarifies the influence of the variation of steric structure on the macromolecular configuration and, consequently, on all related properties. Conversely, it enables one to determine whether the properties in solution may reveal differences in the steric composition of stereoisomeric polymers.

The first answer to these questions was given in one of our recent papers on isotactic and atactic polystyrene.[1] It has been stated that, with the accuracy of the methods employed, the relation between intrinsic viscosity and osmotic molecular weight for fractions of the two types of polystyrene does not practically depend on the variation of steric structure. Measurable differences have been observed only for the values of the second virial coefficient which, at equal molecular weight, is higher for the atactic polystyrene than for the isotactic one.

Despite the particular interest, an analogous comparison for isotactic and atactic polypropylene could not be made till now because of lack of reliable data, chiefly due to the difficulty in obtaining good fractions of both kinds of polymers and in applying certain physical methods, such as osmotic techniques, at high temperatures.

Recently, in a letter to the editors, Chiang published[2] data of intrinsic viscosity and molecular weight, the latter determined by light scattering, of isotactic polypropylene fractions, obtained by a column fractionation technique.

He arrived at the relation:

$$[\eta] = 1.00 \times 10^{-4} \times \overline{M}_w^{0.8} \qquad \text{(isotactic polypropylene)} \qquad (1)$$

where $[\eta]$, in 100 cm^3/g, was measured in decalin at 135°C ($\overline{M}_w$ from about 100,000 to 1,100,000).

TABLE 1. INTRINSIC VISCOSITIES OF ATACTIC POLYPROPYLENE FRACTIONS IN DECALIN AT 135° C

Fractions and osmotic mol. weights	*c (g/100 ml)* a)	η_{sp}/c b)	$[\eta]$ c)
N 234	0·253	3·700	
M = 389,000	$0{\cdot}126_5$	3·345	3·26
	$0{\cdot}084_3$	3·215	
	$0{\cdot}063_2$	3·155	
M 423	0·262	2·415	
M = 252,000	0·131	2·245	2·27
	$0{\cdot}087_3$	2·185	
	$0{\cdot}065_5$	2·160	
N 334	0·285	1·810	
M = 184,000	$0{\cdot}142_5$	1·690	1·72
	0·095	1·650	
	$0{\cdot}071_2$	1·640	
M 63	0·652	1·210	
M = 91,000	0·326	1·110	1·11
	$0{\cdot}217_3$	1·080	
	0·163	1·060	
M 81	0·940	0·940	
M = 70,800	0·470	0·855	0·838
	$0{\cdot}313_3$	0·820	
	0·235	0·810	
M 923	2·485	0·335	
M = 18,200	1·242	0·310	0·310
	0·828	0·300	
	0·621	0·295	

a) Volumes measured at room temperature.
b) Determined with Desreux-Bischoff type viscometer.
c) Corrected values: volumes reduced to 135°C.

In the course of experiments, which will be published in subsequent papers,[3] we have determined the $[\eta]$-M relations in various solvents of highly selected fractions of atactic polypropylene, obtained

by fractional precipitation and then by measuring osmotic molecular weights in benzene or toluene at room temperature.

For some other fractions obtained from the same fractionations, we have now measured the molecular weight from $[\eta]$ in toluene at 30°C and then $[\eta]$ in decalin at 135°C.

In Table 1 experimental data in decalin are reported from which we have derived the most probable equation:

$$[\eta] = 1.58 \times 10^{-4} \times \overline{M}_n^{0.77} \quad \text{(atactic polypropylene)} \qquad (2)$$

for $\overline{M}_n$ from about 20,000 to 400,000.

Although the isotactic polypropylene fractions employed for the measurements do not appear in Chiang's paper[2] to be very narrow, we believe that equation (1) does not markedly differ from that expected in the case of good fractions, owing to the smaller effect of the polydispersion by light scattering measurements and to the relatively high value of the exponent of $\overline{M}_w$.

Hence, it becomes possible to make a comparison between the two types of polymer. Fig. 1, shows equations (1) and (2) with related experimental points, in a log $[\eta]$-log M plot. The difference between the two equations, as shown in the diagram, is only slightly smaller than that which would be expected from the use of the two different methods for the determination of the molecular weights.[4]

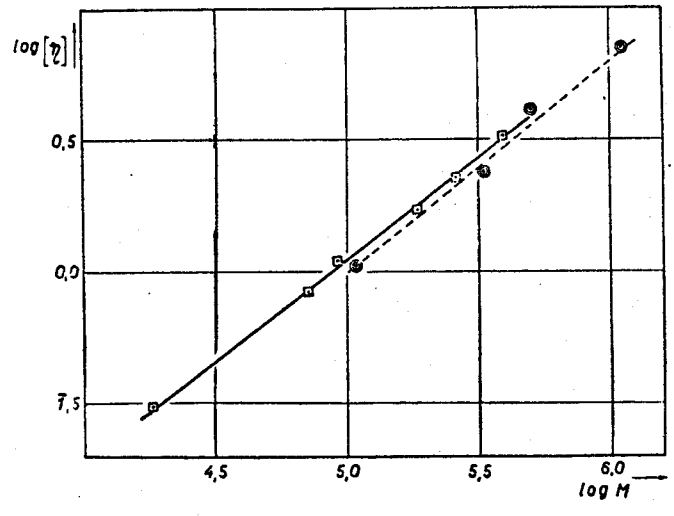


FIG. 1. Relationship between intrinsic viscosity and molecular weight for polypropylene in decalin at 135°C. Broken straight line is drawn according to (1); solid one is drawn according to (2).
⊙ Data of R. Chiang for isotactic fractions
⊡ Our experimental data for atactic fractions

We may, therefore, conclude that, also in the case of the polypropylene, there must be no considerable difference in the viscometric behaviour of isotactic and atactic polymers in solution.

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PREPARATION AND STRUCTURE OF LINEAR HIGH POLYMERS OF HEXYNE-1

by G. NATTA, G. MAZZANTI, G. F. PREGAGLIA and M. PERALDO

(17 Oct. 1958)

[*Gazz. Chim. It.* **89**, 465 (1959)]

ABSTRACT

The polymerization of hexyne–1 was studied with the aid of catalysts acting through an anionic-coordinated mechanism, which are prepared from different titanium salts and triethyl aluminum (Table 1).

The polymers were extracted with various boiling solvents. The polymer fraction insoluble in boiling acetone had a high molecular weight (intrinsic viscosity in toluene at 30°C $\simeq$ 1).

Polyhexyne–1 is easily attacked by molecular oxygen even at room temperature; a treatment under a nitrogen atmosphere for 20 hr in a boiling benzene solution, or else for 6 hr in a boiling xylene solution is accompanied by considerable variations in the I.R. spectrum of the polymer.

The polymer is amorphous as revealed by X-ray examination; the fraction insoluble in boiling acetone produces I.R. spectra which show steric hindrances and intermolecular distances similar to those found in the spectra of isotactic polyhexene–1.

The I.R. spectrum suggests a structure containing several conjugated double bonds, which most likely are of the *trans*-type.

The chemical behaviour indicates the presence in the main chain of several double bonds alternated with single bonds; the limited reactivity with dienophilic agents and the lack of absorption maxima in the U.V. might suggest an incomplete conjugation of the double bonds bound to an incomplete coplanarity.

TABLE 1.

Titanium compound		*Al* $(C_2H_5)_3$	*n-heptane* cm^3	*Monomer* g	*Polymerization conditions*		*Product obtained*		% *acetone extractable oily polymers*	% *high-molecular-weight acetone insoluble polymers*
type	*moles*	*moles*			*T°C*	*Time hr*	*g*	$\frac{g\ polymer}{g\ monomer}100$		
$Ti(OC_3H_7)_4$	0·02	0·05	50	30	80	$1^1/_2$	7·9	26·3	62	37·5
$TiCl_3$	0·0246	0·05	90	30	40	2	6·6	22	24·2	75
$TiCl_3$	0·021	0·05	150	30	20	6	14·2	47·6	12·45	87·5
$TiCl_3$	0·0078	0·0264	150	30	−20/+10	23	9·5	31·6	14·5	85
$TiCl_3$	0·022	0·05	10	42	0	18	27·4	65·3	9·52	90·2
$TiCl_3$	0·0259	0·05	250	50	18	94	42·2	86·4	14·5	85

By the catalytic hydrogenation of polyhexyne–1 a polymer, which shows an I.R. absorption spectrum very similar to that of linear polyhexene–1, is obtained.

On the basis of our results, the polymers of hexyne–1 consist (at least for the most part) of macromolecules having a regular structure of the type:

$$\begin{array}{lll} C_4H_9 & C_4H_9 & C_4H_9 \\ | & | & | \\ C = CH- & C = CH- & C = CH- \end{array}$$

The variations, which can be observed in the I.R. spectrum, after heating to a high temperature, can be attributed to an isomerization phenomenon of the macromolecules, probably due to a change in the steric configuration of the double bonds (*trans*, *cis*-isomerization type).

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STEREOSPECIFIC POLYMERIZATION AND ISOTACTIC POLYMERS OF VINYL AROMATIC MONOMERS

by GIULIO NATTA, FERDINANDO DANUSSO and DARIO SIANESI

(3 Nov. 1958)

[*Makromol. Chemie* **28**, 253 (1958)]

During recent years, considerable research work has been carried out at our institute on the stereospecific polymerization of mono- and polynuclear aromatic vinyl monomers, particularly of nuclear substituted styrenes.

As soon as we obtained isotactic crystallizable, high melting polymers of styrene[1] we considered with great interest the possibility of obtaining stereo-ordered polymers from other aromatic monomers, by employing typical stereospecific catalytic systems, and of studying their physical and technological properties.

At the same time it appeared very promising to carry out a systematic research, in order to determine the relationship between the monomer structure or the kind of substitution and the monomer reactivity in an anionic coordinated polymerization and, eventually, the stereospecificity of the catalytic system.

In the present paper we summarize some of our most interesting results.[2]

By studying the behaviour of many arylsubstituted vinyl monomers, we found that stereospecific polymerization can be applied to almost the whole class of such monomers, except, of course, the monomers containing bonds or groups reacting with the components of the catalyst (e.g. those containing either active hydrogen atoms, or atoms with lone electron pairs: O. S, N, . . .).

With polymerizable aromatic monomers the features of the polymerization appeared to correspond remarkably to those we had

observed[3] in the case of styrene. This enabled us to obtain by polymerization in practice only high polymers having a linear and ordered structure, under conditions leading uniquely to a coordinated anionic process, using catalysts prepared from $TiCl_4$ or $TiCl_3$ and organoaluminum compounds. In this way, it was possible to avoid all other cationic or radical polymerization mechanisms, towards which many of these monomers are extremely sensitive. The polymers obtained consisted therefore essentially of one fraction, that could not be further separated with solvents into fractions having different structural order.

Depending on the structure of the monomer, these polymers are in some cases crystallizable to a high or medium degree of crystallinity, while in other cases they are not crystallizable (at least by conventional annealing or cooling).

It is interesting to note that the stereospecific polymerization of vinyl aromatic monomers can be highly efficient also with catalysts which, with aliphatic α-olefins, are only little or moderately stereospecific. While with aliphatic α-olefins the catalysts from violet, crystalline $TiCl_3$ are more stereospecific than those from $TiCl_4$, in the case of vinyl aromatic monomers the difference is not so evident.

In Table 1 the monomer structure and the main properties of the polymers obtained by stereospecific catalysis are reported. In the last column, data of yield of polymers obtained under the same experimental conditions, are also compared; for this comparison, it seemed preferable to report the result obtained with a catalyst from $TiCl_4$. With this catalyst, experimental data are in general well reproducible, not being dependent on the physical state or particle size of the solid titanium compound, such as $TiCl_3$.

The data of Table 1 show that the character of the crystallizability of the polymers listed is markedly dependent on the type and site of substitution of the corresponding monomer.

It is to be noted that such dependency does not seem to be related to the polar character of the substituent, i.e. the modifications that the substituent may cause to the electronic configuration of the monomer and more particularly the polarizability of the vinyl double bond. It appears, on the contrary, strictly related to the size, the site and the number of substituents, that is, to steric reasons.

Thus, polymers of para substituted styrenes are not crystallizable at all, when the size of the substituent is not very small. The poly (*p*-fluorostyrene) is, in fact, the only crystalline para substituted

polymer we have been able to obtain, evidently because of the small difference between the Van der Waals radii of a hydrogen and a fluorine atom.

Ortho substituted monomers, if polymerizable, give, on the contrary, polymers which are easily crystallizable. The same ability is shown by polymers of di-substituted (e.g. dimethyl) styrenes, even if the para position is involved.

The crystalline polymers listed in the table generally have a very high crystal melting temperature; some of these are higher than the decomposition temperature. Crystallinity degrees are, in some cases, equal to, but in other cases higher than that of isotactic polystyrene. Crystallization rates, at temperatures above glass transition, can be very high, as in the case of ortho-substituted polystyrenes. Thus, contrary to the behaviour of polystyrene, high crystallinities are reached with these polymers in a few seconds at a temperature some ten degrees below the melting temperature.

A preliminary examination of the structures of the crystalline polymers[4] enabled us to conclude that they are formed by isotactic and, consequently, spiralized macromolecules. The identity period along the *c*-axis of the crystals (i.e. helix axis) depends on the monomer structure. While in the case of the poly (*o*-fluorostyrene) the pitch of the helix comprises three monomeric units, as in polystyrene, in the case of the polymers of *o*-methyl, *p*-fluoro, 2-methyl-4-fluorostyrene, and 1-vinylnaphthalene it comprises four monomeric units. For the four polydimethylstyrenes and poly(*m*-methylstyrene), a greater number of monomeric units correspond to the identity period.

These crystallizable isotactic polymers, if examined in the amorphous state, show some small differences in properties, when compared with corresponding amorphous atactic polymers prepared by conventional non stereospecific, e.g. radical, methods.

A quite similar behaviour is shown by the remaining polymers listed in the table: although they are non crystallizable, they show certain differences in many physical properties, when compared with corresponding atactic radical polymers.

In some instances, these differences, apparently very marked, must obviously be partly attributed to the considerable differences in the molecular weights between the two types of polymers. In the polymerization conditions used in this work, the stereospecific process leads, in fact, to considerably high molecular weights, as is roughly shown by intrinsic viscosity data reported in Table 1. Such molecular

weights are generally of the order of magnitude of 10^6, whereas it is very difficult, and in some instances impossible, to reach such high molecular weights by using free radical or cationic polymerization methods.

In many instances, however, the difference in properties, such as the differences observed in I.R. absorption spectra, must certainly be attributed to a difference in the steric regularity of the macromolecules of the two types of polymers.

Thus, on the basis of various results and conclusions on the formation mechanism and on the properties of these non-crystallizable polymers, we believe that they are essentially constituted by macromolecules, which are not only completely linear, but also have a regular steric configuration of the units, like the typical isotactic polymers. Consequently, in these polymers, the physical process of crystallization is remarkably slowed or completely hindered by particular steric hindrances of the substituents.

Following, for instance, general rules holding in crystallization of linear high polymers, crystallization cannot be possible in all cases where an ordered structure should imply a bad space filling, due to the size and positions of the side chains, in such a way as to lead to a density in the crystal phase less than that of the amorphous phase.

Steric hindrance may take place not only with regard to the spiralization of a single macromolecule, which is peculiar for isotactic polymers, but also to the packing of several already spiralized macromolecules in a crystal lattice.

The nature of the substituent not only affects the crystallizability and other physical properties of the polymers, but also affects considerably the reactivity of the monomers in the coordinated anionic polymerization. The conversion data reported for each monomer in the table, all obtained in the same experimental conditions, may be an approximate measure of such reactivity.

A deeper study is, however, being carried out on this point, based on measurements of initial polymerization rates, and aiming at the knowledge of quantitative relations between the monomer structure, or particularly the site and the type of substitution in the styrene nucleus, and the monomer reactivity in coordinated polymerization. It may be, however, now understood that this polymerization process is particularly sensitive to the presence of rather hindering substituents on the nucleus in the proximity of the vinyl group.

An ortho substitution in styrene leads in any case to a considerable decrease in the reactivity of the monomer, which in some cases

TABLE 1.

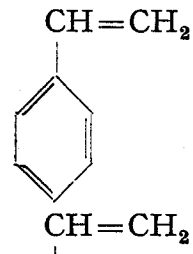
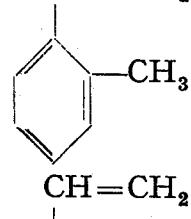
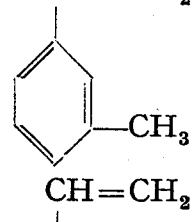
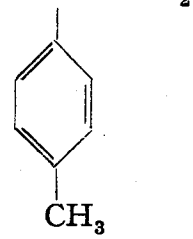
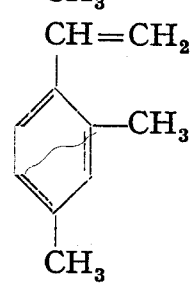
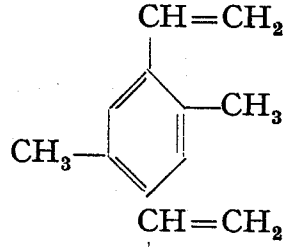
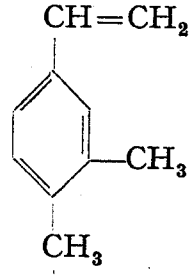
Monomer	*Physical state of the polymer* a)	*Melting temperature (°C)* b)	$[\eta]$ c)	*Conversion yield (%)* d)
Styrene 	cryst.	240	3·5	43·7
o-Methylstyrene 	cryst.	> 360	n. d.e	4·6
m-Methyl styrene 	cryst.	215	3·9	22·7
p-Methylstyrene 	am.	—	2·9	49·3
2,4-Dimethylstyrene 	cryst.	310	3·5	4·4
2,5-Dimethylstyrene 	cryst.	330	2·8	1·6
3,4-Dimethylstyrene 	cryst.	240	3·2	21·2

TABLE 1. (*cont.*)

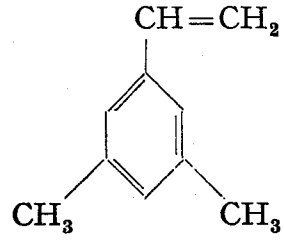
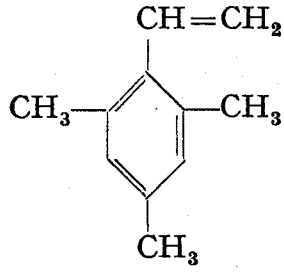
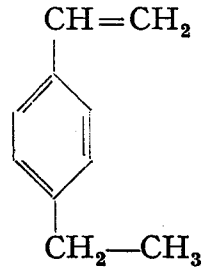
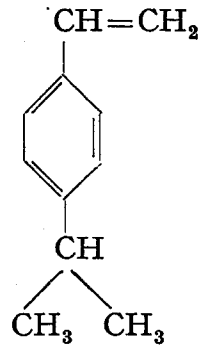
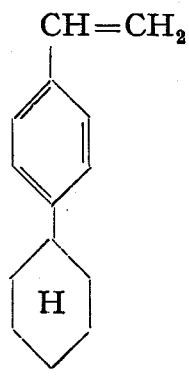
Monomer	*Physical state of the polymer* a)	*Melting temperature (°C)* b)	$[\eta]$ c)	*Conversion yield (%)* d)
3,5-Dimethylstyrene 	cryst.	290	2·6	12·4
2,4,6-Trimethylstyrene 	....	....	....	0
p-Ethylstyrene 	am.	—	3·5	48·5
p-Isopropylstyrene 	am.	—	3·9	24·2
p-Cyclohexylstyrene 	am.	—	2·5	25·0

TABLE 1. (*cont.*)

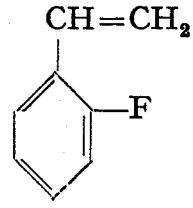
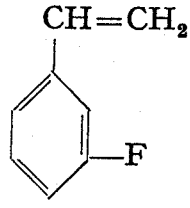
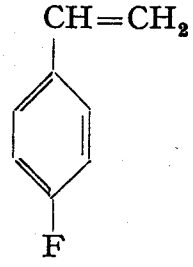
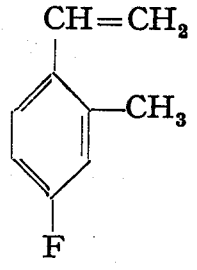
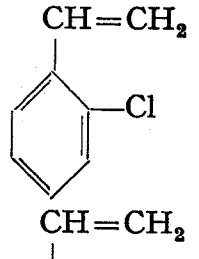
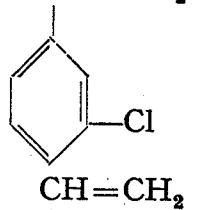
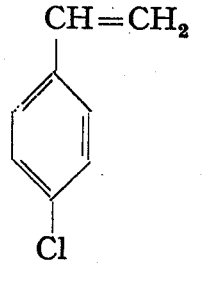
Monomer	*Physical state of the polymer* a)	*Melting temperature (°C)* b)	$[\eta]$ c)	*Conversion yield (%)* d)
o-Fluorostyrene 	cryst.	270	2·3	4·1
m-Fluorostyrene 	am.	—	2·8	24·9
p-Fluorostyrene 	cryst.	265	2·0	39·7
2-Methyl-4-fluorostyrene 	cryst.	> 360	n. d.e	4·3
o-Chlorostyrene 	...	...	...	0
m-Chlorostyrene 	am.	—	3·5	23·2
p-Chlorostyrene 	am.	—	2·1	27·8

TABLE 1. (*cont.*)

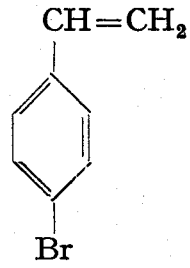
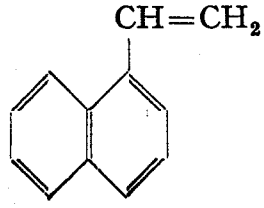
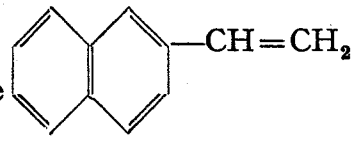
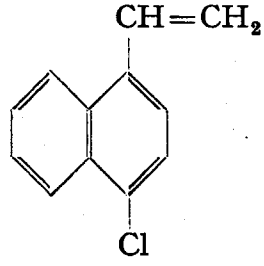
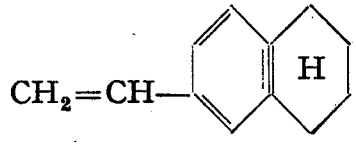
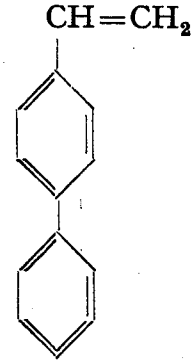
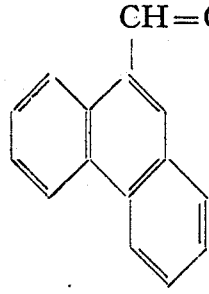
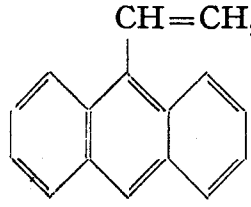
Monomer	*Physical state of the polymer* a)	*Melting temperature (°C)* b)	$[\eta]$ c)	*Conversion yield (%)* d)
p-Bromostyrene 	am.	—	1·8	20·1
1-Vinylnaphthalene 	cryst.	~360	2·3	12·9
2-Vinylnaphthalene 	am.	—	3·4	38·9
1-Vinyl-4-chloro naphthalene 	am.	—	1·7	11·2
6-Vinyl-1.2.3.4-tetrahydronaphthalene 	am.	—	2·2	28·3
4-Vinyldiphenyl 	am.	—	0·7	39·2

TABLE 1. (*cont.*)

Monomer	*Physical state of the polymer*[a]	*Melting temperature (°C.)*[b]	$[\eta]$[c]	*Conversion yield (%)*[d]
9-Vinyl-phenanthrene 	am.	—	0·7	10·6
9-Vinyl-anthracene 	...	...	...	0

a) Cryst., crystalline; Am., amorphous. The crystalline polymers have been recognized by X-ray and polarizing, hot stage microscope examinations. In many cases they are in the crystalline state since the preparation; sometimes, on the contrary, only after suitable thermal treatments. We have considered as amorphous the polymers, whose X-ray diagrams did not show sharp diffraction peaks also after several attempts to crystallize them by thermal treatments on the solid polymer at temperatures higher than that of glass transition.

b) Temperature of complete disappearance of the crystallinity, determined by polarizing, hot stage microscope, with heating rate of 1–2°C/min.

c) Intrinsic viscosity in tetralin at 100°C, in 100 $cm^3\ g^{-1}$, determined on samples obtained as specified in (*d*).

d) Polymerization conditions: $2{\cdot}0\times10^{-3}$ mol $TiCl_4$; $6{\cdot}0\times10^{-3}$ mol $Al(C_2H_5)_3$; 80×10^{-3} mol monomer; reaction volume: 35 cm^3; solvent: benzene; reaction at 70°C for 7 hr.[3]

e) Not determined: this polymer was insoluble also in boiling tetralin.

can also be practically inactive with regard to the catalysts employed. This last behaviour seems to be general for di-ortho substituted styrenes.

Reactivities of meta or para substituted styrenes, in general markedly depend on the polar character of the substituents, save the case of styrenes substituted with groups having considerable steric requirements; for these one may observe irregular decreases in reactivity, which are to be ascribed to steric hindrance phenomena.

In particular, the values of polymerization rates, referred to that of styrene, of several meta and para substituted styrenes fit the Hammet equation.[5] The slope of the straight line, which is a measure of the sensitivity of the reaction to polar substituents, is negative. This clearly shows that, apart from steric hindrance effects, the reactivity of the monomer is enhanced by the presence of electron releasing substituents. This could already have been deduced from the conversion data reported in the table.

Such a result is not in keeping with what one would expect from a normal anionic polymerization; on the contrary, it may be in a good agreement with what was stated earlier[6] on the mechanism of the coordinated anionic polymerization, which implies a coordination step of the carbanion, resulting from the polarization of the olefinic double bond, to the central strongly electropositive metallic atom of the organometallic catalytic complex.

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2. See for example: SIANESI, D., NATTA, G. and DANUSSO, F. communication presented at the VIII. Congresso Nazionale della Soc. Chimica Italiana, Torino, May 26th, 1958 (see paper 73); other papers by F. Danusso et al. to be published in *Chimica e Industria* (see papers 114, 118, 150, 153).

3. DANUSSO, F. and SIANESI, D., *Chim. e Ind.* [*Milano*] **40**, 450 (1958); DANUSSO, F., SIANESI, D. and CALCAGNO, B. *ibid.* **40**, 628 (1958), DANUSSO, F. and SIANESI, D. *ibid.* **40**, 909 (1958).

4. NATTA, G., CORRADINI, P. and BASSI, I. W., communications presented at the VIII. Congresso Nazionale della Soc. Chimica Ital., Torino, 1958.

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6. See, for example, NATTA, G., The catalytic action of complexes in stereospecific polymerization by means of coordinated anionic catalysis, *Ricerca Sci.*, Suppl. **28** (1958).

99

MOLECULAR WEIGHT AND INTERACTION AFFINITY WITH SOLVENTS FOR ATACTIC POLYPROPYLENE FRACTIONS

by F. DANUSSO, G. MORAGLIO and V. GIANNELLA

(8 Nov. 1958)

[*Rend. Accad. Naz. Lincei* (8) **25,** 498 (1958)]

ABSTRACT

The osmotic pressures in benzene or in toluene of atactic polypropylene fractions obtained in a previous fractionation (see paper 101) have been measured.

The law of variation of the reduced osmotic pressure with concentration proved to be different in the two solvents used; however, in any case one can justify it from theoretical considerations. The establishment of this law has given us the means of accurate calculation for the molecular weight of the fractions, and for the value of the second virial coefficient of the two solvents, vs. the molecular weight. The range of molecular weights of the fractions examined was shown to be between 24,000 and 335,000, corresponding to a range of degrees of polymerization between 570 and 7960.

The interaction affinities (at infinite dilution) of polypropylene in toluene and benzene have been calculated from the values of the second virial coefficient.

Toluene is a better solvent than benzene, and this appears to be connected with the less aromatic character of toluene with respect to benzene, in agreement with a comparison of the solvent power towards other hydrocarbon polymers.

100

THE RELATION BETWEEN INTRINSIC VISCOSITY AND MOLECULAR WEIGHT OF ATACTIC POLYPROPYLENE IN DIFFERENT SOLVENTS

by F. DANUSSO and G. MORAGLIO

(8 Nov. 1958)

[*Rend. Accad. Naz. Lincei* (8) **25,** 509 (1958)]

ABSTRACT

This paper describes viscometric measurements with diluted solutions of atactic polypropylene fractions, with a known molecular weight (see paper 99), performed in cyclohexane, toluene, and benzene at 30°C, and in isoamyl acetate at 34°C. The relationships between intrinsic viscosity and molecular weight, which have been thus determined for each of the four solvents possessing very different solvent power, appear to be consistent with the known law of the homogeneous exponential type. In particular in isoamyl acetate, this relationship assumes the expression typical of the solutions in Θ solvents, in agreement with other experimental runs, which would indicate the pseudoideal character of the solutions of atactic polypropylene in isoamyl acetate at 34°C.

We have calculated the average statistical dimensions of the polypropylene macromolecules in the various solvents and at various molecular weights, based on the Fox and Flory theory. In particular it was found in the case of isoamyl acetate at 34°

$$\left(\frac{\bar{r}_0^2}{M}\right)^{\frac{1}{2}} = 930 \times 10^{-11} \qquad (\text{for } \Phi = 2{\cdot}1 \times 10^{21}).$$

From the comparison with the average statistical data of other polymers, it has been deduced that the configurational behaviour of atactic polypropylene in solution appears to be very similar to that of other known polymers of the vinyl type, such as polystyrene, polyisobutene and polymethylmethacrylate. The comparison is more expressive when based on the value relative to the degree of polymerization:

$$\left(\frac{\overline{r}_0^2}{x}\right)^{\frac{1}{2}} = 603 \times 10^{-10}.$$

101

FRACTIONATION OF ATACTIC POLYPROPYLENE BY FRACTIONAL PRECIPITATION

by F. DANUSSO and G. MORAGLIO

(13 Nov. 1958)

[*Rend. Ist. Lomb. Sci. e Lettere* **92** A, 591 (1958)]

ABSTRACT

The fractionations of three different samples of atactic polypropylene were performed by the technique of fractional precipitation at 30°C. In view of the low density of polypropylene, it appeared to be convenient to use only high-density chlorinated solvents, thus obtaining the separation of the phase concentrated in the polymer by floating.

Fractionations have proved that good fractions can be obtained from atactic polypropylene, but this occurs only up to a certain molecular weight limit, above which, even by improving considerably the operation techniques, fractions are obtained still having a considerable residual polydispersion.

This inconvenience seems chiefly dependent on the large area and on the type of polydispersion of the initial samples, rather than on the defect of linearity or on anomalies of interaction of the macromolecules.

102

STEREOSPECIFIC POLYMERIZATION OF STYRENE. NOTE V: EFFECTS OF TEMPERATURE WITH CATALYSTS OBTAINED FROM $Al(C_2H_5)_3$ AND $TiCl_4$

by F. DANUSSO, B. CALCAGNO and D. SIANESI

(25 Nov. 1958)

[*Chimica e Industria* **41**, 13 (1959)]

ABSTRACT

The effect of temperature on the whole process of isotactic polymerization of styrene, with catalysts prepared by reacting $Al(C_2H_5)_3$ with $TiCl_4$, appears to be rather complex. By following kinetic conclusions, reached in previous papers of this series, we examined experimentally the effect of temperature from each of its main aspects, i.e. effect: (a) on catalyst formation; (b) on the pure polymerization reaction; (c) on catalyst aging during polymerization.

Thus, optimum conditions of temperature were determined, to reach the highest activities and to increase the stability of the catalyst during the course of the polymerization. An activation energy of 10,500 cal $mole^{-1}$ was calculated for the overall process, which is likely to be solely attributed to the polymerization reaction.

103

ELASTOMERIC PROPERTIES OF ETHYLENE-PROPYLENE COPOLYMERS

by G. NATTA and G. CRESPI

(12 Dec. 1958)

[*Chimica e Industria* **41**, 123 (1959)]

ABSTRACT

The properties of new linear amorphous copolymers of ethylene with aliphatic alpha-olefins are described. These copolymers represent a new class of substantially saturated elastomers, which show better properties than other previously known saturated rubbers.

The mechanical and elastic properties of other saturated elastomers and of polyethylene–polypropylene mixtures are reported here. It is clearly evident, from such properties, that ethylene–propylene copolymers are essentially amorphous and possess low cohesion forces. The elastic moduli, calculated with various systems of measurement, are of the order 10^6–10^7 dyne/cm^2 at room temperature.

The rebound values vs. temperature are reported with regard to the elastic properties of these elastomers; from these values it results that:

(1) for copolymers containing about 50 per cent of ethylene, the rebound, at different temperatures, assumes values which are close to those of natural rubber.

(2) the minimum rebound temperature is about —40°C; this is the reason why these elastomers can be used also at markedly lower temperatures than room temperature.

(3) the rebound properties improve with an increase of the ethylene content, due to the higher flexibility of the copolymers rich in ethylene.

(4) the minimum rebound temperature is a function of the ethylene molar content in the copolymer.

This last observation can be utilized also for analytical purposes.

104

DETERMINATION OF METALS BOUND TO ISOTACTIC POLYPROPYLENE CHAINS

by G. NATTA, L. GIUFFRÉ and I. PASQUON

(13 Dec. 1958)

[*Rend. Accad. Naz. Lincei* (8) **25**, 417 (1958)]

ABSTRACT

Previous kinetic studies on the polymerization of alpha-olefins with the catalytic system, alpha-$TiCl_3$–$Al(C_2H_5)_3$, have shown the existence of two chain transfer phenomena: one having a rate depending on the concentration of the aluminum alkyl and the other having a rate which was determined by the amount of the titanium compound introduced in the polymerization system.

Both these chain-transfer processes show a tendency to form polymeric chains bound to aluminum atoms. With this work, we have tried, using analytical methods, to determine the presence of such aluminum alkyl compounds which are bound to the polymeric chains, establishing their amount relative to the moles of polymerized propylene.

The results obtained on these analyzed polymeric fractions, allowed us to conclude that in the polymerization of propylene to isotactic polymer, the chain-trainsfer process, whose rate is a function of the square root of the concentration of aluminum alkyl, introduces —C_2H_5 end groups in the polymeric chains. Such groups are bound to the aluminum, whose amount found in the polymer is related to that of alpha-$TiCl_3$ with which the polymerization was effected.

105

ENTHALPY AND ENTROPY OF FUSION OF ISOTACTIC POLYPROPYLENE

by F. DANUSSO, G. MORAGLIO and E. FLORES

(13 Dec. 1958)

[*Rend. Accad. Naz. Lincei* (8) **25**, 520 (1958)]

ABSTRACT

The enthalpy of fusion ΔH_u of isotactic polypropylene was determined by the method of the decrease in melting point with the addition of diluents and by the application of the known relationships derived from thermodynamic-statistical theories of polymer solutions.

The enthalpy of fusion was found to be 2600 cal/unit (± 100). On the basis of the melting point of the pure polymer, an entropy of fusion ΔS_u was calculated of 5·8 cal/unit °K ($\pm 0{\cdot}2$).(*)

The heat of fusion of polypropylene is similar to that of polyethylene, if it is referred to the weight of the substance, whereas its melting point is higher than that of polyethylene due most likely to their different polymeric crystalline structure. The ΔS_u value, on the contrary, conforms with that of other linear polymers, such as polyoxyethylene and polychloroprene, whose structural unit consists of three joined atom groups.

(*) In subsequent work by the same Authors, more reliable data were found, in relation to difficulties arising in the particular case of polypropylene (broad melting interval, need of extrapolation for a "true" equilibrium melting temperature, etc.). Values of ΔH_u were found ranging from 1700 to 2200 cal/unit and consequently of ΔS_u ranging from 3.7 to 4.8 eu/unit.

106

DI-ISOTACTIC POLYMERS

by G. NATTA, M. FARINA and M. PERALDO

(13 Dec. 1958)

[*Rend. Accad. Naz. Lincei*, (8) **25**, 424 (1958)]

Four years ago, during the 11 Dec. 1954 meeting of this Academy, we announced the synthesis of a new class of polymers, obtained by the polymerization of alpha-olefins, having an exceptional regularity of structure.[1]

For these polymers we proposed the name "isotactic", which is now generally used in the macromolecular literature.

Because of the great interest which these polymers have aroused, both in the scientific and in applied fields, we extended the study of stereoisomerism to macromolecules whose main chain consists of a regular succession of pairs of carbon atoms having different substituents and both capable of enantiomorphous steric configurations.

Due to the fact that the most effective stereospecific catalysts known at present consist of systems acting through a coordinate mechanism, we investigated olefins which were deuterated in position 1. The mono-deuterated olefin is chemically the same as an alpha-olefin, but its polymer has a monomeric unit with two differently substituted asymmetric carbon atoms. For this purpose we have prepared the *cis*- and *trans*-deutero-propenes, $CHD{=}\ CHCH_3$.

As will be described in a forthcoming paper, the monomers were obtained by the reaction between D_2O and the corresponding lithium-propenyls. The preparation of the lithium-propenyl was accomplished by the method described by E.A. Braude and co-workers.[2]

The infrared spectra of the two $1d_1$-propenes show that the steric configuration is the same as the one of the starting bromo-derivatives, as expected from the work of Braude on some derivatives of *cis*-propenyl-lithium.[3]

The isotopic purity of the monomers was very close to or higher than 95 per cent, while its steric purity was lower depending also on the purity and stability of the starting bromo-derivatives. The $1d_1$-*trans*-propene polymerized by us had a steric purity of 95 per cent; the $1d_1$-*cis*-propene had a steric purity of 85 per cent. We worked with amounts of the order of $^1/_{10}$ g, so it may be expected that on a bigger scale both the isotopic and steric purities could be improved.

The polymerization was performed with semi-micro techniques and in the absolute absence of air and water vapour. It was carried out with the aid of the catalytic system triethyl-aluminum and alpha-$TiCl_3$ in n-heptane.

An amount of 52 N cm^3 of the *cis*-isomer, 257 N cm^3 of the *trans*-isomer and 82 N cm^3 of a mixture *cis/trans* in the ratio 2/1 have been separately polymerized in the presence of 0·225 g of triethyl-aluminum, 0·065 g of alpha-$TiCl_3$ in n-heptane, at room temperature for times between 20 and 40 hr.

TABLE 1.

Solvents used in the fractionation	*Fractions obtained by extraction % by weight*		
	poly (cis-*propene* $1d_1$)	*poly* (trans-*propene* $1d_1$)	*poly* (cis-trans-*propene* $1d_1$)
Acetone	28·6	9·6	11·9
Ether	4·2	3·1	2·6
n-Heptane	4·2	3·5	6·2
n-Octane	50·0	53·4	55·5
Residue	13·0	30·4	23·8

The polymers were purified from the catalyst by the treatment of anhydrous butyl alcohol followed by precipitation in acetone. They were later fractionated by subsequent extraction with the following solvents: ethylether, n-heptane, n-octane, at their corresponding boiling points, following already known techniques.[4] The ether, n-heptane and n-octane fractions were examined by I.R. analysis. The n-octane residues were not analyzed because from a previous study on polypropenes[5] it was found that the n-octane extract had practically the same steric purity and melting point as the n-octane residue with a slightly higher chemical purity. The n-octane fractions had the same X-ray spectra as a sample of highly crystalline isotactic polypropylene, while their I.R. spectra, as might be expected, were different. The

I.R. spectra of the poly-1d_1-*cis*-propene and of the poly 1d_1-*trans*-propene are completely different, as shown in Fig. 1. The sharp dichroism observed in the I.R. spectra of stretched samples of the two polymers, indicates that these consist of chains in which all the atoms are arranged regularly. Thus, the two polymers which, as shown by X-ray spectra, have the same chain structure with respect to the carbon atoms, are diastereoisomers.

By polymerizing mixtures of the two isomers we obtained products for which the intensity of the I.R. absorption bands corresponding to the spectrum of the homopolymer, which was present in smaller quantity, decreases very rapidly. This can be explained by statistical considerations because generally successions of two or more identical monomeric units are necessary to observe the vibrations of the corresponding diastereoisomer.

On the contrary some absorption bands as, for instance, the peak observed for the poly-1d_1-*cis*-propene in the range 7·35μ–7·40μ, can be observed even if the monomeric unit is isolated between different units, as shown by the copolymers between the 1d_1-(*cis* or *trans*)-propene and 1d_2-propene. We will refer to this subject in more detail in another paper. From these absorption bands it is possible to estimate the ratio between the two monomeric forms present in the polymer.

The formation of the diastereoisomers indicates that during the polymerization there is not a notable isomerization of the monomers, even if a certain variation in the chemical and stereoisomeric composition of the residual gases has been observed. This variation can be caused by the catalytic isomerization process, which is not necessarily connected with the polymerization process.

As has been already stated, the differences in the I.R. spectra (the X-ray spectra of the polymers of 1d_1-*cis*-propene and 1d_1-*trans*-propene being equal), can be ascribed to a different and sterically regular disposition of the deuterium atom with respect to the CH_3 group in the two types of crystalline polymers.

If we assume that the two polymers are isotactic with respect to the β-carbon atom ($CHCH_3$), then two different regular dispositions of the carbon atom bonded to the α-carbon atom (CHD), are possible.

In Fig. 2 the two possible configurations are reported using the same representation as the one used in the first paper on isotactic polymers; i.e. by supposing that the main chain of the polymer is displayed on a plane in a zig-zag form.

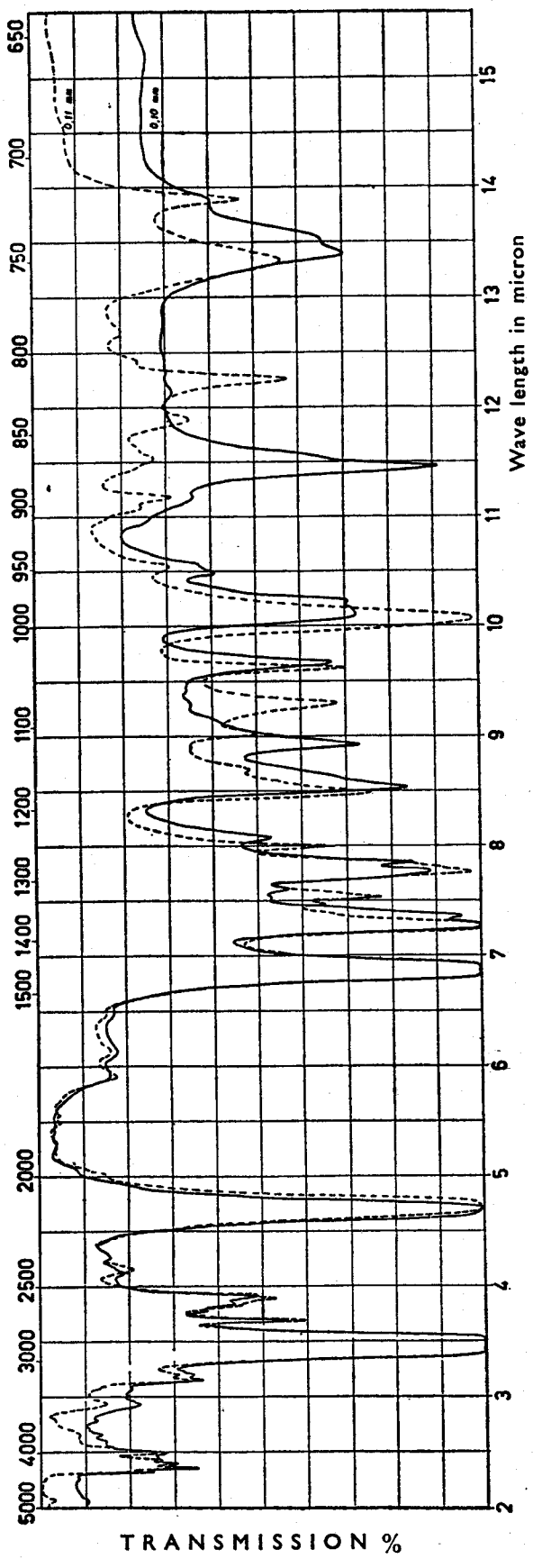


FIG. 1. I.R. spectra of n-octane extracts of poly (*cis*-propene $1d_1$): full line; and of poly(*trans*-propene $1d_1$): dotted line

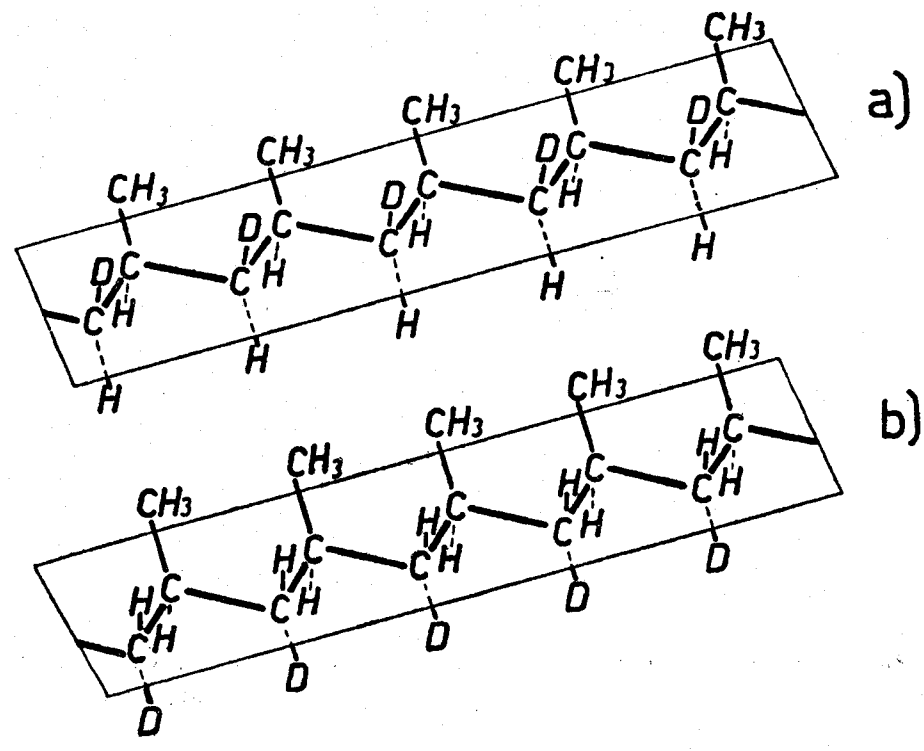


FIG. 2. Representation of a chain of $1d_1$ polypropylene: *(a)* threo-di-isotactic configuration; *(b)* erythro-di-isotactic configuration

In one case (Fig. 2a) the deuterium atoms are on the same side of the CH_3 group, while in the other case (Fig. 2b) they are on the opposite side.

In order to define the contemporaneous steric regularity of the isotactic type, which both the α- and β-carbon atoms can exhibit, we have proposed the name of "di-isotactic" polymers.

To distinguish between these two types of structures, we propose to extend in the polymer field the use of the prefixes "erythro" and "threo".

In the case of erythro-di-isotactic polymers, the CH_3 group and the deuterium atom are respectively at one side and at the opposite side with respect to the plane in which the main chain is displayed at zigzag; while in the case of threo-di-isotactic polymers the two substituents are on the same side with respect to the plane.

The two types of isomers are represented by the Fischer projection in Fig. 3, while in Fig. 4 is depicted the shape they assume in the crystal.

It is of interest to observe that the I.R. spectra of the amorphous ether-soluble fraction of the two polymers are also different; each spectrum exhibits, with a lower intensity, the absorption bands of the corresponding di-isotactic polymer when it is examined in the melted state. On the other hand the two spectra of the amorphous part have a group of very similar bands, which, on the contrary, are not present

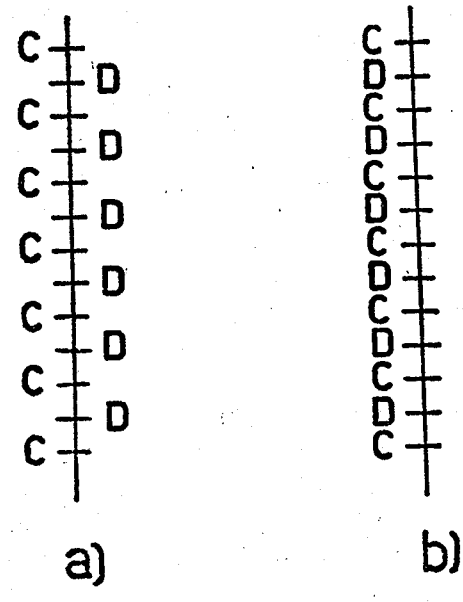


FIG. 3. Representation according to Fischer of a chain of polypropene $1d_1$: *(a)* threo-di-isotactic configuration; *(b)* erythro-di-isotactic configuration

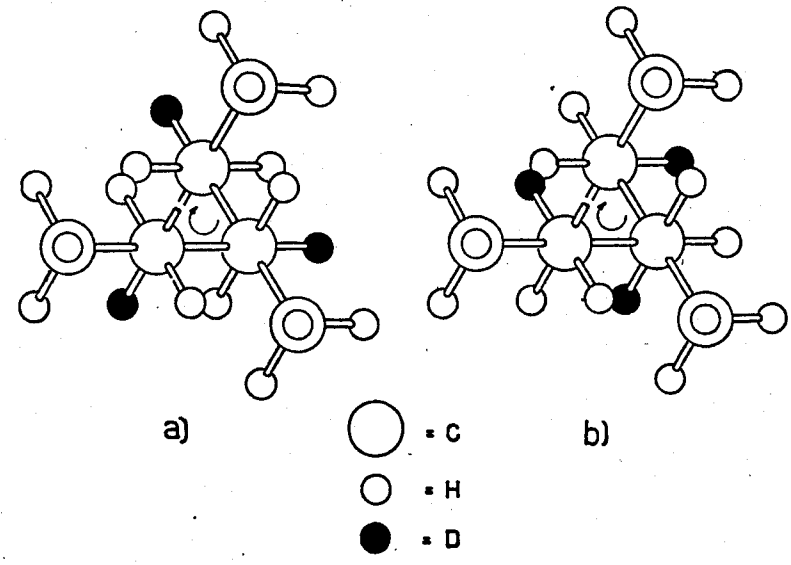


FIG. 4. Projection on a plane normal to the chain axis of a left-handed helix of polypropene $1d_1$: *(a)* threo-di-isotactic configuration; *(b)* erythro-di-isotactic configuration. The carbon atoms of the CHD groups are marked by the tertiary carbon atoms of the CH—CH_3 groups

in the spectra of both di-isotactic fractions. These bands can be associated with particular inversion-containing elements of the atactic structure, which could produce the same absorptions, independently of the nature of the monomer. The intensity of these bands calls for a high number of inversions. These same bands, on the contrary, are very weak in the spectra of the n-heptane fraction, which, as

is well known, consists of stereoblock polymers with a chain-length sufficient to give a certain crystallinity which can be detected also in the I.R. spectrum.

The results can be explained by the fact that, even in the atactic fraction, there is a constant or, at least, a prevalent mechanism for the opening of the double bond.

Knowing the structure of the di-isotactic polymer obtained from a given monomer, it is possible to establish the type of opening, if one assumes for the monomer a constant approach to the active centre of the catalyst. In fact, from the *trans*-monomers, through a *trans*-opening, the erythro di-isotactic polymer is obtained, and through a *cis*-opening, its threo diastereoisomer is obtained; from the *cis*-monomer are respectively obtained the threo and erythro form.

A more accurate study of the I.R. spectra and an examination of neutron diffraction spectra can provide the necessary information to determine the type of opening.

The extension of these ideas to monomers and to polymerization processes giving syndiotactic polymers, lead us to believe that the syndiotactic type of polymers might be identical when using either *cis*- or *trans*-monomers. In such a case polymers will be obtained which are syndiotactic with respect to both the asymmetric carbon atoms, to be named "di-syndiotactic". It is possible to foresee that the stereoisomeric phenomena, which have been found for the here-described deuterated polymers, can be extended to other polymers whose monomers are of the general type CHR=CHR'; by the stereospecific polymerization of *cis*- or *trans*-monomers it will be possible to obtain different sterically regular polymers.

Such difference would not be limited only to the case of the erythro and threo di-isotactic polymers, which can also have different crystalline structures, but could even be extended to the amorphous polymers which are generally formed along with the crystalline polymers.

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RESONANCE ENERGY OF POLYACETYLENE

by P. CORRADINI

(13 Dec. 1958)

[*Rend. Accad. Naz. Lincei* (8) **25**, 517 (1958)]

ABSTRACT

The resonance energy of polyacetylene is calculated in order to relate this value with some peculiar properties of the polymer, which differ from those of the higher homologues (polybutyne, polyhexyne). The average resonance energy for each bond, calculated on the basis of a polymer with an infinite number of acetylenic units in the chain, resulted only a little lower than that of benzene (5·5 kcal/bond). The length of the C—C bond along the chain can thus be assumed to be 1·40 Å. On such a basis we have confirmed the already known X-ray data and explained the insolubility of the polymer, even if scarcely cross-linked, in the usual solvents, and the solubility and the non-planarity of the chains of the higher homologous polymers of polyacetylene.

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STEREOSPECIFIC POLYMERIZATIONS OF CONJUGATED DIOLEFINS. NOTE II: THE POLYMERIZATION OF BUTADIENE WITH CATALYSTS PREPARED FROM ALUMINUM ALKYLS AND SOLUBLE VANADIUM CHLORIDES

by G. NATTA, L. PORRI and A. MAZZEI

(15 Dec. 1958)

[*Chimica e Industria* **41**, 116 (1959)]

ABSTRACT

This paper refers to the polymerization of butadiene with the aid of catalysts prepared from $AlEt_3$ and vanadium chlorides soluble in the polymerization solvent (VCl_4 or $VOCl_3$). An examination of the precipitates, which are formed in the catalyst-forming reaction, is also reported.

The crude polymerization products obtained with the aid of these catalysts chiefly consist of practically pure *trans*-1,4 crystalline polymers (*trans*-1,4 content >99 per cent; m.p. 140–5°C); they contain minor amounts of sterically less pure *trans*-1,4 polymers having a lower melting point and of amorphous polymers.

These last are practically absent when using only the heterogeneous part of the catalyst, repeatedly washed with heptane by decantation.

Diagrams are reported here which indicate how the catalytic activity (measured as amount of polymer obtained in a given time) varies when varying the Al/V ratio of the systems: $AlEt_3$-VCl_3, $AlEt_3$-$VOCl_3$, $AlEt_2Cl$-VCl_4, $AlEt_2Cl$-$VOCl_3$.

Comparative data are reported on the polymerization rate of the systems obtained from $AlEt_3$ and VCl_4, $VOCl_3$, VCl_3 respectively. The polymerization rates decrease in the order: catalysts from VCl_4 > catalysts from $VOCl_3$ ≫ catalysts from VCl_3.

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THE STEREOSPECIFIC POLYMERIZATION OF VINYLETHERS

by G. NATTA, G. DALL'ASTA, G. MAZZANTI, U. GIANNINI and S. CESCA

(5 Jan. 1959)

[*Angew. Chem.* **71**, 205 (1959)]

ABSTRACT

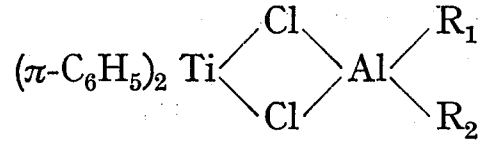
This paper deals with the study on catalysts able to promote stereospecific cationic polymerizations, in the homogeneous phase, of vinylalkylethers to polymers having an isotactic structure. In previous papers it had been observed that the possibility of polymerizing vinylalkylethers in a stereoregular way, was linked to a rather slow and controlled behaviour of the polymerization reaction. Such a behaviour is also favoured by the extreme purity of the reagents, by the low polymerization temperature and by the gradual addition of the monomer to the catalytic system. From this point of view the greatest emphasis must be attributed to the nature of the catalyst.

It was found that, going from compounds having a high cationic activity, such as aluminum trihalides (which polymerize vinylalkylethers rapidly and in a slightly ordered way) to those possessing an anionic activity, such as triethyl aluminum (which does not polymerize vinylethers), one observes the highest stereospecificity in the polymerization of vinylalkylethers when intermediate compounds of the type $AlCl_2C_2H_5$ or $AlCl(C_2H_5)_2$ are used. This fact can be attributed to the decrease of the cationic nature derived from the substitution of some halogen atoms with organic groups followed by the consequent reduction of the polymerization rate.

Stereospecific catalysts of this type are here called "modified Friedel-Crafts catalysts". If one keeps in mind this concept, it becomes possible to find catalysts for the stereospecific polymerization of vinyl-

alkylethers, by changing the central metal or the substituents of many catalysts. Thus, for instance, $TiCl_2(CH_3COO)_2$ or $TiCl_2(OR)_2$ are active. Even in the case where the organic groups which substitute all the halogen atoms are acidic groups (e.g. in Ti-tetraacetates), every catalytic activity for the polymerization of vinylethers is extinguished.

An analogous concept is valid for the catalytic bimetallic complexes, based on aluminum and titanium:



(where R_1 and R_2 are either chlorine atoms or alkyl groups). Such compounds are prepared by the reaction of dicyclopentadienyl titanium dichloride with aluminum triethyl or with aluminum dialkyl chloride.

The compound in which R_1 and R_2 are both chlorine atoms can polymerize alkylvinylethers in a highly stereospecific way; that compound in which R_1=Cl and R_2=C_2H_5 shows, however, a low polymerization activity and the resulting polymer is slightly crystalline. Finally, that one in which R_1 and R_2 are both C_2H_5 groups does not polymerize vinylalkylethers at all.

It is of interest to observe that in the polymerization of ethylene with these three types of catalytic complexes, an inversion of the polymerization activity occurs.

The study of the influence of temperature on the stereospecificity of the polymerization of vinylbutylether was effected particularly in the presence of bimetallic complexes, which were prepared from aluminum trialkyl and dicyclopentadienyl-titanium-dichloride (molar ratio 2:1). These complexes were not isolated. Whereas at temperatures higher than 0°C, a cationic polymerization of vinylethers to atactic amorphous products occurs, at —30°C the polymerization does not take place. By further lowering of the temperature (—50°C; —78°C), an increase in the amounts of isotactic polymer is obtained. This may lead one to think about two different operating polymerization mechanisms; one at high temperature and another one at low temperature.

Finally, the physical and chemical properties of isotactic vinylisobutylether are described. The I.R. spectrum of this polymer is compared with that of amorphous polyvinylisobutylether.

A cationic coordinated mechanism is assumed for these polymerizations of vinylalkylethers. Whereas for a stereospecific polymerization of mono-olefins, the presence of a crystalline solid phase is required in order to orient the monomer when it enters into the growing chain, vinylethers can be also polymerized stereospecifically in the homogeneous phase. This is to be attributed to the presence of two active centres in the monomer molecule, namely (oxygen and the double bond), analogously with what was observed in diolefins.

The specific orientation of the monomer at the moment of its addition to the growing chain is ascertained by its double anchorage to the catalyst by means of the coordinated association of the double bond and of the dative bond of oxygen (by its free electron pairs), to aluminum.

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SMECTIC MESOMORPHOUS MODIFICATION OF ISOTACTIC POLYPROPYLENE

G. NATTA, M. PERALDO and P. CORRADINI

(10 Jan. 1959)

[*Rend. Accad. Naz. Lincei*, (8) **26**, 14 (1959)]

In a preceding communication to this Academy, we referred briefly to the crystalline structure of isotactic polypropylene, prepared with stereospecific polymerization methods discovered in our Institute.[1]

In this note we wish to point out the possibility of obtaining a metastable solid modification of isotactic polypropylene, which we shall call "modification II". This modification is, because of some physical properties peculiar to it, different from the stable modification (modification I) which has already been described in our preceding communications. Such a "modification II" may be easily obtained by the rapid cooling in cold water of polymer films a few tens of a millimetre thick, previously heated above their melting point (176°C).

Modification II may be rapidly and completely transformed into modification I, by heating it at temperatures close to those in which the melting process begins (140–150°C). After heating at temperatures lower than 140°C, the transformation, even if it is still rapid, reaches limit values more and more decreasing so that, at a temperature lower than 70°C, samples are not subjected to any considerable change. For this reason, wishing to obtain modification II free from modification I, it is much better to perform a rapid cooling of the melted polymer by operating on thin films.

Similarities and differences of structure existing between modifications I and II were determined by X-ray and I.R. exa-

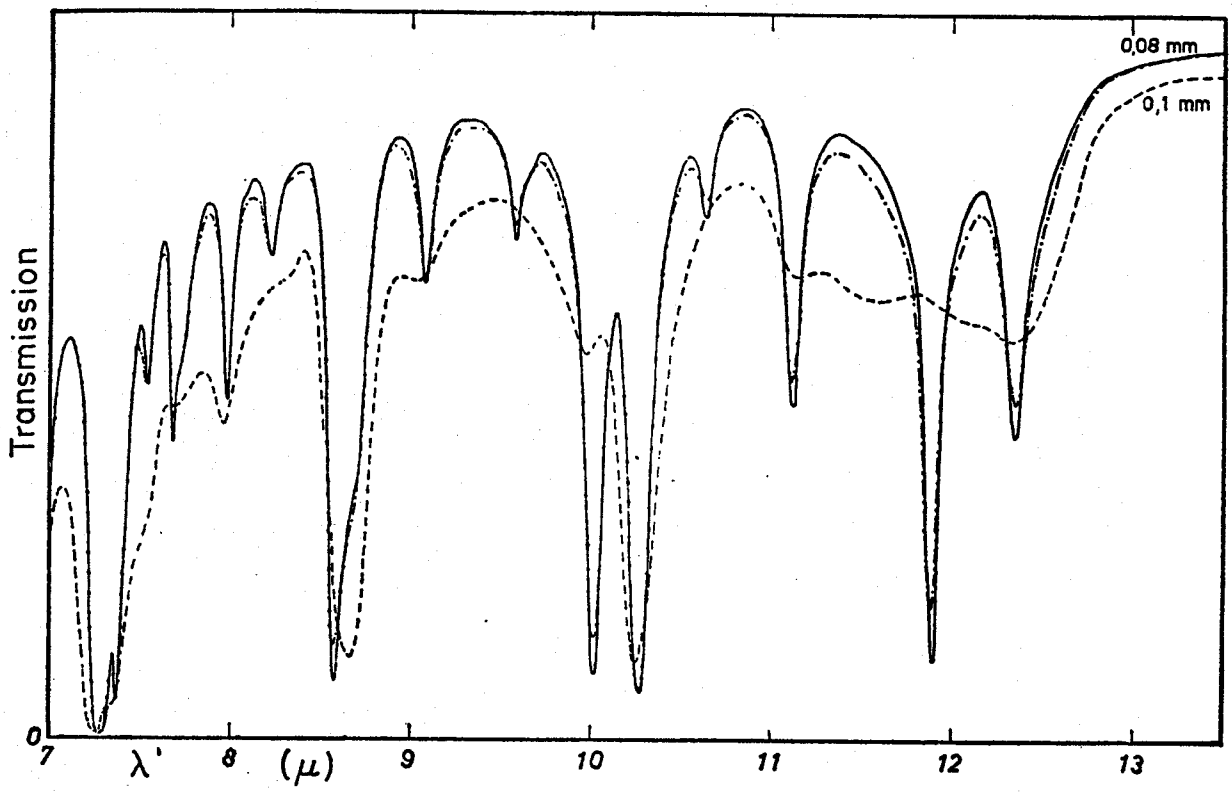


FIG. 1. I.R. absorption spectra of a sample of isotactic polypropylene: ——— modification I; —.—.— modification II; – – – – melted

minations of samples of isotactic polypropylene, which had been subjected to different thermal treatments.

In Fig. 1 are compared the I.R. absorption spectra (in the region 7 to 13μ) of a sample of isotactic polypropylene, that was obtained by rapid cooling of the melted polymer (modification II), of the same sample after a 5-min heating at 140°C (modification I) and in the melted state.

Figure 2 shows a comparison between the X-ray (Cu$K\alpha$) diffraction spectra, registered with a Geiger counter from $2\vartheta = 5°$ to $2\vartheta = 30°$, of a sample of isotactic polymer in both modifications I and II and of a sample of amorphous atactic polymer.

It is interesting to observe that the density of the sample containing modification II (0·88) is far lower than that of the same sample after annealing and containing modification I (0·92), while it is higher than the density of the amorphous atactic polypropylene (0·85). As can be seen from the figures, the X-ray spectra are also appreciably different.

The I.R. spectra of the two modifications are, on the contrary, very similar to one another, and they show just small fre-

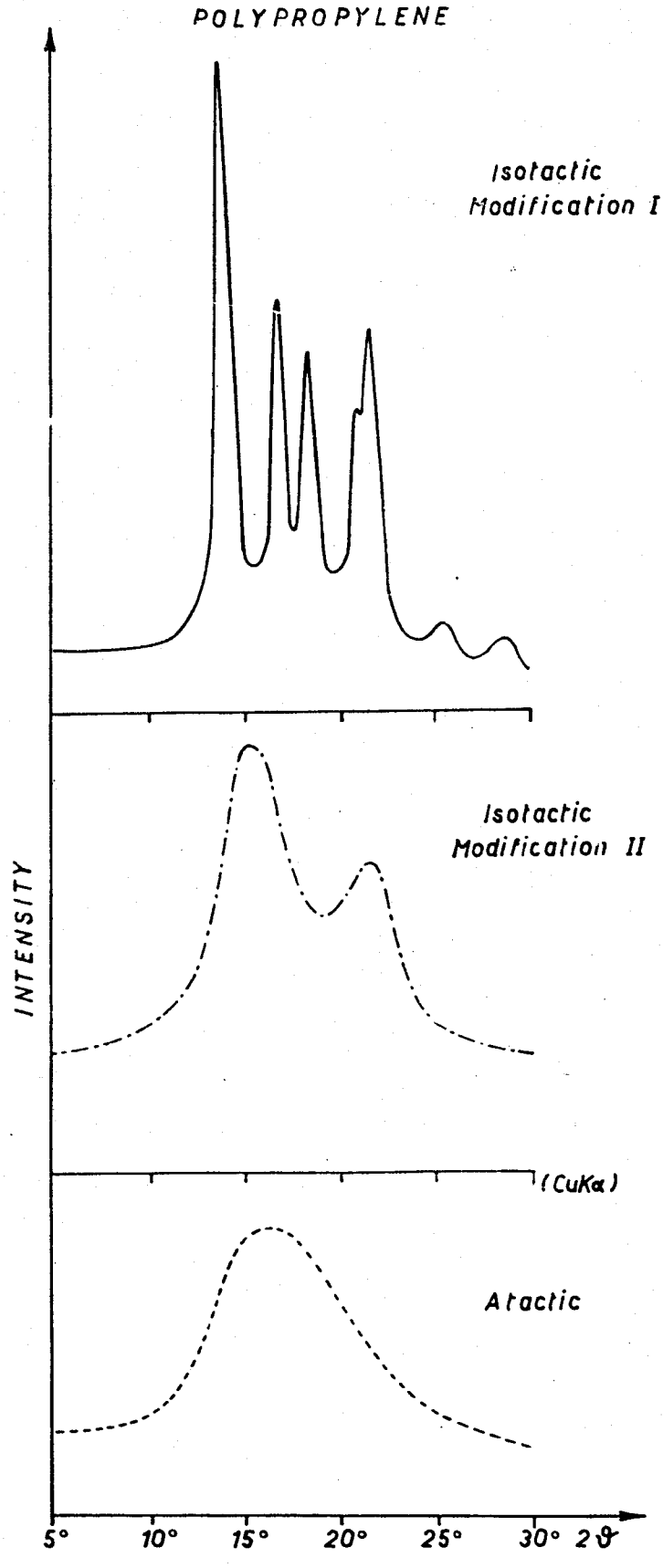


FIG. 2. X-ray diffraction spectra (CuK*a*) of isotactic and of amorphous atactic polypropylene samples: ———— modification I; —.—.—.— modification II; – – – – amorphous atactic

quency and intensity differences. It had been observed that the I.R. spectra of modification I of isotactic polypropylene was essentially determined by a threefold helix conformation of the macromolecules, whereas, no effect due to interactions among neighbouring macromolecules in the crystal had been observed.[2] The remarkable similarity of the I.R. spectra of the two modifications shows that the chains, even in modification II, have a threefold helix conformation for a remarkable fraction of their length. The differences observed in the density and in the X-ray spectra must therefore be attributed to a different side packing of the macromolecules, which, as we have already seen, affects slightly the I.R. spectrum.

In fact, the three first peaks of the X-ray spectrum of modification I, which are diffracted from crystallographic planes parallel to the chain axes, are reduced, in the X-ray spectrum of modification II, to a single and very wide halo which is not due, we believe, to the superposition of the enlarged diffractions of these peaks. On the contrary, the 4th peak of modification I, which corresponds to a plane non parallel to the chain axis, is enlarged and it is in a position which is seemingly not modified and it is absent in the spectrum of the atactic polymer. This indicates a lack of regularity in the packing of the macromolecules among themselves, but not necessarily a lack of parallelism, which parallelism is a necessary condition to obtain a sufficiently compact association.

As a matter of fact, modification II of the isotactic polymer may be perfectly oriented under stretching; in this state it gives an X-ray fibre spectrum in which the wide halo with a maximum at 5·85 Å is oriented on the equatorial section of the film, thus confirming that it is caused by the interference of waves diffracted perpendicularly to the fibre axis, as the three first peaks of modification I. The identity period which can be measured on the fibre spectrum is 6·5 Å, which is the same as that of modification I. This period is sharply defined, contrary to the widening of the points of the reciprocal lattice in the directions perpendicular to it.

The corresponding I.R. spectrum shows a very good degree of orientation and it is substantially the same as that given by the stretched samples of modification I.

From our experimental results, it is possible to suggest the following conclusions:

(1) Modification II contains segments of molecules of isotactic polypropylene with a threefold helix conformation, arranged in parallel bundles.

(2) The side packing of the polymeric chains corresponding to an average distance among the chains of about 6·4 Å, is less compact and it lacks the regularity characteristic of modification I which was previously described by us.

We believe that the structure of modification II, contrary to that of modification I, may be suitably described if one supposes that chain segments having a right- and left-handed threefold helix conformation are disorderly distributed in the directions perpendicular to the chain axes, even if they are parallel to themselves. Thus, macromolecules should be associated in many small bundles, which should be able to become parallel when samples are oriented under stretching.

The results obtained from these studies, besides allowing a structural definition of a paracrystalline smectic modification[3] of polypropylene, have also allowed us, by some critical observations on the worth and on the possibility of comparing the methods which may be used, to determine the degree of crystallinity of polypropylene.

These observations most likely should not be considered as limited to the polymers examined here, but to be of a general application.

The determination of the degree of crystallinity from density measurements is valuable only when the coexistence of no more than two modifications, the amorphous and the crystalline one, is possible; that is when two differently ordered modifications, even if in the metastable state, cannot coexist.

The measurement of the intensity of the I.R. bands that are absent in the same polymer in the amorphous state, cannot always be considered as a sufficient criterion to determine the degree of crystallinity of a polymer considered as a measurement of its degree of three-dimensional regularity.

In fact, these bands may be due, as in polypropylene, to the existence of regularly spiralized chains, and are almost independent of the type of side order of the chains. The regularity of the chain conformation may be caused by the tendency of the chains to become parallel among themselves, even if, by kinetic causes, it is not possible to realize a three-dimensionally ordered lattice.

In fact, in the polypropylene modification obtained by quenching, in which the crystalline modification I does not appear, it is possible to observe, by I.R., an apparent crystallinity. This is not very much lower than the one measured on the same samples after annealing, which show a high degree of crystallinity also by X-rays.[4]

With regard to polypropylene, the I.R. method gives the con-

centration of the three-fold helices (modification I+modification II), whereas the X-ray method is more suitable to determine the concentration of the thermodynamically more stable phase (modification I).

While the X-ray methods used to measure the degree of crystallinity are more suitable for the determination of the regularity of the side packing of the chains, the three methods all together (X-rays, I.R., and density) permit an even better and more complete interpretation of the different types of co-existing regularities.

From this study it results that metastable smectic modifications with an intermediate order between the crystalline three-dimensionally ordered state and the completely amorphous disordered one may exist in the polymers having an ordered isotactic structure.

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THE KINETICS OF THE STEREOSPECIFIC POLYMERIZATION OF α-OLEFINS

by G. NATTA and I. PASQUON

(27 Jan. 1959)

[*Advances in Catalysis* **9**, 1 (1959)]

ABSTRACT

In this work we have reported on all the data concerning the kinetics of the stereospecific polymerization of α-olefins (in particular of propylene), compiled up to 1959.

After a general introduction dealing with the nature of the catalytic systems and with the mechanism of the stereospecific polymerization, we have described the behaviour of catalytic systems based on α-$TiCl_3$, for they are among the most stereospecific ones in the polymerization of α-olefins to isotactic polymers.

The different steps of the overall polymerization process have already been discussed, with particular emphasis on the termination steps of the growth of the polymer chains: these studies were made using different methods.

The runs which were carried out in order to evaluate the number of the active centres present on the surface of the catalyst are also described. These determinations have allowed us to determine the mean life-time of the polymeric chains; by knowing this value, we have been able to point out conditions which one must follow in order to obtain heteroblock polymers consisting of long alternating sequences of different monomers.

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PROGRESS IN FIVE YEARS OF RESEARCH IN STEREOSPECIFIC POLYMERIZATION*

by GIULIO NATTA

(27 Jan. 1959)

[*S. P. E. Journal* **15**, 373 (1959)]

More than four years have elapsed since the first announcement of stereospecific polymerization of alpha-olefins.[1] This discovery opened a new immense field of research which attracted large numbers of chemists and technicians in Europe, America and Asia.

This immense work has brought remarkable fruits; most of them were foreseen by us when, in 1954, we announced the first highly stereospecific syntheses. In fact, we forecast the importance of steric regularity on the properties of the obtained polymers.

PROGRESS IN STEREOSPECIFIC CATALYSIS

Alpha-olefins: in our initial work on these olefins we clearly indicated the conditions for obtaining highly stereospecific catalysts, and polymers having a remarkable steric purity.[2] Later work confirmed our early findings: highly stereospecific polymerization of alpha-olefins takes place with heterogeneous catalysts and the highest yields in isotactic polymers are obtained with the aid of catalysts formed by a crystalline component (preferably a halide of a highly electropositive transition metal in a low valence state) and a metal-organic compound of a strong electropositive metal having a very small ionic radius. These yield complexes with the transition metal compounds and molecules of these complexes are tenaciously adsorbed on some points of the surface of the solid, crystalline component.[3]

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* Lecture given at the 15th Annual Techn. Conference, S. P. E., New York, 1959.

Many researchers have considered on the same level the stereospecificity in the polymerization of α-olefins and the production of linear polymers of ethylene with the aid of Ziegler catalysts. Some have also erroneously spoken of "isotactic polyethylene", without realizing that isotacticity is a particular regularity in steric arrangement, connected with the possibility of existence of enantiomorphous forms of the monomeric units, due to phenomena of stereoisomery. (Linear polyethylene cannot be isotactic since it does not contain regular sequences of asymmetric carbon atoms.)

An accurate study of Ziegler type catalysts has demonstrated that perfectly linear polyethylenes, having high and very high molecular weights can be obtained with the aid of a great number of completely soluble catalysts, such as the products of the reaction between transition metal alcoholates and aluminum alkyls[4] and certain organometallic soluble complexes, some of which have been isolated by us in pure crystalline form.[5] On the other hand with the aid of such soluble catalysts, it is not possible to obtain isotactic poly-α-olefins.

Progress in the field of α-olefin polymerization has been achieved in order to regulate molecular weights and their distribution. Besides the methods using hydrogen, many other processes have been found which are equally efficient, such as that based on chain transfer with alkyl groups of dissolved organometallic compounds of suitable structure.[6]

TABLE 1. STEREOSPECIFIC POLYMERIZATION OF PROPYLENE
(TEMPERATURE 75°C; PROPYLENE PRESSURE 2.8 ATM; SOLVENT n-HEPTANE)

Catalyst			*Percentage of isotactic polymer**	$[\eta]$
Organometallic compound (mols)		$TiCl_3$ *(mols)*		
$Al(C_2H_5)_2$	$6{\cdot}2\times10^{-3}$	$3{\cdot}1\times10^{-3}$	84·5	2·9
$Be(C_2H_5)_2$	$9{\cdot}5\times10^{-3}$	$3{\cdot}2\times10^{-3}$	96·0	2·7
$Be(C_2H_5)_2$	$5{\cdot}4\times10^{-3}$	$4{\cdot}5\times10^{-3}$	92·8	3·4
$Be(C_2H_5)_2 9{\cdot}10^{-4}+Al(C_3H_5)_3{\cdot}O(C\text{-}H_5)_5$	$4{\cdot}2+10^{-3}$	$11{\cdot}6\times10^{-3}$	96·0	2·5
$Be(C_2H_5)_2 9{\cdot}10^{-4}+Al(C_3H_5)_3{\cdot}O(C\text{-}H_5)_5$	$4{\cdot}2\times10^{-3}$	$11{\cdot}6\times10^{-3}$	94·5	2·9
$[(C_2H_5)_2TiAl(C_2H_5)_2]_2$	$4{\cdot}15\times10^{-3}$	$3{\cdot}7\times10^{-3}$	96·7	3·9

* As % of isotactic polypropylene we assume the % of polymer not extractable with boiling *n*-heptane.

The rate of such transfer is a function of the instantaneous concentration of the metal-alkyls present in solution (e.g. in the case of triethyl aluminum, it is a function of the square root of the concentration).[7] Kinetic studies,[8] which were first developed on the α-$TiCl_3$-$Al(C_2H_5)_3$ system, have been later extended to other systems. These studies allowed us to explain the mechanism of chain transfer and chain termination which regulate the molecular weight.[9]

In the case for example of the regulation by a high concentration of aluminum trialkyls or hydrogen, the degree of polymerization depends, other conditions being equal, on the square root of the aluminum alkyl concentration or on the square root of the hydrogen partial pressure, and is practically independent of the monomer partial pressure when it is higher than 1 atmosphere:[10]

$$\overline{DP} = \frac{1}{K_1 + K_2\sqrt{C_{Alk}} + K_3\sqrt{P_{H_2}}}$$

where C_{Alk} indicates the aluminum alkyl concentration and P_{H_2} the hydrogen partial pressure.

The regulation of the molecular weight is of remarkable importance for particular applications of poly-α-olefins, in which melt viscosity plays an important role, e.g. for application in the textile field. The use of highly pure and highly crystalline $TiCl_3$, and of organometallic compounds yielding scarcely dissociable complexes allowed us to obtain directly by polymerization, crude propylene polymers of remarkable steric purity, containing more than 95 per cent of macromolecules insoluble in boiling heptane, which are mostly insoluble also in boiling n-octane.[11]

The nature of the organometallic compound has a remarkable influence on the steric purity of the polymerizate. The more firmly the organometallic compound is associated with the crystalline phase, the higher is stereospecificity.

If several organometallic compounds are present at the same time, stereospecificity is determined by the more strongly associated one. This allows, for instance, to maintain the high stereospecificity which is observed when employing beryllium alkyls alone, even adding an excess of an Al-trialkyl-etherate.[12] Recently we have obtained high stereospecificities by replacing simple organometallic compounds with

TABLE 2. PHYSICAL PROPERTIES OF HIGHLY ISOTACTIC UNORIENTED POLYPROPYLENE

$[\eta]$ = 2-2.5 (100 cm^3/g)

Specific gravity	0·915–0·920 g/cm^3
Crystallinity (X-ray methods)	80–85%
Melting point (polarizing microscope)	175–176°C
Yield strength ASTM D 412	400–410 kg/cm^2
Elongation at break, ASTM D 412	25–50%
Stiffness, ASTM D 747	15,000–16,000 kg/cm^2
Hardness (Rockwell) ASTM D 785	R 110–115
Vicat softening point (5 kg load) DIN 57302	125–135°C

other complexes which are chemisorbed by the surface of the transition metal compound[13] (see Table 1).

The analytical method proposed by us in previous papers,[2] according to which highly isotactic propylene polymers were isolated as residue after extraction of the crude product with boiling heptane, proved to be reliable also in subsequent studies. In fact, a further fractionation, for instance by boiling octane, does not lead to significant variations in melting temperature, and yields fractions having different molecular weights but having, in practice, the same steric purity.[14]

In Table 2 the properties of highly isotactic polymers are listed. The crystallinity of highly isotactic polymers, M.P. 175-176°C, determined

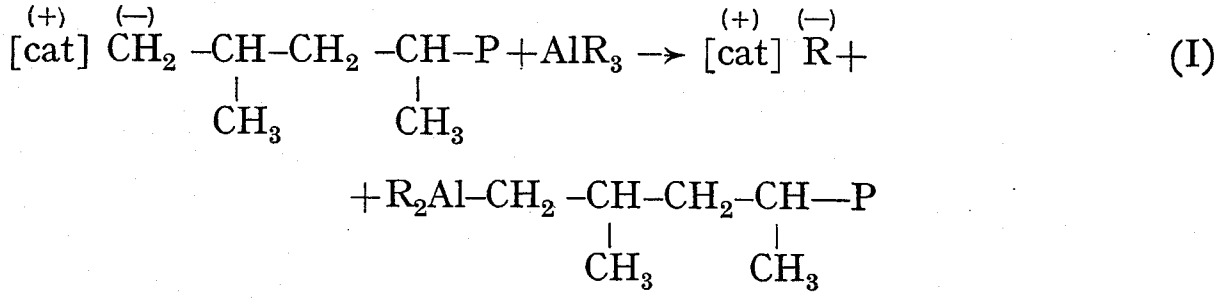
TABLE 3. ISOTACTIC AND STEREOBLOCK POLYPROPYLENES

Solubility		*Melting Temperature*	*X-ray Crystallinity* %	*Irregularities** %
Extractable with Boiling	*Non-extractable with Boiling*			
	trichloroethylene	176	75—85	0
	n-octane	174—175	65—68	0,6—1.3
n-octane	2-ethylhexane	174—175	60—66	0.6—1.3
2-ethylhexane	*n*-heptane	168—170	52—64	3.8—5.1
n-heptane	*n*-hexane	147—159	41—54	10.8—18.0
n-hexane	*n*-pentane	110—135	25—37	25.2—39.4
n-pentane	diethylether	106—114	15—27	37.1—41.4

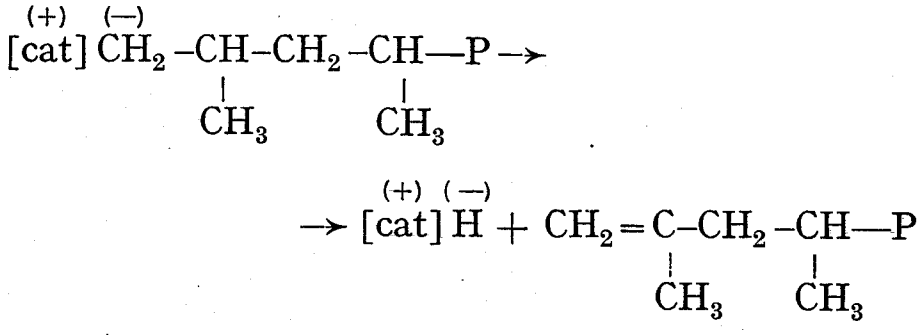
* Calculated according to Flory's theory assuming a heat of fusion of 2600 cal/monomeric unit.

by X-rays, can reach values of 80–85 per cent if the molecular weights are not too high.

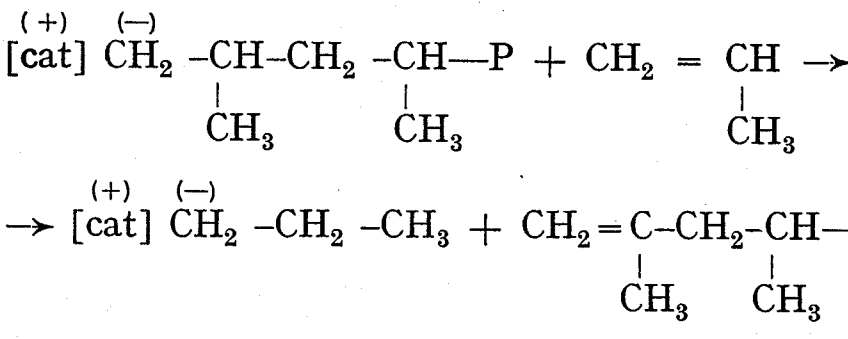
Analytical determinations made at the Polytechnic Institute of Milan demonstrated that the polymeric chains obtained in the presence of aluminum-alkyls are mostly linked to aluminum. This occurs because the most important processes limiting the molecular weight of the polymer, when operating at not too high temperature, are kinetically comparable to a chain transfer with the alkyl groups of the Al-alkyls in solution (I) and not to the dissociation process to hydride (II) and to the chain transfer with the monomer (III). A great part of the chains stays in this way bound to the aluminum during the whole polymerization.



(I)



(II)



(III)

A characteristic feature of the polypropylenes obtained with the aid of these catalysts after decomposition of these last, is the presence in the polymeric chains of terminal groups of two different kinds. At one end of the chain there is usually an alkyl group, derived from the aluminum alkyl used in the preparation of the catalyst or a n-propyl

group. At the other end of the chain there is a vinylidene group or an isopropyl group, this latter deriving from the decomposition at the end of the polymerization of the organometallic compounds bound in the polymeric chains.[15]

In the polypropylenes produced with catalysts $TiCl_3 + Al(C_2H_5)_3$ the most frequent end groups during the polymerization are:

$$\left.\begin{array}{l}\text{Catalyst}\\ \\ R_2Al-\\ \\ CH_2=CCH_3-\end{array}\right\}\text{-}CH_2\text{-}CHCH_3(CH_2\text{-}CHCH_3)_nCH_2\text{-}CHCH_3\text{-}\left\{\begin{array}{l}-CH_2CH_3\\ \\ \\ -CH_2CH_2CH_3\end{array}\right.$$

and after decomposition of the catalyst with alcohol or water:

$$\left.\begin{array}{l}(CH_3)_2\text{-}CH\\ \\ CH_2=CCH_3-\end{array}\right\}\text{-}CH_2\text{-}CHCH_3(CH_2\text{-}CHCH_3)_nCH_2\text{-}CHCH_3\text{-}\left\{\begin{array}{l}-CH_2CH_3\\ \\ -CH_2CH_2CH_3\end{array}\right.$$

If the molecular weight is regulated by a high alkyl concentration, or by means of hydrogen, the number of isopropyl end-groups in the total polymer increases.

If the catalytic complex can be easily dissociated, with separation from the active center of compounds containing metal alkyls, the inversions of steric configuration in the polymeric chains are more frequent.[17] The stereoblock polymers possess quite different properties from those of highly isotactic polymers and of atactic polymers. The percentage of steric irregularities in the different polypropylene fractions can be calculated on the basis of the heat of fusion (2600 cal/mol unit),[16] recently determined in this Institute (see Table 3).

A decrease in crystallinity, deriving from an increase in the number of inversions, causes a decrease in melting temperature, but no remarkable variations in the second order transition, which depends on the non-crystalline part. With an increasing crystallinity, the unfavourable effects exerted by the amorphous part on the dynamic characteristics at temperatures nea the second order transition are reduced.

The second order transition of amorphous polypropylene is the

highest among those of linear poly-α-olefins and may represent, in the case of low crystallinity polymers, an inconvenience for certain uses. The lowest glass transition temperature is instead shown by linear polyethylene.

Copolymerization leads to irregularities, which cause a reduction in crystallinity and in melting temperature, in a way quite similar to that of polymers containing steric irregularities; but while in the latter case the second order transition temperature is practically unchanged, in C_2—C_3 copolymers one can, on the contrary, observe a decrease in the second order transition temperature, which is the higher, the larger the ethylene content in the copolymer.[18] While in random copolymers of α-olefins with ethylene, crystallinity tends to disappear with ethylene contents higher than 20 per cent and lower than 80 per cent, the properties of heteroblock copolymers are quite different. The ethylene-propylene copolymers possess remarkable crystallinity even for ethylene contents which, in an ideal copolymer, would lead to a complete disappearance of crystallinity. The ethylene–propylene copolymers having long heteroblocks not only have a good crystallinity, but also better properties at low temperature; its temperature of complete melting is only a few degrees lower than that of pure isotactic polypropylene.[19]

The use of polymers having a high steric purity is particularly important in the fiber field.

Laboratory research work carried out in Italy in these last four years has been accompanied by the gradual development of a series of pilot plants of increasing capacity. These will be followed, in a short time, by a commercial production of 10-million lb/year of textile fibers, an amount which will be easily doubled. Staple fibers of different types and high-tenacity continuous yarns will be produced in a Montecatini plant at Terni, while polypropylene for use as a plastic material is produced at Ferrara.

The Italian Industry soon recognized the importance and vastness of the new fields opened by the discovery of stereospecific catalysis. It was thus necessary not only to expand the research work carried out at the Milan Polytechnic Institute, but also to create new research centers to share the tasks connected with the study of the stereospecific polymerization of α-olefin and of other monomers, with the preparation of copolymers, the properties of the polymers and the nature of the catalytic complexes. In addition to the scientific studies being carried out in the University Laboratories of Milan, Pisa and others, the

Research Institutes of the Montecatini Co., in particular at Ferrara, Terni and Novara, are studying the commercial development of the new processes.

OPTICALLY ACTIVE ISOTACTIC POLYMERS

Very interesting results from the scientific viewpoint, have been achieved by P. Pino at the University of Pisa in the preparation of polymers from optically active monomers. Starting from optically active olefins, polymers were obtained having a higher degree of crystallinity than that of polymers obtained by racemic monomers, and a different melting temperature. The optical activity of these polymers is very much higher than that of the corresponding monomers. In the case of poly-5-methylhexene-1, it is higher by more than 100 times that of the monomer and is of opposite sign.The study of optically active catalysts and of their influence on stereospecificity and crystallinity was developed both at Milan and at Pisa: the results obtained having a scientific interest will be described in papers to be published soon.

NEW POLYMERS OF DI-ISOTACTIC TYPE

At the Milan Polytechnic Institute, products belonging to a new class of stereo-ordered polymers have been prepared. These polymers have a linear paraffinic chain of the –CHR–CHR′ type, in which carbon atoms linked to different substituting groups follow one another alternately. Crystalline, stereo-ordered polymers of this type were described by us as derived, respectively, from *cis* and *trans* CHD = $CHCH_3$ monomers.[20] When operating with stereospecific catalysts, and starting from the *cis* or from the *trans* stereoisomer, crystalline polymers are obtained which show certain differences in some of their physical properties. The infrared spectra, for instance, are remarkably different as can be seen in Fig. 1.

New nomenclature problems have been faced, in order to characterize these new polymers, which we have called "di-isotactic." Polymers in which the configurations of both asymmetric carbon atoms are ordered, can exist in different configurations. In the case of isotactic polymerization, the two types of structure indicated in Fig. 2 (by supposing the chain stretched on a plane) are possible.

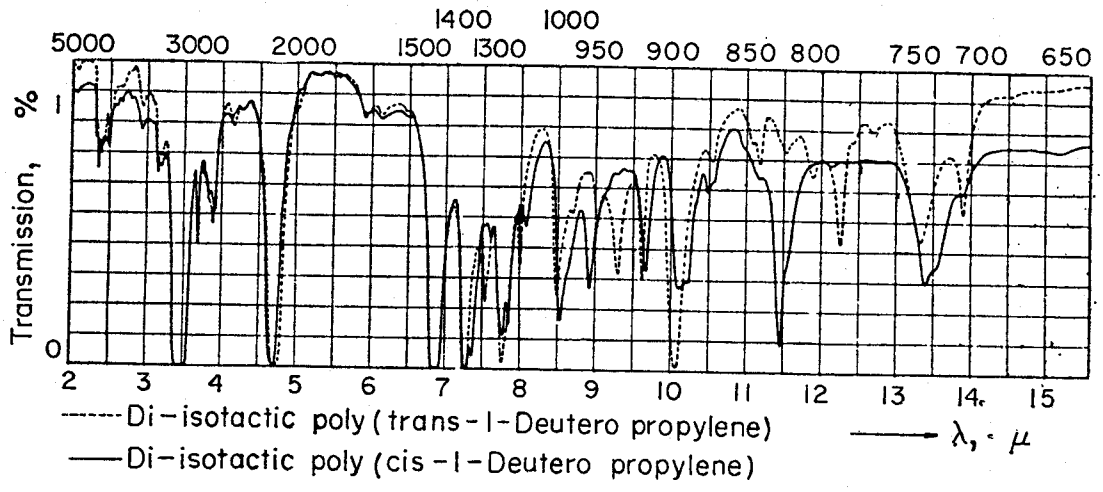
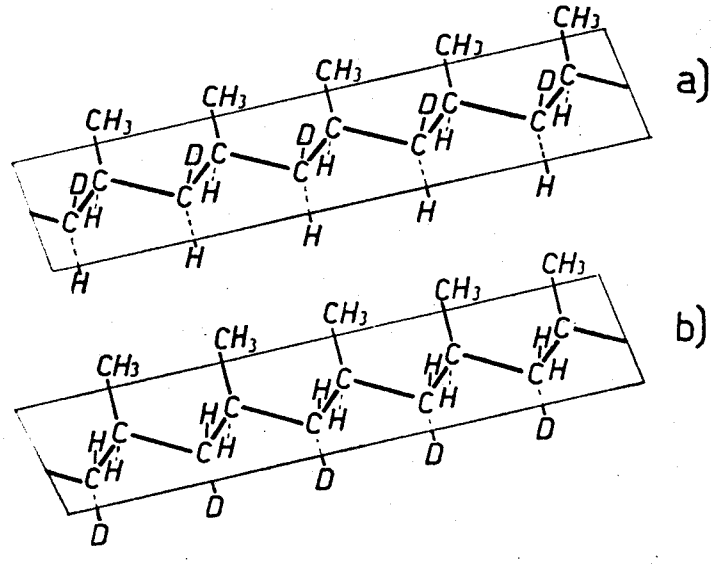


FIG. 1.



DI-ISOTACTIC POLYMER

a) threo poly (1-deutero propylene)

b) erythro poly (1-deutero propylene)

FIG. 2.

Figure 3 shows end views of the three-fold helices of these two stereoisomeric di-isotactic polymers. Only the left-handed helices are represented (the carbon atoms of the CHD groups cannot be seen being hidden by the tertiary carbon atoms of the $-CHCH_3$ groups).

We propose the terms: "threo-di-isotactic" for the polymer that, when the chain is displayed at zigzag in a plane, has all the substituting

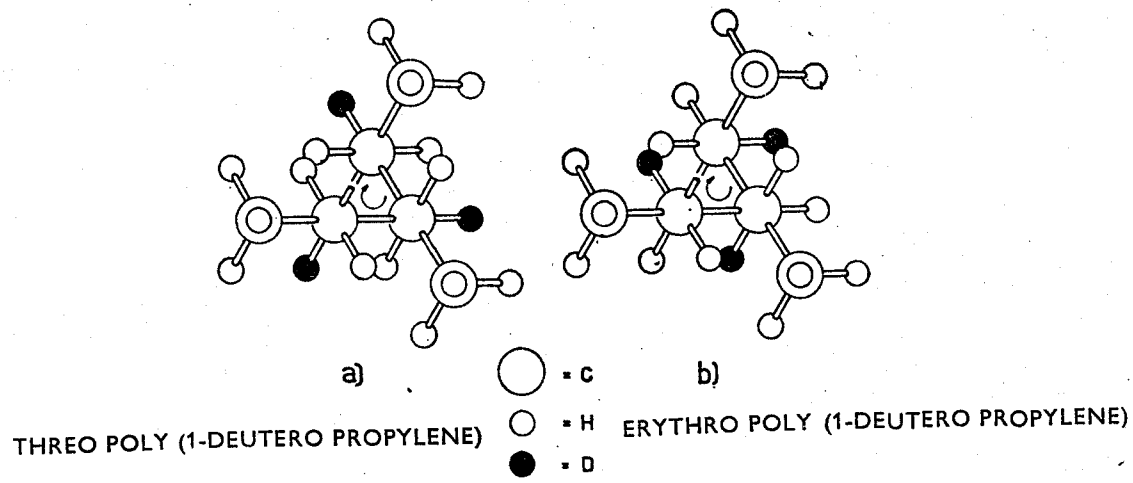


FIG. 3.

groups on the same side of the plane; and "erythro-di-isotactic" when it has one substituting group on one side, and the other on the opposite side. Both these isomers were isolated by us, as well as the mono-isotactic polymers obtained by random copolymerization of a mixture of the *cis* and *trans* isomers of the monomer.

CRYSTALLINITY OF ISOTACTIC POLYMERS

Isotacticity is a property exclusively connected with the steric structure of the main chain and not necessarily with crystallinity. Therefore, the extent of crystallinity is not sufficient to indicate the degree of isotacticity. The degree of crystallinity depends on the heat and mechanical treatments undergone by the polymer and reaches values which may result very differently according to the method employed for its determination.

A crystalline isotactic polymer remains isotactic even in the liquid state, when heated at a temperature higher than that of melting of the crystals; the same happens also at low temperature if, by rapid quenching, its normal crystallization is hindered. In this case, below the second order transition temperature, many isotactic polymers can be obtained as an amorphous glass, only slightly different, in certain physical properties, from a linear atactic polymer. In the case of isotactic polypropylene, an unstable crystalline smectic modification can be obtained by quenching it, having different lattice structure and low relative density (0·88). This modification presents approximately the same infrared spectrum as, and a degree of crystallinity only slightly lower

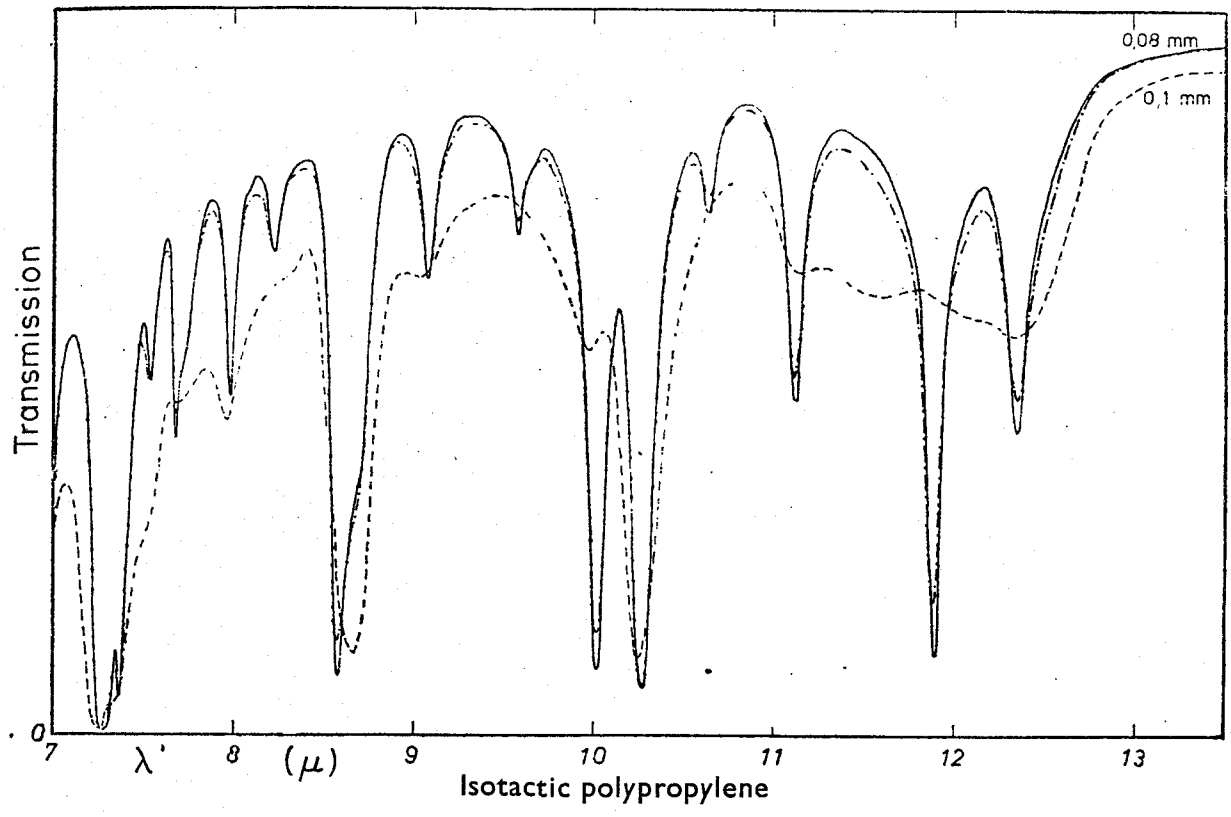


FIG. 4.

than that of the stable crystalline modification obtained from the same sample by annealing (Figs. 4 and 5).

The X-ray examination shows that the unstable modification has the same helix chain structure and the same identity period along the chain as the stable modification, but a different (random) parallel packing of the enantiomorphous chains in the three-dimensional lattice.[21] This explains the possibility of obtaining from highly isotactic polypropylene, more transparent films than polyethylene films. In this latter, in fact, a considerable difference in the specific gravity and in the diffraction index between amorphous and crystalline polymer makes it impossible to obtain highly transparent films, because they contain regions of different crystallinity having dimensions greater than the wave length of light.

Research work recently developed at the Milan Polytechnic Institute, and the results of which are in press, have demonstrated that the crystallinity bands in the 2–15 microns region in the infrared spectra of isotactic polymers (contrary to what happens in other spiralized polymers, such as the proteins and cellulose) are only due to vibrations connected with a three-fold helix conformation of the macromolecule and not to the interactions between monomeric units of different chains.

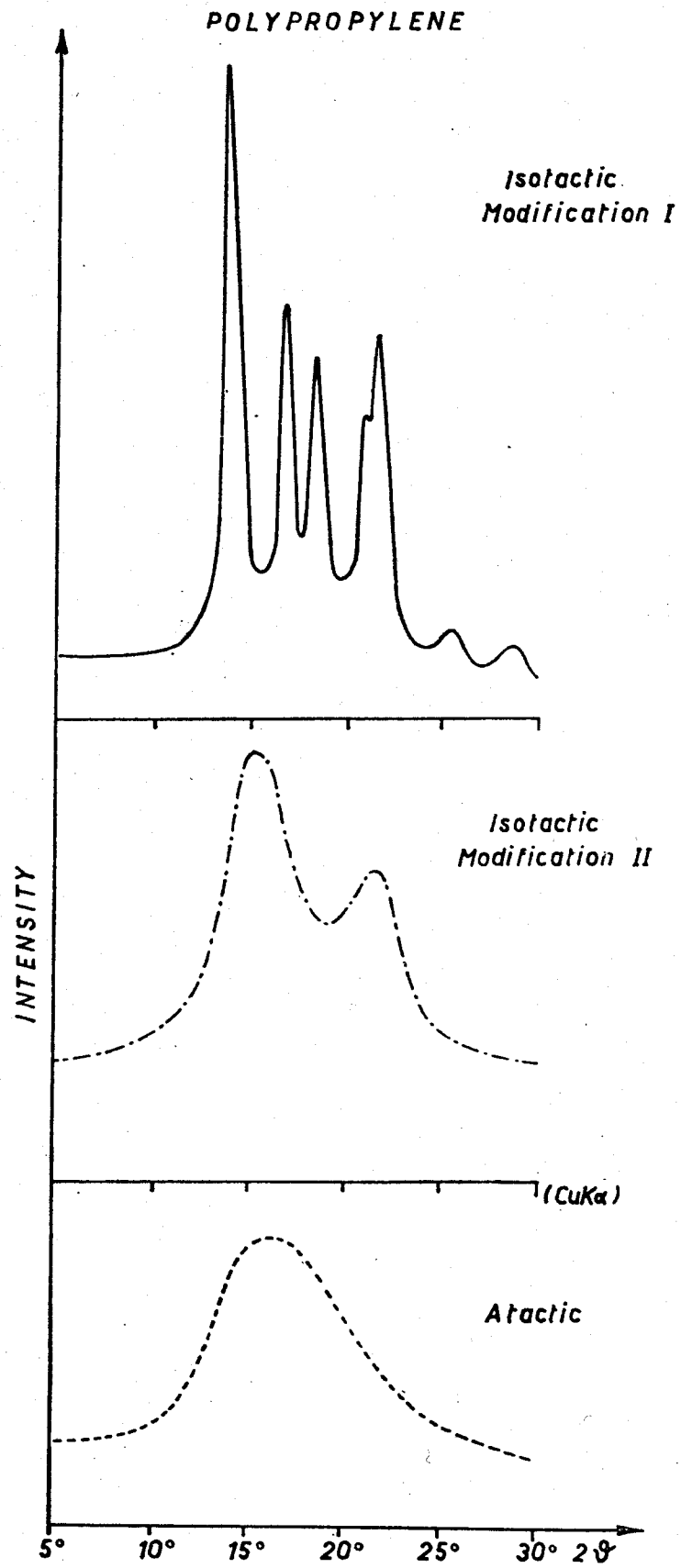

POLYPROPYLENE
Isotactic
Modification I
Isotactic
Modification II
Atactic
INTENSITY
(CuKα)
5°
10°
15°
20°
25°
30°
2ϑ

Figure 5.

TABLE 4. CRYSTALLINE ISOTACTIC, AROMATIC POLYMERS.

Monomer	*Intrinsic Viscosity*	*Melting Point °C*
styrene	3·5	240
o-methyl-styrene	—	>360
m-methyl-styrene	3·9	215
2–4 dimethyl-styrene	3·5	310
2–5 dimethyl-styrene	3·5	330
3–4 dimethyl-styrene	3·2	240
3–5 dimethyl-styrene	2·6	290
o-fluoro-styrene	2·3	270
p-fluoro-styrene	2·0	265
2-methyl-fluoro-styrene	—	>360
3-vinyl-naphthalene	2·3	360

Infrared bands due to crystallinity can therefore be observed also in the absence of a regular association of several chains (which is necessary to impart a crystallinity detectable by X-rays) provided that there exists a regular spiralization in each chain. Moreover, it may be observed that in certain random isotactic aromatic copolymers, which appear crystalline by X-rays, but having different "isomorphous" (i.e. vicariable in the chain) monomeric units following each other along the chain, the infrared bands of crystallinity disappear.[22]

The absence of crystallinity in α-olefin isotactic polymers having linear side chains with more than four carbon atoms, demonstrates that crystallinity by itself is not sufficient to define the isotacticity of a polymer. The copolymerization with stereospecific catalysts gives different results as for crystallinity, according to the type of monomers employed and the operating conditions.

Monomeric units having shape and dimension only slightly different from each other can vicariate in a way quite similar to that known in the lattices of solid solutions between isomorphous substances, and thus yield crystalline copolymers with lattice constants slightly different from those of the homopolymer of the prevalent monomer. As in the case of tridimensional lattices of low molecular weight substances, isomorphism and iso-dimorphism phenomena can occur also in crystallized polymeric chains, provided the monomeric units deriving from different monomers have very similar structure and dimensions, and can thus substitute each other varying

only slightly the identity period and the cross-sectional area of the chain helices. Phenomena of iso-di-morphism are expected to occur when the two homopolymers can crystallize in different forms (e.g. with identity periods containing a different number of monomeric units). When, however, the monomeric units do not show "isomorphism," crystallinity may occur in different cases as follows: (1) When the percent of comonomeric units is small; (2) When copolymerization does not occur at random, but forms long isotactic blocks.

The melting temperature of isotactic homopolymers depends, first of all, on steric factors and is not related to the melting point of the monomers. Branched olefins have melting temperatures lower than those of linear isomeric olefins, but the isotactic polymers of many branched olefins have melting points much higher than those of the corresponding linear olefins.[23]

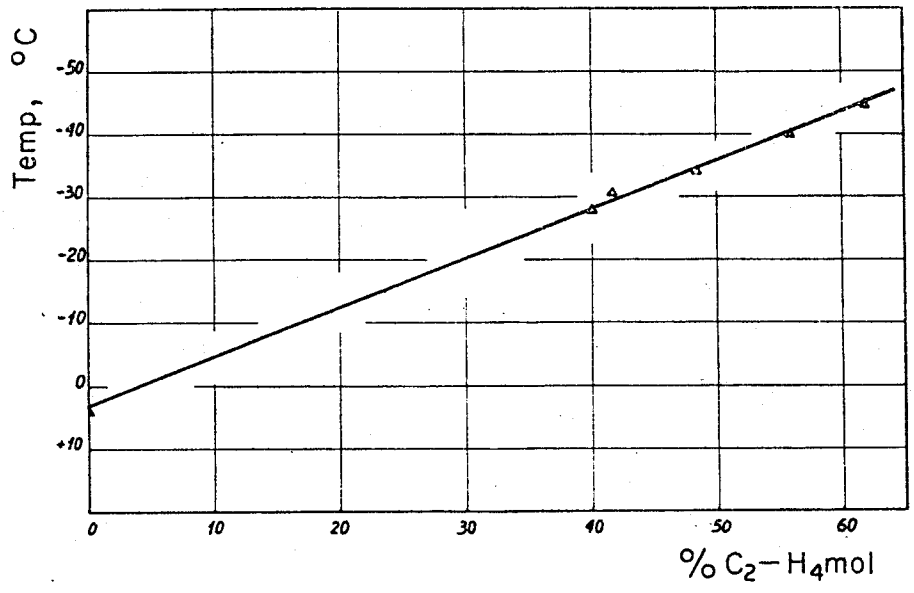


FIG. 6.

A similar behaviour is also found for certain isotactic aromatic polymers (see Table 4). Isotactic polymers having high crystallinity were obtained from certain aromatic monomers; some of these polymers, in respect of normal isotactic polystyrene, show a higher crystallinity and a higher crystallization rate.[24] Crystallinity in isotactic polymers is hindered when the side chains are very mobile or when, even if not mobile, they present a bulkiness which does not permit a good, compact packing, without large bond deformations or a too close

approaching of the atoms to each other relating to Van der Waals distances.

It might be stated that whenever hydrogen bridges or attractions of a chemical nature favouring the packing of chains are absent, a polymer cannot crystallize when hypothetical packings of the chains would lead to the formation of crystals having specific gravities lower than those possessed by the same polymer in the liquid or glassy state. This may be why many isotactic polymers do not crystallize at all, or crystallize only with difficulty.

We must, however, distinguish between impossibility and difficulty to crystallize. The latter can be due to steric hindrances, such as interactions between main chain and side groups. The difficulties met with in the crystallization of isotactic polymethacrylates are caused by the low mobility of the chain and find their counterpart in some aromatic polymers which also crystallize with difficulty. Irregularities in the chain lead to a decrease in crystallinity. The same results are obtained, as far as crystallinity is concerned by introducing steric irregularities (gradually transforming the isotactic polymer into a stereoblock polymer and into an atactic polymer) or by copolymerization with different monomeric units.

Quite different is the behaviour of the polymers, as far as the second order transition is concerned. An atactic polymer has approximately the same second order transition of the not crystallized portion of an isotactic polymer or of a stereoblock polymer. A copolymer presents a second order transition which is intermediate between those of the two homopolymers. This explains the variation of the mechanical properties of ethylene-propylene copolymers with composition. Figure 6 shows the minimum rebound temperature of the random copolymers. This is the reason for the great interest in the field of elastomers of the copolymers containing ethylene.

Figure 7 shows the rebound properties of the random C_2—C_3 copolymers having different composition, as a function of temperature. It is interesting to note that when a copolymer obtained with the aid of highly stereospecific catalysts contains such a number of irregularities as to hinder crystallization, many of its properties (particularly mechanical properties) are practically identical with those of a linear head-to-tail copolymer having the same composition, but obtained by means of a catalyst having low or no stereospecificity. The absence of a regular spiralization of the main chain causes the absence of crystallinity bands in the infrared spectra.

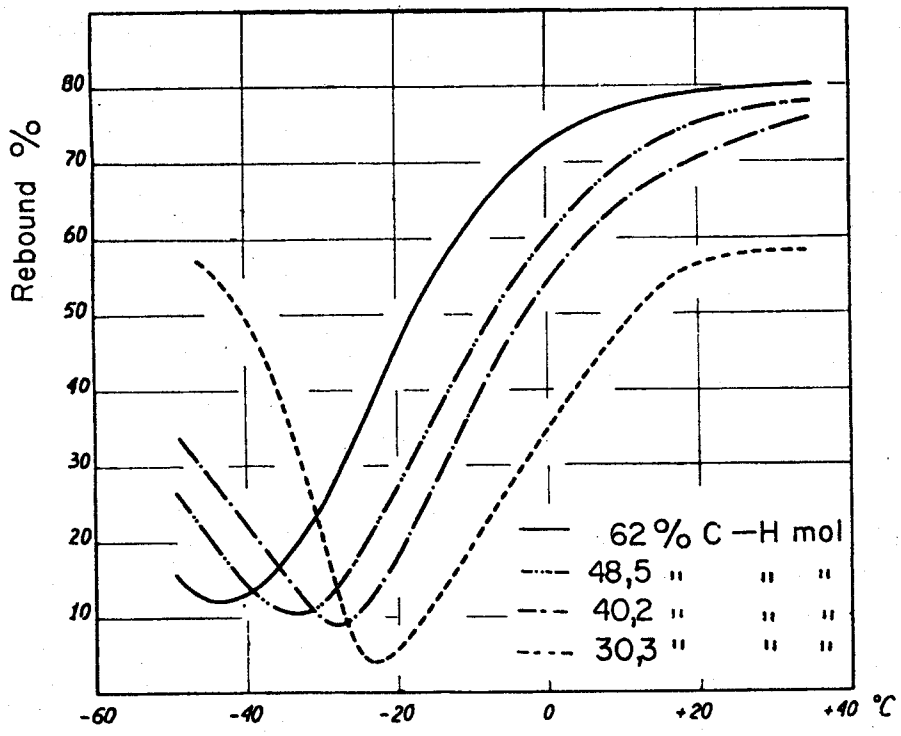


FIG. 7.

When working with stereospecific catalysts, the monomer reactivity ratios are nearer to each other and this is an advantage in the polymerization process, making it easier to obtain homogeneous copolymers[25] (see Table 5).

A characteristic feature of coordinated, anionic copolymerization, as well as of other ionic polymerizations, is that the product of reactivity ratios has a value near 1. This has been verified also in the case of copolymerization of aromatic monomers[26] (see Table 6).

ISOTACTIC POLYMERS OF VARIOUS NON-HYDROCARBON MONOMERS

The same catalysts that polymerize α-olefins in a stereospecific manner can behave similarly with vinyl monomers containing silicon or tin in the side chain[27] and with certain monomers containing halogen atoms linked to aromatic groups.

The use of heterogeneous catalysts is necessary for these stereospecific polymerizations as we have already pointed out for α-olefins. The particular steric orientation of the monomeric units is probably related to the structure of the activated, intermediate complex formed by the monomer with the catalyst.

Polarization of the vinyl double bond, the preferred orientation of the intermediate product and the constancy in the type of opening of the double bond are related with a sterically specific chemisorption of the monomer on an active center formed by an asymmetric organometallic complex which is part of a solid, ordered surface connected with a layer lattice. The study of the polymerization of *cis* and *trans* CHD = CH·CH_3 monomers, forming "di-isotactic" polymers, makes

TABLE 5. ETHYLENE AND PROPYLENE REACTIVITY RATIOS IN COPOLYMERIZATION IN THE PRESENCE OF CATALYSTS PREPARED FROM TRIALKYL ALUMINUM AND DIFFERENT TRANSITION METAL HALIDES

Metal halide	$r_{C_2H_4}$	$r_{C_3H_6}$	$r_{C_2H_4} \cdot r_{C_3H_6}$
$VOCl_3$	17·95	0·065	1·17
VCl_4	7·08	0·088	0·63
VCl_3	5·61	0·145	0·81
$TiCl_4$	33·36	0·032	1·07
$TiCl_3$	15·72	0·110	1·73
$TiCl_2$	15·72	0·110	1·73

TABLE 6. REACTIVITY RATIOS OF SOME VINYL AROMATIC MONOMERS IN COPOLYMERIZATION IN THE PRESENCE OF CATALYSTS PREPARED FROM $TiCl_4$ AND $Al(C_2H_5)_3$

Monomers	r_1	r_2	$r_1 \cdot r_2$
styrene-*p*-methylstyrene	0·82	1·15	0·95
styrene-*m*-methylstyrene	2·0	0·5	1·0
styrene-*p*-ethylstyrene	1·0	1·0	1·0
styrene-*p*-chlorostyrene	2·2	0·5	1·1

it possible to state that, in stereospecific catalysis, not only the mode of presentation of the monomer on the catalyst, but also the type of opening of the double bond, and therefore the configuration of both the —CHD— and the —CH·CH_3— groups, is determined. Monomers that contain, besides a vinyl double bond, another double bond conjugated with the first, or an atom having a lone electron pair able to associate itself chemically with the catalytic complex can show a quite different behaviour.

In these cases the preferential orientation, necessary for a stereospecific polymerization, can be caused by the coexistence of two interactions, the one given by the vinyl group and the other by the other group or atom conjugated with the first.[28] These interactions impose a particular structure on the intermediate activated complex. This is why in these cases it is possible to have stereospecific polymerizations also with the aid of soluble catalysts.

In our early investigations we had obtained, by homogeneous catalysis, crystalline isotactic and syndiotactic polymers, with 1–2 arrangement, and atactic, amorphous polymers of diolefins.[29]

Recently, T. G. Fox and coworkers of the Rohm and Haas Co. have disclosed the preparation of isotactic and syndiotactic polymers of methacrylates, by means of anionic polymerization using soluble catalysts, formed by organometallic compounds of lithium.[30] J. D. Stroupe and H. E. Hughes have established the structure of the isotactic polymers thus obtained.[31] Isotactic polymers of vinyl ethers were prepared by us[28] with the aid of various soluble catalysts of a more or less cationic type, different from those initially used by Schildknecht[32] (see Table 7). In many cases we obtained higher crystallinity.

The knowledge of these new types of stereospecific catalysts permits us a better explanation of the mechanism of stereospecific polymerization. In a preceding paper, I defined anionic coordinated the polymerization with catalysts formed by complexes containing organometallic compounds of strongly electropositive metals and low-valence compounds of transition metals.[33] In the United States there is a tendency to call this type of polymerization "coordinated", omitting the term "anionic".

Such a simplification may lead to some misunderstandings, because there are cationic polymerization processes which should be considered as coordinated, taking place with catalysts which are complexes. It is not possible, on the other hand, to limit ionic polymerization to only those cases in which a complete dissociation in ions takes place, because the greatest part of the polymerization processes which are usually considered as typically cationic, do not satisfy this requirement.

The attribute "anionic" or "cationic" for coordinated polymerization should be related to the polarity of the terminal carbon atom of the polymer linked to the catalytic complex. If this atom presents a negative polarity, the catalysis should be considered of the anionic, coordinated type. If on the contrary, it presents a positive polarity, the catalysis should be considered of the cationic, coordinated type.

The α-olefin polymers obtained under conditions leading to chain transfer with the monomer, generally contain in the first case macromolecules having a vinylidene end group; in the second case they mostly contain an internal double bond or a vinyl group.

TABLE 7. POLYMERIZATION OF ISOBUTYLVINYLETHER AT —78°C IN HOMOGENEOUS PHASE, IN THE PRESENCE OF DIFFERENT ALUMINUM COMPOUNDS

Catalyst	*Properties of the polymer*
$Al(C_2H_5)_3$	no polymer
$Al(C_2H_5)_2Cl$	crystalline, substantially insoluble in boiling acetone, $[\eta]$ in toluene at 30°C = 2·1
$Al(C_2H_5)Cl_2$	crystalline, substantially insoluble in boiling acetone, $[\eta]$ in toluene at 30°C= 2·3
$AlBr_3$	almost completely amorphous, soluble in boiling acetone, $[\eta]$ in toluene at 30°C = 0·9

There are typically cationic complexes, such as those obtained from $AlCl_3$ or $TiCl_4$ and an alkyl-halide, and typically anionic ones such as those obtained from titanium di- or trivalent salts and lithium, beryllium or aluminum alkyls.

There are, furthermore, complexes showing intermediate properties between those of cationic and anionic catalysts. The complexes formed by low-valence compounds of transition metals with $AlCl_3$ possess properties which are nearer to those of cationic catalysts, while the complexes of the same type obtained with metal-alkyl-halides have intermediate properties. Some of those complexes show stereospecific properties. For instance, the $AlCl_3$-$Ti(Cp)_2Cl$ complex polymerizes vinyl ethers to crystalline polymers.[34]

When the chlorine content is decreased through partial to total substitution by alkyl groups, the tendency to polymerize vinyl ethers also decreases, while the ability to polymerize ethylene increases (see Table 8). Complexes richer in alkyl groups also polymerize α-olefins, if a suitable crystalline support is present.

STEREOISOMERIC POLYMERS OF DIOLEFINS

Our research work in the field of diolefin polymerization using catalysts containing organometallic aluminum compounds began with a study of butadiene polymerization by means of a catalyst consisting of $Al(Et)_3$ only.

Together with the discovery of highly stereospecific catalysts for the polymerization of α-olefins, the discovery of highly stereospecific catalysts for the polymerization of diolefins was developed. The general conditions for the polymerization of diolefins with catalysts of that type were indicated by us.

Thus the first crystalline butadiene and isoprene polymers, with high content in *trans*–1,4 units were obtained and their preparation is the subject of patents. With the same catalysts which are highly stereospecific in the polymerization of α-olefins, we easily obtained highly pure (> 99 per cent) *trans*–1,4 polymers.[35] Using catalysts formed by soluble complexes containing O, N, etc., we similarly obtained isotactic, syndiotactic, and atactic polymers having a 1,2 arrangement.[29]

We also succeeded in obtaining high yields of crystalline butadiene polymers having a high content of *cis*–1,4 units. The organometallic catalysts containing titanium, prepared by us in our early work, even if prepared with particular Al–Ti ratios, always yield crude polymers containing, besides the *cis*–1,4 units, also *trans*–1,4 and 1,2 units.

The use of catalysts prepared from TiI_4 as described by the Phillips Co.[36] permits us to increase the total content of *cis*–1,4 units in comparison with the crude polymers obtained from $TiCl_4$, but not to obtain pure, crystalline polymers.

Early in our investigation we had assumed that the poor stereospecificity of catalysts obtained from soluble titanium halides was due to the fact that such catalysts do not present a homogeneous composition and contain active centers of different types and different stereospecific activities. This assumption was confirmed by low temperature fractionation, which enabled us to isolate from their solutions crystalline *cis*–1,4 butadiene polymers by means of fractional crystallization at —30 to —40°C., to establish their lattice structure and to observe their ability to crystallize, as natural rubber does under stretching at room temperature or above.[37]

Using catalysts of a particular type, containing only one type of active center, crude butadiene polymers having a *cis*–1,4 content

TABLE 8. CATALYTIC ACTIVITY OF DIMETALLIC COMPLEXES IN THE POLYMERIZATION OF ETHYLENE AND OF ISOBUTYL-VINYL-ETHER

	Polymerization of isobutyl-vinyl-ether					*Polymerization of ethylene*				
Catalyst	*Mols of monomer / Mols of catalyst*	*Temp.*	*Time*	*Yield*	*[η] in toluene at 30°C*	*Polymer properties*	*Time*	*Press.*	*Temp.*	*g of crystalline polyethylene/mol of catalyst*
		°C	hr				hr	atm	°C	
$(C_5H_5)_2TiCl_2AlCl_2$	400	—78	2	97	2·03	see under A*	21	40	85	690
$(C_5H_5)_2TiCl_2AlClC_2H_5$	290	—78	3	34	2·15	see under B**	8	40	95	3400
$(C_5H_5)_2TiCl_2Al(C_2H_5)_2$	35	—78	15	0	—	—	8	40	95	3700

A * = Crystalline polymer. Fraction insoluble in boiling acetone = 91 per cent
B ** = Crystalline polymer. Fraction insoluble in boiling acetone = 55 per cent

TABLE 9. PHYSICAL PROPERTIES OF VULCANIZED POLYBUTADIENES WITH HIGH CONTENT IN *cis*—1,4 STEREOISOMER (PURE GUM RECIPE)

cis-1,4 content	*88-90%*	*96-98%*
Mooney viscosity, ML 4	90-95	70-80
Tensile strength, psi	800-1100	2500-2800
Elongation at break, %	900-1000	850-950
Modulus at 300% elong., psi	140-180	140-180
Resilience at 20°C, %	80-85	85-88
Hardness, Shore A	45-50	45-50
Compounding recipe:		
Polybutadiene		100
Stearic acid		2
Zinc oxide		3
Sulphur		1
Vulcafor MBTS (di-2-benzothiazyl disulphide)		1·3
Nonox D (phenyl-β-naphthylamine)		1
Cure: 145°C × 45 min.		

TABLE 10. PHYSICAL PROPERTIES OF VULCANIZED POLYBUTADIENES WITH DIFFERENT CONTENT IN *cis*—1,4 STEREOISOMER (CARBON BLACK RECIPE)

cis-1,4 content	*88-90%*	*96-98%*
Mooney viscosity, ML 4 of raw polymer	50-55	45-50
Tensile strength, psi	2200-2500	3300-3600
Modulus at 300% elong., psi	1000-1100	1100-1300
Elongation at break, %	500-600	450-550
Resilience at 20°C, %	55-60	60-65
Resilience at 90°C, %	60-65	65-70
Hardness, Shore A	60-65	60-65
Compounding recipe:		
Polybutadiene		100
Stearic acid		2
Zinc oxide		5
Vulcan 3 (HAF)		50
Sulphur		2
Vulcafor MBTS (di-2-benzothiazyl disulphide)		1
Nonox D (phenyl-β-naphthylamine)		1
Cure: 145°C × 45 min.		

higher than 97 per cent were obtained, both at the Donegani Institute of Novara and in Milan. The influence of steric purity on the properties is remarkable (see Tables 9 and 10).

Polybutadiene, vulcanized in the absence of reinforcing fillers, yields a rubber which has low initial elastic modulus and high tensile strength

only if it is capable of acquiring high crystallinity under stretching. Highly pure *cis*–1,4 polybutadiene is the product nearest in elastic properties to *cis*–1,4 polyisoprene (i.e. to natural rubber). One of the difficulties encountered in the use of polybutadiene was that high molecular weight polymers are difficult to process and difficult to depolymerize by thermal or mechanical treatments. It is now possible to regulate the molecular weight directly in the polymerization step and also to achieve a desired distribution of the molecular weights.

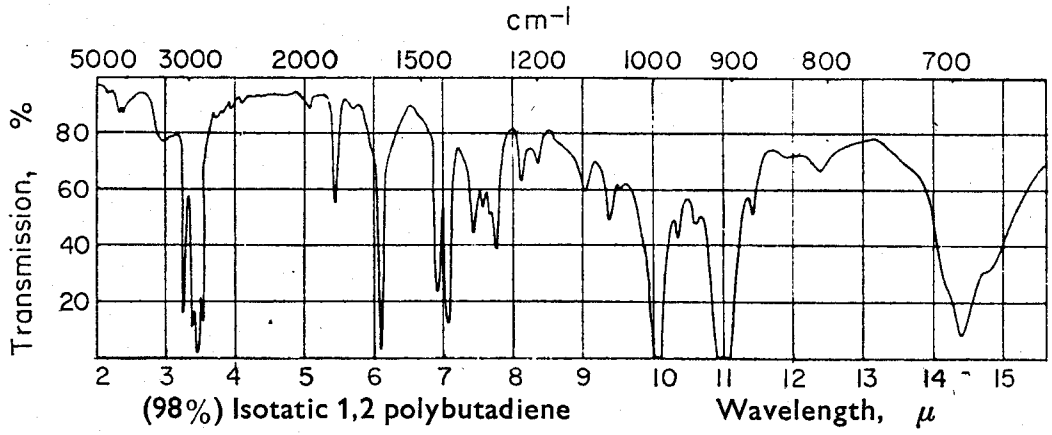


FIG. 8.

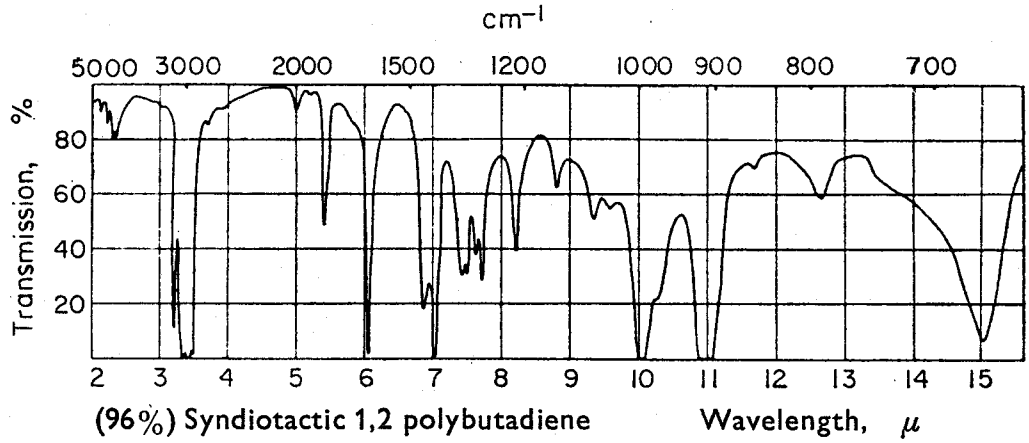


FIG. 9.

The infrared spectra of isotactic and syndiotactic 1, 2 and *trans*-1,4 polybutadienes are reported in Figs. 8, 9 and 10 respectively. We think it useful to report these infrared spectra since different coefficients appear to have been used in the United States and in Europe to determine the stereoisomeric purity of polybutadienes by infrared methods. Thus, infrared spectra of butadiene polymers have been reported,[38] from which the authors have decided on a *cis*–1,4 content of 95 per

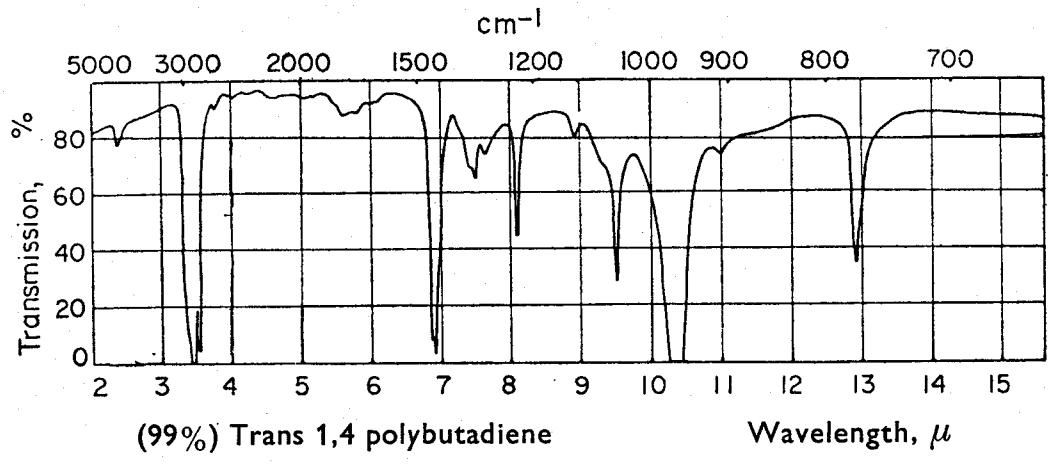


FIG. 10.

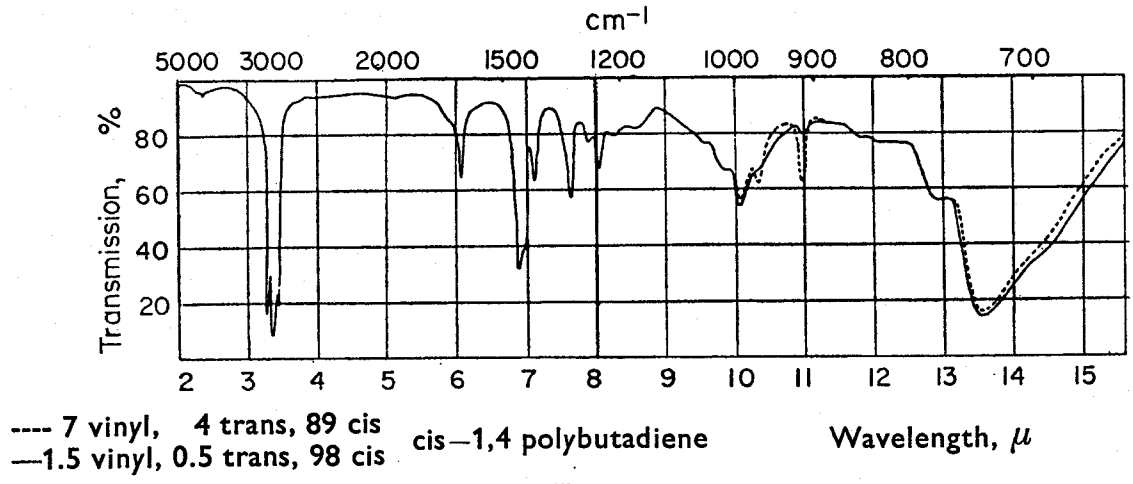


FIG. 11.

cent while by interpreting the said spectra according to our coefficients, a *cis*–1,4 content of only about 88 per cent results.

In Fig. 11 the infrared spectra of two samples having different *cis*–1,4 contents are compared. The contents of the different structures, as determined with our coefficients, are indicated.

The greatest practical interest arises from highly pure *cis*–1,4 polymers having a controlled molecular weight. They present good processability and very good mechanical properties, even in the absence of reinforcing fillers, and very good resilience even at low temperature.

The study of the polymerization of diolefins and of other monomers, with preparation of crystalline polymers of different steric structure, demonstrates that the difference in properties between various polymers of different structure not only depends on whether they present crystallinity or not, but rather depends in a predominant way on the specific type of steric structure.

Whenever different steric configurations are possible, it is not sufficient, in order to define the polymer, to indicate that it is able to crystallize, but it is also necessary to establish the type of steric regularity and the steric purity.

The same polymer with a given steric configuration and a given steric purity, which can be obtained in different crystalline modifications, can show different properties depending on the actual crystalline structure (e.g. in the case of polypropylene, polybutene, *trans*–1,4 polybutadiene), but the differences in mechanical properties deriving from the type of crystal structure are less important than those deriving from differences in the steric configuration.

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STEREOSPECIFIC POLYMERIZATION OF VINYL MONOMERS CONTAINING AN ELEMENT OF THE 4TH GROUP

by P. LONGI, F. BERNARDINI and L. COLOMBO

(29 Jan. 1959)

[*Rend. Ist. Lomb. Sci. e Lettere* **93**A, 134 (1959)]

ABSTRACT

Linear head-to-tail high-molecular-weight polymers of vinyl monomers containing an element of the 4th group and having the general formula

$$(CH_3)_3M—(CH_2)_3—CH = CH_2$$

where M is carbon, silicon or tin, were obtained with the aid of catalysts prepared from triethyl aluminum and titanium tetrachloride. When M was carbon or silicon, we obtained polymers that, after extraction with boiling solvents, gave highly crystalline fractions, which consisted of isotactic polymers having a high melting temperature and fractions consisting of stereoblock isotactic macromolecules, having a lower crystallinity and lower melting temperature, and finally furnished fractions of non-crystallizable macromolecules, which appeared amorphous by X-ray examination.

All the crystalline fractions of hydrocarbon polymers or of silicon-containing polymers, when examined by X-rays, showed an identity period of 6·5 Å along the chain, corresponding to that shown by other isotactic polymers containing three monomeric units arranged in a three-fold symmetry helix.

On the contrary, the polymer obtained from 5-trimethylstannyl-pentene–1 resulted in a completely amorphous product soluble in boiling diethylether.

TABLE 1. FRACTIONATION AND PHYSICAL PROPERTIES OF POLYMERS WHOSE MONOMERS HAVE THE GENERAL FORMULA:
$(CH_3)_3M—(CH_2)_3—CH=CH_2$

Run no.	*M*	*I* *Acetone extract* %	*II* *Ether extract*				*III* n-*Heptane extract*				*IV* *Residue*			
			%	$[\eta]$	d^{30}	*M.P.* °C	%	$[\eta]$	d^{30}	*M.P.* °C	%	$[\eta]$	d^{30}	*M.P.* °C
1	C	15·9	81·7	0·44	0·840	—(*)	2·4	2·1	0·854	125	—	—	—	—
2	C	8·6	78·5	0·55	0·838	—(*)	12·9	4·0	0·849	125	—	—	—	—
3	Si	33·35	64·5	0·42	0·859	127·5	2·15	1·29	0·867	131·5	—	—	—	—
4	Si	9·3	82·0	0·77	0·857	127·5	4·9	1·36	0·868	132	3·8	1·36	0·873	133
5	Sn	16·5	83·5	0·27	1·310	—	—	—	—	—	—	—	—	—
6	Sn	18·0	82,0	0·43	1·308	—	—	—	—	—	—	—	—	—

$[\eta]$ Intrinsic viscosity at 135°C in tetralin, 100 m³/g.
M.P. Melting point measured with the polarizing microscope; heating at a rate of 1°C/min.
(*) The determination of the melting point was not possible due to insufficient crystallinity.

Some of the properties of the above-mentioned polymers are compared in Table 1.

Independently of the type of atoms present in the monomeric unit, the least soluble fractions show a higher density and molecular weight; in the case of a structure that is at least partially crystalline, they show a higher melting temperature.

As reported in Table 1, the substitution of a silicon atom in each monomeric unit of poly-6,6-dimethyl-heptene-1 does not cause considerable variations in the melting temperature of those fractions having the same solubility and also practically the same crystallinity. Even the density of the above-mentioned fractions does not vary considerably.

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STEREOSPECIFIC POLYMERIZATION OF VINYLAROMATIC MONOMERS. NOTE I: ALKYL-SUBSTITUTED STYRENES

by D. SIANESI, M. RAMPICHINI and F. DANUSSO

(13 Feb. 1959)

[*Chimica e Industria*, **41**, 287 (1959)]

ABSTRACT

The polymers obtained by stereospecific polymerization processes from different substituted styrenes are examined. The following monomers were polymerized: *o*-methylstyrene, *m*-methylstyrene, *p*-methylstyrene, 2,4-dimethylstyrene, 2,5-dimethylstyrene, 3,4-dimethylstyrene, 3,5-dimethylstyrene, *p*-ethylstyrene and *p*-isopropylstyrene.

Stereospecific polymerization techniques can be generally applied to these monomers; however, the resulting polymers from some of these monomers are not crystallizable to any large extent. Crystalline polymers, having in any case isotactic structure and high crystal melting temperature, may reach in some instances high degree of crystallinity and have high crystallization rates. Non crystallizable polymers are obtained from *para* monosubstituted styrenes; on the other hand, the polymers of dimethylstyrenes are crystallizable, even if substituted in the *para* position.

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A NEW ORGANOMETALLIC CRYSTALLIZABLE COMPLEX CONTAINING TITANIUM AND ALUMINUM. ITS CATALYTIC PROPERTIES IN THE POLYMERIZATION OF OLEFINS

by G. NATTA, G. MAZZANTI, P. CORRADINI, U. GIANNINI and S. CESCA

(14 Feb. 1959)

[*Rend. Accad. Naz. Lincei* (8) **26**, 150 (1959)]

ABSTRACT

The reaction of bis-cyclopentadienyl titanium monochloride with an excess of $Al(C_2H_5)_3$, gives a diamagnetic, chlorine-free, crystalline complex, to which, on the basis of its chemical analysis and its molecular weight determination, we assigned the formula $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$.

The constants of its unit cell were determined by X-ray examination of the single crystals; on the basis of this finding and also of the chemical behaviour of the complex, we drew up its structural formula.

The $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$ complex can promote by itself the polymerization of ethylene, and in the presence of $TiCl_3$, it acts as a catalyst for the polymerization of propylene, yielding, relative to the catalytic system, $TiCl_3$–$Al(C_2H_5)_3$, higher molecular weight polypropylene, with a higher content in isotactic macromolecules.

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CRYSTALLINE STRUCTURE OF γ-TITANIUM TRICHLORIDE

by G. NATTA, P. CORRADINI and G. ALLEGRA

(14 Feb. 1959)

[*Rend. Accad. Naz. Lincei* (8) **26,** 155 (1959)]

ABSTRACT

It has been known that $TiCl_3$, in the crystalline state, presents three modifications, which we have denominated as α, β, γ[1]. The α- and γ-modifications are also known as violet modifications and consist of superimposed bidimensional macromolecules, in which the titanium atoms are linked with each other by a pair of bridged chlorine atoms (Fig. 1). These macromolecules, which have a layer shape, have been called by us "structural layers". In the two said modifications, these macromolecules have the same steric structure, only differing in their mode of packing.

The crystal structure of the β-modification, which is also known as the brown modification, is characterized, on the contrary, by linear macromolecules in which two subsequent titanium atoms are linked by three bridged chlorine atoms (Fig. 2).

Among the violet modifications, the α-one had been already described by Klemm[2] and subsequently more accurately by Reed and McWood,[3] on the basis of a lattice in which the structural layers, consisting of two layers of chlorine atoms that include a layer of titanium atoms, follow one another in such a way that anions yield a well-defined hexagonal close packing.

The main properties of γ-$TiCl_3$ are also described in this paper.

From the examination of the powder spectrum of this modification, we were able to observe, along with various analogies with the spectra

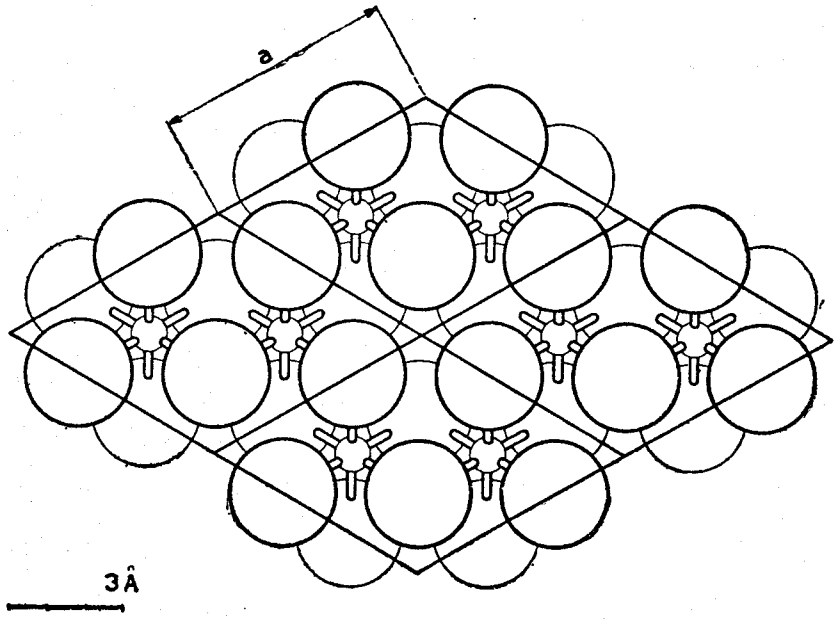


FIG. 1. Model of the structure of α-$TiCl_3$, according to Reed and MacWood. The big balls indicate the chlorine atoms, the small ones the titanium atoms.

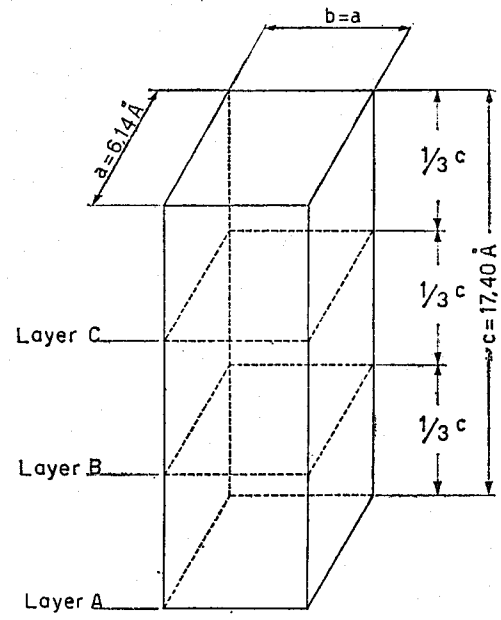


FIG. 2. Unit cell of γ-$TiCl_3$. The layers of type (a), (b), (c), reported in FIG. 3, repeat along the c-axis, thus determining a cubic compact packing of the chlorine atoms.

of the α- and β-modifications, the absence of a very intense line at $d = 2{\cdot}73$ Å, which is characteristic of the α- and β-modifications. In its place one can observe the appearance of a very intense line, at $d = 2{\cdot}51$ Å. Therefore, it appeared sensible *a priori* to look for a new type of close packing of chlorine atoms, whose ionic radius is much

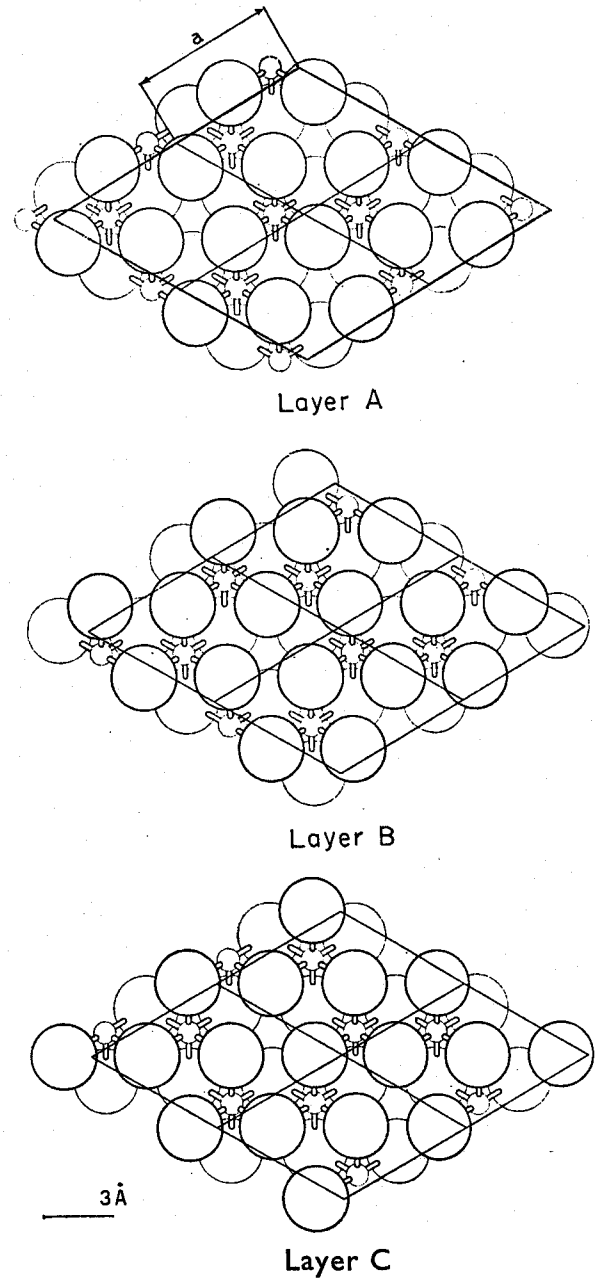


FIG. 3. Space distribution of the titanium atoms (small balls), and of the chlorine atoms, in the structural layers which follow one another in the unit cell of γ-$TiCl_3$, according to FIG. 2.

higher than that of the cations, which could justify the appearance of this most characteristic reflection of the present modification. We found this type of packing in the cubic close packing of the anions; in fact our calculations have interpreted both the position and the intensity of this reflection and of the most part of the other intense ones.

The presence, in the powder spectrum, of the reflection at $d = 5{\cdot}91$ Å, already observed in the α-modification and absent in the β-modification, was clearly caused by the diffraction of the titanium atoms, which in the α-modification repeat themselves every two layers of

chlorine atoms. This alternation must, therefore, be present even in the case of γ-$TiCl_3$, in which, consequently, structural layers of the same type as those observed in α-$TiCl_3$ are to be expected.

Our subsequent detailed calculation has confirmed these hypotheses. The resulting hexagonal unit cell has the following constants:

$$a = b = 6{\cdot}14\,\text{Å};\ c = 17{\cdot}40\,\text{Å};\ \gamma = 120°,$$

and contains six monomeric units [$TiCl_3$].

The examination of the type of weak reflections, characterized by the relationship between the indexes:

$$h - k = 3n \pm 1,$$

(reflections which are practically due only to the diffraction of the titanium atoms), has allowed us to determine the coordinates of the titanium atoms within the unit cell, and the space group (see Table 1). Fig. 3 shows the mode of packing of the structural layers in the crystalline state; this structural model leads to a good agreement between observed and calculated intensities, including the weaker reflections.

TABLE 1. COORDINATES OF THE Cl AND Ti ATOMS WITHIN THE UNIT CELL OF γ–$TiCl_3$ (SPACE GROUP $P3_112$) (4)

		x	y	z
Cl:	1st set (6*c*)	1/9	—1/9	z
	2nd set (6*c*)	4/9	—4/9	z
	3rd set (6*c*)	—2/9	2/9	z
Ti:	1st set (3*a*)	1/9	—1/9	0
	2nd set (3*a*)	—2/9	2/9	0

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THE COORDINATED ANIONIC POLYMERIZATION OF PROPYLENE TO ATACTIC AND STEREOBLOCK HIGH MOLECULAR WEIGHT POLYMERS. NOTE I: CHARACTERISTICS OF THE CATALYTIC SYSTEM: $VOCl_3$-$Al[CH_2CH(CH_3)_2]_3$

by I. Pasquon, E. Giachetti and L. Giuffré

(3 March 1959)

[*Chimica e Industria* **41**, 281 (1959)]

ABSTRACT

The $VOCl_3$–$Al[CH_2CH(CH_3)_2]_3$ catalytic system favours the formation of polypropylenes that are rich in atactic and stereoblock fractions.

In this paper, the following aspects of the problem have been particularly examined:

(1) The study, by chemical and X-ray analyses, of the catalyst obtained by the reaction of vanadium oxychloride with tri-isobutyl aluminum at 80°C.

(2) The influence of the method of preparation of the catalyst on the polymerization of propylene.

(3) The influence of the Al/V ratio on the activity of the catalyst.

Among the most interesting results obtained, the following ones deserve to be mentioned:

The solid catalyst obtained by using different conditions of preparation is amorphous by X-rays and it contains metal carbon bonds.

The activity of the catalytic system is influenced remarkably by the following factors:

(a) order of addition of the reagents;

(b) presence or absence of olefin during the preparation of the catalyst;

(c) time elapsed at the temperature of preparation of the catalytic system, before its use in the polymerization;

(d) Al/V ratio. The highest activity is observed when Al to V molar ratios are equal to about 1·2.

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STRUCTURE AND REACTIVITY OF VINYL AROMATIC MONOMERS IN COORDINATED ANIONIC POLYMERIZATION AND COPOLYMERIZATION

by GIULIO NATTA, FERDINANDO DANUSSO and DARIO SIANESI

(14 March 1959)

[*Makromol. Chemie* **30**, 237 (1959)]

The stereospecific polymerization of vinyl hydrocarbons to isotactic polymers has been extended, since the beginning of our research, to the field of vinyl aromatic monomers[1].

In the course of a systematic research programme, about thirty vinyl aromatic monomers have been prepared in our laboratory[2] and polymerized with catalysts from Al alkyls and Ti halides, following reaction conditions selected from the deeper study of the styrene isotactic polymerization[3, 4].

We recently described[5] the properties of the polymers obtained and briefly discussed the influence of the structure of the monomers on their reactivity and on the physical properties of the corresponding polymers. We report here in some detail the results on the relative reactivities of vinyl aromatic monomers in stereospecific polymerization and copolymerization.

The results, especially those concerning substituted styrenes, can be interpreted in terms of polar and steric effects of the substituents; hence, the possibility of reaching a clearer understanding of the mechanism of this unusual polymerization.

An extensive experimental investigation showed us[6] that in stereospecific polymerization with the above mentioned catalytic systems all vinyl aromatic monomers, which were polymerized, follow the kinetic laws which we have found to hold in the case of unsubstituted styrene[4].

Although we have to deal with heterogeneous catalytic systems, acting with an ionic mechanism, the polymerization can be experimentally carried out in such conditions as to assume constant or regular features, and studied with relatively simple, isothermal methods.

Depending on the nature of the catalytic reagents and the conditions under which they are brought in contact, the catalyst may be either stable or unstable during the polymerization. But even in the latter case it is possible to isolate and study the factors influencing the essential polymerization reaction, independently of the other factors determining the overall process. It is thus possible to obtain reliable results, which offer the possibility of reaching valid theoretical conclusions[3].

The polymerization reaction is, *per se*, a first order reaction with regard to both the monomer and the catalyst, having an activation energy of the order of 10,000–14,000 cal mol^{-1}.

In order to establish a scale of reactivity of differently substituted monomers in the overall polymerization process, we have determined the *relative reactivity a* of each monomer (in its homopolymerization).

The relative reactivity a of each monomer was defined as the ratio between its overall rate constant k_{mon} and the corresponding constant of the styrene k_{styr}, at a same temperature:

$$a = \frac{k_{mon}}{k_{styr}} \tag{1}$$

Being in general:

$$v = -\frac{dm}{dt} = k \cdot c \cdot m \tag{2}$$

we have in some instances determined a by dilatometric measurements[4] as the ratio between initial polymerization rates in separate equivalent polymerizations of each of the two monomers; in other cases a has been calculated from conversion data at a same reaction time, by the equation (derived from (2)):

$$a = \frac{\log (1-\eta_{mon})}{\log (1-\eta_{styr})} \tag{3}$$

where η_{mon} and η_{styr} are the conversion yields of the two monomers, in the same experimental conditions. The a values of several monomers are listed in Table 2.

On the other hand, beside the knowledge of the reactivities toward the overall process, it is of fundamental interest to determine the

relative reactivities of the monomers in the elementary process of chain growth.

By polymerizing a mixture of monomers, we have obtained products whose copolymeric nature has been proved by us, also on the basis of X-ray and infrared-ray examinations. Thus we have been able to calculate conventional *reactivity ratios* r_1 and r_2 for several monomers, copolymerized with styrene. In order to analyse the products easily and to check their homogeneity, labelled styrene was used as co-monomer.

In Table 1 the reactivity ratios of some monomeric systems are reported. The corresponding composition curves have a regular shape, which is typical of an ideal copolymerization. The ideal character of the copolymerization is also evidenced by the $r_1 \cdot r_2$ values, which are very close to unity, and also confirmed by particular infrared studies, showing, in the cases so far examined, a random structure of the co-polymers.

TABLE 1. REACTIVITY RATIOS OF SOME SUBSTITUTED STYRENES AT 40 °C.
(monomer 1 = styrene)

Monomer 2	r_1	r_2	$r_1 \cdot r_2$
p-methylstyrene	0·82 (±0·1)	1·15 (±0·05)	0·95
m-methylstyrene	2·0 (±0·2)	0·5 (±0·1)	1·0
p-ethylstyrene	1·0 (±0·2)	1·0 (±0·2)	1·0
p-fluorostyrene	1·5 (±0·2)	0·7 (±0·1)	1·0
p-chlorostyrene	2·2 (±0·2)	0·5 (±0·1)	1·1
p-bromostyrene	1·7 (±0·3)	0·5 (±0·2)	0·85

A particular, interesting result is that the values of the reactivity ratio r_2 in copolymerization are practically identical with the values of relative reactivity a in homopolymerization. In Table 2 the r_2 values for several monomers (all referred to styrene) are compared with those of a.

It should be noted that the found a and r_2 (or r_1) values of each monomer are not greatly different, even when they are determined using rather different catalytic systems, having different activity (e.g. $TiCl_4 + Al(i.C_4H_9)_3$; $TiCl_3 + Al(C_2H_5)_3$; $TiCl_3 + Be(C_2H_5)_2$). They actually depend only on the polymerization temperature.

An ideal character of the copolymerization has already been ad-

mitted for copolymerization following an ionic mechanism[7]. On the other hand, the equality $a = r_2$ has never been so clearly observed previously.

TABLE 2. RELATIVE REACTIVITIES IN POLYMERIZATION, AND REACTIVITY RATIOS IN COPOLYMERIZATION OF SOME SUBSTITUTED STYRENES WITH REGARD TO THE STYRENE AT 60 °C

Substituent in the styrene	a^a	$r_2{}^b$
H	1	1
o-methyl	0·10	0·13
m-methyl	0·43	0·48
p-methyl	1·2	1·16
2,4-dimethyl	(0·08)	0·14
2,5-dimethyl	(0·03)	(0·03)
3,4-dimethyl	0·48	—
3,5-dimethyl	0·23	—
2,4,6-trimethyl	0	0
p-ethyl	1·1	1·05
p-isopropyl	0·49	—
p-cyclohexyl	0·50	0·58
o-fluoro	0·20	0·18
m-fluoro	0·50	0·47
p-fluoro	0·74	0·72
o-chloro	0	—
m-chloro	0·40	0·43
p-chloro	0·45	0·49
p-bromo	0·50	0·48[d])
p-methoxy	2–3[c])	1·6
β-C_4H_4(2-vinylnaphthalene)	0·67	—

a) Calculated from experimental values of polymerization rate or conversion.
b) Calculated for ideal case from experimental composition of a copolymer, prepared by low conversion 1:1 copolymerization.
c) Estimated value: the monomer interacts with the catalyst.
d) At 40°C.

In fact, in a conventional ionic polymerization, with a chain mechanism, the overall rate is in general thought to be chiefly determined by the initiation rate[8], as well as being influenced by a termination rate, and is not representative of the value of the propagation rate. This is, on the contrary, the completely determining factor of the reactivity ratios in copolymerization.

The ideality of our copolymerization and the identity between a and r_2, show that in our polymerization conditions:

(a) the relative tendency of a monomer to enter in a polymer chain depends only on the structure of the entering monomer, but not on the nature of the terminal unit of the growing macroion.
(b) in classical terms (of conventional chain reactions) no differentiation is detectable between an initiation and a propagation step;
(c) in the same terms, and also according to kinetic results, a true termination step is never evidenced.

In other words our polymerization apparently proceeds, from the point of view of the monomer consumption, through a single type of step. We have, therefore, practically to deal with a stepwise addition process, in which the ultimate length of the macromolecules of the polymer may be determined by some elementary reactions, already recognized,[3] having the features of transfer reactions.

In order to understand better the mechanism of the fundamental addition reaction, it is of great significance to examine the relationship between structure and reactivity for the monomers studied.

For this purpose, the data of Table 2 were arranged following a Hammett plot (excluding, of course, all ortho substituted monomers)[9]. Figure 1 shows that, for halogen or *p*-n-alkyl substituted styrenes and for some other monomers, a linear relation may be considered to hold between log a, or log r_2, and the σ constant values corresponding to each type of substituent in the phenyl nucleus.

A few other monomers (*p*-isopropylstyrene and *m*-methyl substituted styrenes) on the contrary have a or r_2 values lower than those which would be predicted from the above linear relation.

The behaviour of these last monomers could be ascribed to factors of steric hindrance. Even if in the case of simpler reactions steric effects are not normally observed in examinations of meta or para substituted compounds, it is not surprising to find them in a reaction which has a stereospecific character and is promoted by heterogeneous catalysts. An evident confirmation of the importance of steric requirements in our polymerization is given by the very low reactivity of ortho (and even more of di-ortho) substituted styrenes, some of which are completely inactive.

The validity of the Hammet rule for a significant group of monomers indicates a regular response of the reaction to the electronic configuration of the monomer.

The most interesting result is, however, the negative slope of the straight line of Fig. 1 ($\varrho = \sim -1{\cdot}0$), indicating that the reaction is

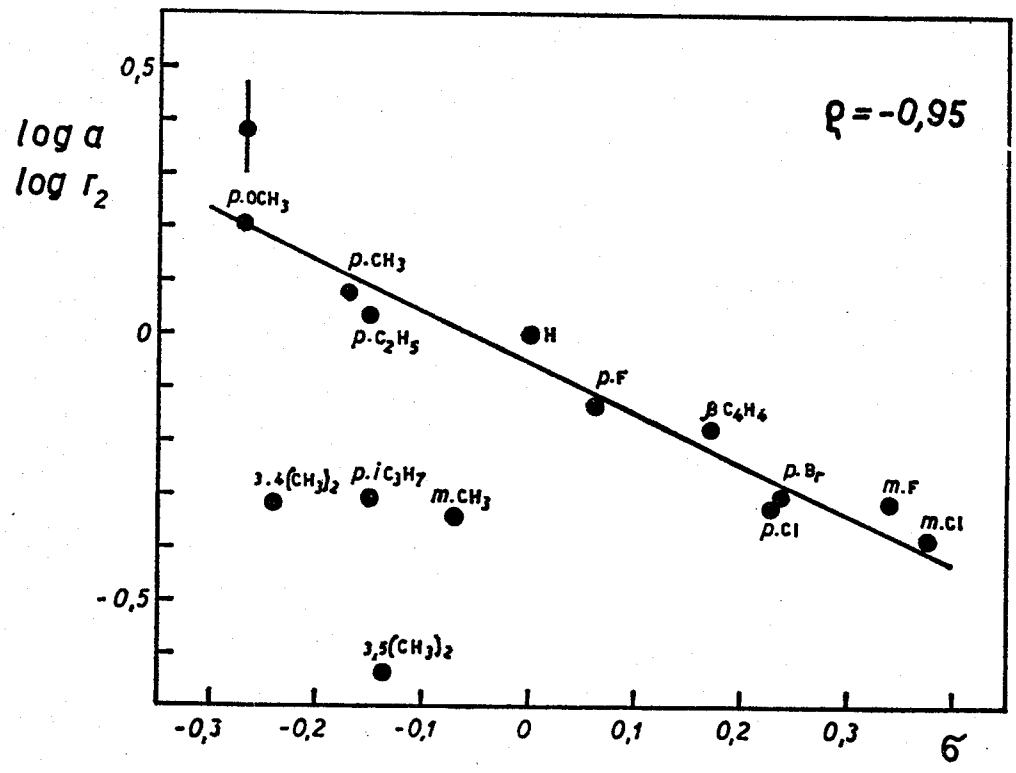


FIG. 1. Mean values of relative reactivity and reactivity ratio of Table 2, ordered following the Hammett plot

favoured in the case of monomers having an electron releasing substituent. The greater the electronic density on the double bond, the more reactive the monomer is, as if an electrophilic attack on the double bond were kinetically determinant.

Considering only r_2 values, this might at first sight appear as a typical feature of the cationic polymerization[10], in which a positive growing ion attacks the monomeric double bond.

However, in a conventional cationic polymerization, as far as it is known, it should first be noted that:

(a) ideal copolymerization may sometimes take place, but the equality $a = r_2$ has never been till now found to hold;

(b) following our further data obtained with conventional cationic catalysts, r_2 values of the same meta or para substituted monomers above examined all fit on a straight line in a Hammet plot, while in Fig. 1 exceptions in defect were observed;

(c) ortho-substituted monomers (as well as the α-substituted ones, as α-methylstyrene) have high reactivities, while in our polymerization they are completely inactive or show very low reactivities.

Furthermore, many arguments were found and evidenced in some of our preceding papers (see for example Refs. 11 12 13) which strongly sup-

port that the polymeric chain must be built up by addition of polarized $\overset{(-)}{CH_2}\text{–}\overset{(+)}{CHR}$ monomeric units to the activated $\overset{(-)}{CH_2}$– end group of a growing chain. Some of these may be summarized as follows:

(a) the nature of certain bonds in the catalytic complexes, in which carbon atoms act as a ligand and are connected to highly electropositive metal atoms;

(b) the close analogy to simpler addition reactions of olefins to similar organometallic compounds or complexes;

(c) the value of the activation energy of the polymerization;

(d) the presence in the polymers, as end groups, of the alkyl or aryl groups which were initially bound as ligands to the organometallic catalytic complexes;

(e) the presence of vinylidenic end groups in the macromolecules of aliphatic polyolefins, as a result of a H^- transfer from the —CHR— group of the terminal monomeric unit of the growing chain to the catalyst or to an entering monomer molecule;

(f) the presence of radioactive carbon atoms in the polymers, when labelled CO_2 is used to stop the polymerization.[17]

The fact that the stereospecific polymerization of vinyl aromatic monomers is intrinsically of the anionic type (with a negative growing ion), but does not respond to the polarity of the substituents according to a conventional anionic polymerization (favoured by electron attracting substituents) may appear to be quite peculiar. But it can find an interpretation in the mechanism already proposed for a "coordinated anionic polymerization",[12] in which a fundamental role is thought to be played by a previous step of coordination of the monomer to the transition metal of the catalyst.

According to our experimental results, as well as to evidence of the structure of some catalytic complexes[13] and to results on the stereospecific polymerization of α-olefins, the mechanism of the single addition step of our polymerization may be interpreted as follows.

The methylenic end of the alkyl groups, contained in the catalytic complex, or of the growing polymeric chain, is bound to the electron deficient catalytic complex, the bond having a partially ionic character, at least in its activated state. Thus, the negative terminal group of the chain can be thought of as bound to the metals of the complex, probably in a closer manner to the more electropositive one (e.g. Al).

When a monomer molecule approaches the catalytic centre, addition may occur following two fundamental stages.

1. According to the common rules of the heterogeneous catalysis, a chemisorption of the monomer should take place on a region of the surface of the catalyst where a transition metal atom acts as a coordinating centre. The coordination must be accompanied or immediately followed by polarization of the vinyl double bond, due to local field conditions. As an actual result of this stage, a positive charge must be localized on the α-carbon atom of the vinyl group*.

2. The positive carbon atom of the monomeric unit turns toward the negative terminal of the growing chain. Then, neutralization and covalent bond formation take place, followed by approaching of the new chain end to the more electropositive metal atom, so that the initial situation is restored.

The experimentally observed favourable effect of electron-releasing substituents on the reactivity in the case of vinyl aromatic monomers, would depend on the controlling nature of the first stage, in which the vinyl group acts as a nucleophilic reagent favouring the coordination of the monomer to the more electron-deficient part of the complex.

In a conventional anionic polymerization (e.g. catalyzed by sodium alkyls), on the contrary, as a consequence of a previous attack of the growing carbanion, a negative charge would be stabilized on the α-carbon atom and an increase of electron density on the vinylic double bond would be unfavourable to the addition reaction.

As a consequence also of the outlined mechanism, in our polymerization the coordination stage effected by electron-deficient bimetallic complexes may further imply geometric requirements and arrangements, which may be at the same time the origin of the stereospecificity, but also the reason of the lower reactivity observed with sterically hindered monomers.

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* It is known[14] that as a consequence of a nucleophilic attack on the styrene in the presence of the cation of a monovalent, strongly electropositive metal (e.g. Na, Li), the negative charge is localized on the α-carbon atom. In the formation of phenylethylic organometallic compounds with a polyvalent, less electropositive metal (e.g. Sn), the metal is bound to the methylenic group on β-position.[15] In the case of the formation of phenylethylic aluminum compounds (by reacting styrene with tri-isobutyl aluminum) an equilibrium composition of α- and β-substituted isomers is obtained, displaced toward the latter isomer.[16] It is therefore possible to foresee that, by coordinating a styrene molecule to a complex containing Ti and Al, a polarization of the double bond must occur as an electron displacement toward the β-position.

It is interesting to note that, in the case of stereospecific polymerization of α-olefins, the reactivity of the monomers appears to decrease in the order: ethylene, propene, butene, 3-methyl butene, 3,3-dimethyl butene. Considering only the polar effect of the substituents, this behaviour would be reversed with respect to that observed with vinyl aromatic monomers, but typical of a normal anionic polymerization. This would mean that for the α-olefins the formation of a π-complex, followed by polarization of the double bond and by a nucleophilic, kinetically controlling attack of the negative growing anion, could be envisaged. However, steric effects must play an important role in the establishment of the above reactivity scale.

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THE COORDINATED ANIONIC POLYMERIZATION OF PROPYLENE TO ATACTIC AND STEREOBLOCK HIGH MOLECULAR WEIGHT POLYMERS. NOTE II: KINETICS OF POLYMERIZATION WITH THE CATALYTIC SYSTEM $VOCl_3$-$Al[CH_2CH(CH_3)_2]_3$

by I. PASQUON, M. DENTE and F. NARDUZZI

(26 March 1959)

[*Chimica e Industria* **41**, 387 (1959)]

ABSTRACT

The polymerization rate of propylene, obtained with the aid of the catalytic system under consideration, decreases by increasing the polymerization reaction time.

We have demonstrated that for sufficiently low ratios of Al to V, e.g. <2–$2{\cdot}5$ at 80°C, such a decrease is closely related to the polymerization process itself.

The analysis of the data obtained suggests that the decrease in rate is caused chiefly by a continuous decrease, during the polymerization, of the rate of diffusion of the monomer to the surface of the catalyst. The continuous lowering of the diffusion rate, in its turn, should be caused by the continuous building up of the polymer around the particles of the catalyst.

Some relationships interpreting the above-described phenomena have been postulated. These relationships concur fully with the experimental

results obtained under various conditions.

In addition the data obtained have allowed us to draw the following conclusions:

(a) the size of the particles of the catalyst increases with the increase of the aging period, at 80°C, of the preformed catalyst.

(b) The size of the particles decreases with the increase of the Al/V ratio.

(c) The catalytic activity, referred to the surface unit of the catalyst and prepared with Al/V ratios = 1 or 2 and aged at 80°C, keeps practically constant when the aging period increases.

(d) The polymerization rate is of the first order with respect to the amount of catalyst and to the concentration of the olefin in the catalyst-solution interface region.

(e) The apparent energy of activation of the overall polymerization process, determined between 15 and 70°C on the basis of the initial rates, resulted to be equal to about 2800 cal/mol.

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STEREOSPECIFIC POLYMERIZATION OF CONJUGATED DIOLEFINS. NOTE III: THE POLYMERIZATION OF BUTADIENE WITH THE $Al(C_2H_5)_3$-$TiCl_4$ CATALYST SYSTEM

by G. NATTA, L. PORRI, A. MAZZEI and D. MORERO

(6 Apr. 1959)

[*Chimica e Industria* **41**, 398 (1959)]

ABSTRACT

This paper refers to the examination of the $AlEt_3$–$TiCl_4$ catalyst system and of the polymers obtained by polymerizing butadiene with the aid of this system.

In particular the authors dwell upon the methods that permitted them to isolate, from the crude polymerization products, high *cis*-1,4 polybutadienes, which are able to crystallize under stretching at room temperature.

The gradual addition of $AlEt_3$ to a $TiCl_4$ solution in an aliphatic solvent, gives rise to the formation of a precipitate whose composition varies with the Al/Ti ratio. At an Al/Ti ratio of 1–1·3 the precipitate obtained essentially consists of crystalline $TiCl_3$ and contains very small amounts of Al. The X-ray spectra of the $TiCl_3$ thus obtained (called β-$TiCl_3$ by the authors) appear identical with that of the brown $TiCl_3$, obtained by the action of dark sparks on gaseous mixtures of $TiCl_4$ and H_2.

The precipitates obtained at ratios Al/Ti $\geq$ 2 are amorphous, as revealed by X-rays; they contain Ti, Cl, ethyl groups and Al. The Cl/Ti ratio is lower than 3 and decreases with the increase of the $AlEt_3/TiCl_4$ ratio; the Al/Ti ratio is about 0·3.

The solid and the liquid phase of the catalyst obtained at $AlEt_3/TiCl_4$ ratio 1–1·3, considered separately, do not show catalytic activity; this can be easily explained considering that the solid phase consists of $TiCl_3$, which is inactive when aluminum alkyls are absent.

In the catalysts prepared at ratios Al/Ti $\geq$ 2 the solid phase keeps its catalytic activity even after being separated from the liquid phase and repeatedly washed with fresh solvent. At these ratios, the solid phase seems constituted, according to the analysis, by Al–Ti complexes, which evidently are active even in the absence of free aluminum alkyls in solution.

In the polymerization of butadiene in the presence of the $AlEt_3$–$TiCl_4$ system, both the polymer yield and the composition of the polymers vary with the Al/Ti ratio. Yield is the highest at Al/Ti ratios of 1–1·3. Some polymerization results as well as I.R. analysis of the polymers obtained, are reported in Table 1.

At low Al/Ti ratios (<0·5) the product contains internal double bonds of the *trans* type and appears as a white powder, only partially soluble in benzene; the polymer is probably due to cationic-type initiators.

The product obtained at ratio 1–1·3 has a rubber-like aspect, is amorphous by X-rays at room temperature, and its *cis*–1,4 unit content is higher than that of the raw polymers obtained at different ratios. At an Al/Ti ratio of about 2, the polymerization product is plastic and not rubber-like any longer; the I.R. analysis reveals that it consists of about 65 per cent of *trans*–1,4 units, and X-rays show that this product has a partial crystallinity of the *trans*–1,4 type.

When the Al/Ti ratio has intermediate values between those considered, products of intermediate composition are obtained.

The products obtained at various Al/Ti ratios were fractionated by diethyl ether extraction (after acetone extraction to remove oils). The results of such a fractionation (Table 2) can be summarized as follows:

1. Polymers obtained at Al/Ti ratio of 1–1·3 are ether soluble for 40–55 per cent; the residue to the extraction is partially crosslinked. The I.R. spectra of the soluble and insoluble fractions are practically the same; the fractions are both amorphous by X-rays. The presence of not negligible percentages of *trans*–1,4 units ($\sim$ 40 per cent) and the absence of crystallinity due to this type of unit indicate that, in these polymers, the *trans*–1,4 units are copolymerized with the *cis*-1,4 units.

2. The polymers obtained at Al/Ti ratio $\geq$ 2 contain about 30 per

TABLE 1. POLYMERIZATION OF BUTADIENE WITH $Al(C_2H_5)_3$–$TiCl_4$ CATALYST AT VARIOUS Al/Ti RATIOS

Run no.	*$Al(C_2H_5)_3$ moles*	*moles $Al(C_2H_5)_3$ /moles $TiCl_4$*	*Solvent cc.*	*Polymerization time, hr*	*Solid polymer g*	*I. R. analysis*		
						trans–1,4 %	*cis–1,4 %*	*1,2 %*
1	0·0071	0·5	heptane 90	1·45′	32	91	6·5	2·5
2	0·0071	1	iso-octane 120	3·30′	55	46	50	4
3	0·0107	1·2	petroleum ether 85	1	19	40	56	4
4	0·0107	1·2	cyclohexane 125	1·30′	21·3	41	57	2
5	0·0215	1·3	heptane 125	3·40′	42	44	52	4
6	0·0215	1·3	heptane 130	3	30	46	50	4
7	0·0107	2	iso-octane 80	2·45′	28	57	38	5
8	0·0112	2·5	heptane 130	3	15	66	28·5	5·5
9	0·0142	2·5	heptane 120	6	19·8	65	29	6
10	0·0134	3	heptane 110	2	6	69	22·5	8·5
11	0·036	4	heptane 100	4·45′	18	64	25	11
12	0·022	5	cyclohexane 120	3·10′	0·75	31	21	48
13	0·022	5	heptane 100	5	11	52	36·5	11·5
14	0·0546	6	heptane 120	4·45′	3	60	25	15
15	0·0364	8	heptane 100	15	12	62	29	9

In the runs performed at the Al/Ti ratio > 2 (except run 12), catalysts were employed from which the liquid phase was removed by decantation.

TABLE 2. FRACTIONATION OF POLYBUTADIENES OBTAINED WITH THE AID OF THE $Al(C_2H_5)_3$–$TiCl_4$ SYSTEM

Run no.	*Acetone extract* %[b]	*Ether extract*[a]				*Residue*				
		%	*trans-1,4* %	*cis-1,4* %	*1,2* %	%	*trans-1,4* %	*cis-1,4* %	*1,2* %	*X-ray analysis*
1	4·97	16·8	63	30	7	78·23	66	28	6	amorphous
2	10·20	31·5	47	49	4	51·4	49	47	4	amorphous
3	6·46	40·5	40·5	56	3·5	53·04	40	55	5	amorphous
4	2·8	57·2	40	58	2	40	40	57	3	amorphous
5	11·95	34·8	40·6	55·4	4	53·25	50	44	6	amorphous
6	16·8	39·4	39·4	56·3	4·3	43·8	48	47	5	amorphous
7	3·65	23·5	33	60	7	72·85	90	5	5	crystal. *trans*-1,4
8	2·5	26·6	31	60	5	70·9	90	6	4	crystal. *trans*-1,4
9	9·5	37	32	62	6	53·5	91	5	4	crystal. *trans*-1,4
10	18·2	30·2	29·6	56	14·4	51·6	91	4	5	crystal. *trans*-1,4
11	2·50	41·5	24	59	17	56	91	5	4	crystal. *trans*-1,4
12	26	26·5	27	46·2	26·8	47·5	93	3	4	crystal. *trans*-1,4
13	12	42·7	29	55	16	45·3	93	2	5	crystal. *trans*-1,4
14	10·2	48·2	25·5	57	17·5	41·6	94	2	4	crystal. *trans*-1,4
15	7·45	17·2	30	50	20	75·35	94	2	4	crystal. *trans*-1,4

a) Amorphous by X-rays.
b) Of oily consistency.

cent of ether soluble fraction. This fraction is rubber-like, is amorphous by X-rays at room temperature and consists of about 65 per cent of *cis*–1,4 units. The residue from the extraction is crystalline and *trans*–1,4.

The product obtained at a ratio of 1–1·3 and the ether soluble fraction of the product obtained at ratio 2, even if amorphous at room temperature, at low temperature ($< -30°C$) show a particular diffraction spectrum, which is not originated by *trans*–1,4 crystallinity. This spectrum (which is much more evident in the ether fraction obtained at Al/Ti ratio ≥ 2) was attributed to crystallinity of the *cis*–1,4 type. Such a crystallinity at low temperature seemed to indicate the presence of essentially *cis*–1,4 macromolecules, along with others having a mixed *cis–trans* structure. In order to clarify their composition, the ether soluble fraction obtained at Al/Ti ratio ~ 2 was subjected to fractionation by crystallizations from solutions in diethyl ether at a temperature from –30°C to –40°C. By this method and after several crystallizations, it was possible to separate fractions having a *cis*–1,4 unit content of 93–95 per cent. These polymers show a final melting temperature at about –1°C which is essentially equal to that of polybutadienes having a content of 98–99 per cent, obtained with the aid of the homogeneous systems $AlEt_2Cl$-Cobalt compounds. The authors deduce from this that substantially pure *cis*–1,4 macromolecules are present in the fraction isolated by them.

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ISOTACTICITY AND CRYSTALLINITY OF VINYL POLYMERS

by G. NATTA and D. SIANESI

(11 Apr. 1959)

[*Rend. Accad. Naz. Lincei* (8) **26,** 418 (1959)]

ABSTRACT

Many stereo-ordered polymers have been recently prepared by employing stereospecific polymerization processes; among these, isotactic polymers of α-olefins and of several vinyl monomers have been widely described.[1] Owing to their exceptionally regular structure, these polymers generally show, in a high degree, the ability to crystallize. In the case of some other similar monomers, however, by employing the same stereospecific catalysts, amorphous polymers have always been obtained. Thus, in the series of α-olefins, when the normal alkyl chain, bound to the vinyl group, exceeded three carbon atoms, the polymers thereof, e.g. poly-hexene, appeared amorphous, even after they had been subjected to various heating treatments to induce crystallinity.

Vinyl ethers[2] and acrylic or methacrylic esters,[3] too, by stereospecific polymerization, produced polymers which were either crystallizable or not, depending on the nature of the alkoxy groups. In a recent paper,[4] for instance, crystallizable polyacrylates were described as being the only ones having a branching at the α-carbon atom. We encountered a great number of similar results in the field of vinylaromatic monomers;[5] an extensive examination revealed, in fact, that a variety of differently substituted styrenes underwent stereospecific polymerization, giving rise to products which were either crystallizable or not, depending on the kind of substitution in the styrene nucleus. Thus, as

a general rule, crystallizable polymers were obtained from ortho-substituted and from di-methylsubstituted styrenes, while, on the contrary, all para-substituted styrenes (with the exception of *p*-fluoro-styrene), produced under the same reaction conditions, amorphous polymers. Non-crystallizable polymers were also obtained from meta-halogen substituted styrenes, while the obtained poly(meta methyl-styrene) was easily crystallizable. Furthermore, whereas α-vinyl naphthalene produced a crystalline polymer, its β-isomer gave always amorphous products.

All these summarized results point to clear evidence that the monomer structure is a critical factor in determining whether the polymer is crystallizable or not.

The general question then arises as to which effect may be responsible for the lack of crystallinity shown by several polymers, though prepared by stereospecific processes. This behaviour could be ascribed either to a failure of stereospecificity in the polymerization mechanism or to the occurrence, in the solid polymer, of steric phenomena, preventing the stereo-ordered macromolecules from crystallizing. For the first case, one should admit that the presence of a certain kind of substitution in the monomers would oppose the regular growth of the macromolecules, leading possibly, to the formation of disordered polymers, unable to crystallize. Evidence has been accumulated, however, that the crystallizability of the polymers does not depend on the chemical nature of the substituents present, but, on the contrary, is strictly related to the steric requirements of the branching groups. This statement, as well as other results and observations on the formation mechanism and on the properties of the non crystallizable polymers, led us[6] to the more plausible explanation that the physical process of crystallization of these polymers is prevented. In fact, steric hindrance can arise from a bulky side group, operating either against the spiralization of a single macromolecule, or against the packing of several already spiralized macromolecules in a crystal lattice thus hindering the isotactic polymer in crystallizing.

We have now been able to obtain clear experimental evidence that vinylaromatic polymers, prepared by stereospecific processes, even if amorphous are actually constituted of stereo-ordered, isotactic macromolecules. This result has been reached by converting amorphous polymers into crystallizable ones, through chemical modifications of the side groups of the preformed polymeric chain.

In practice, amorphous poly(para-chlorostyrene), poly (para-

bromostyrene), poly(meta-chlorostyrene), and poly(meta-fluorostyrene) prepared by employing catalysts from Ti-halides and Al-alkyls, have been submitted to hydrogenation of the benzene nuclei, together with halogen removal. The hydrogenated polymers obtained were very easily crystallizable; they showed the same X-ray diffraction diagrams and the same crystal melting temperature (about 370°C) as a crystalline polymer obtained from pure vinyl-cyclohexane with the aforesaid stereospecific catalysts. The same crystalline polymer was also obtained by hydrogenating a sample of isotactic polystyrene. Infrared absorption spectra of all these polymers practically coincided. A preliminary examination of the structure of the crystalline poly(vinyl-cyclohexane), demonstrated that this polymer is formed by isotactic macromolecules. The identity period (6·5 Å), along the helix axis, comprises four monomeric units.

A further convincing result was obtained by hydrogenation of a sample of amorphous poly(para-methylstyrene), prepared by stereospecific polymerization. The hydrogenated product, probably poly(4-methyl-vinylcyclohexane), appeared to be an easily crystallizable isotactic polymer, having a melting temperature above 360°C.

Thus, polymers which were amorphous, have been converted into other polymers which, because of the different kind of side substitution, were found to be crystallizable, and showing moreover an isotactic structure. Since the existing polymeric backbone and the steric arrangement of the tertiary carbon atoms along the chain, could not be subjected to modifications during the above chemical treatment (which had they occurred, would have led to an increase in the steric disorder), this result has enabled us to state with certainty that in the unmodified amorphous polymers the isotactic structure was already present.

The stereospecific polymerizations were carried out, as detailed in preceding papers[7], in benzene solution, with catalysts obtained by reacting Al (i. $C_4H_9)_3$ and $TiCl_4$in a molar ratio 3:1.

Hydrogenations have been carried out, in cyclohexane medium, with Raney-Ni at 190–200°C and 150–180 atm hydrogen pressure. The hydrogenated products were separated in good yields and purified by repeatedly dissolving them in cyclohexane followed by precipitation in methanol. Intrinsic-viscosity measurements have shown that during the hydrogenation a noticeable degradation of the polymers took place, e. g., poly-para-chloro-styrene, $[\eta]$ in tetralin at 100°C = 2·1;

obtained poly-vinylcyclohexane, $[\eta]$ in toluene at 30°C = 0·55.

Vinylcyclohexane (b.p. 127°C) was obtained by the pyrolysis[8] at 450°C of 2-cyclohexyl-ethylacetate.

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STEREOSPECIFIC POLYMERIZATION OF VINYLAROMATIC MONOMERS. NOTE II: HALOGEN-SUBSTITUTED STYRENES

by D. SIANESI, R. SERRA and F. DANUSSO

(17 Apr. 1959)

[*Chimica e Industria* **41**, 515 (1959)]

ABSTRACT

The polymerization of several nuclear halogen-substituted styrenes, carried out by co-ordinated anionic processes, gives polymers having ordered structure.

Isotactic polymers have been prepared from *o*- and *p*-fluorostyrene and from a mixture of these monomers. These polymers possess high or medium degree of crystallinity, high rate of crystallization and a high melting point. Polymers from 2-methyl-4-fluorostyrene are also easily crystallizable.

Polymers of *m*- or *p*-substituted chloro- and bromo-styrenes do not crystallize in an evident way.

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A NEW ITALIAN ACHIEVEMENT IN THE TEXTILE FIELD: POLYPROPYLENE FIBRES

by G. NATTA

(17 Apr. 1959)

[*Chimica e Industria* **41**, 647 (1959)]

One often wonders whether the discovery of a new synthetic fibre creates anything but a series of complications in a field already invaded by a number of synthetic fibres belonging to several chemically different compounds.

The consumer can easily get confused by the numerous, approximately 150, commercial names of synthetic fibres produced in Europe, United States, and Japan, ending mostly with *on, il, en, in.*

It is already difficult to predict the practical interest and future prospects of principal fibres; the solution of practical problems connected with their use, whether alone or mixed with other fibres, with their dyeing, etc., is equally difficult, yet other textiles, some of which are completely different from others, are constantly appearing on the market.

First of all I should clarify a very important aspect of the problem. What is needed today, is not a new synthetic fibre of the type and cost of those already known, but one which is essentially different from the previous ones with good properties, and of a lower cost than that of the most valuable fibres known.

As we shall see, polypropylene is indeed different from other polymeric materials used for the production of synthetic fibres, and in addition, when produced on a large scale, it costs less than other ones.

In fact it is produced by the polymerization of a very simple monomer, whose cost is very low, namely: propylene. Polypropylene fibres are obtained by melt spinning followed by subsequent stretching. They show excellent mechanical properties and they are the lightest of all the fibres known, even though they are highly crystalline, and this in spite of the fact that, for most solids, the crystalline state is the most dense.

It is also of interest to clarify the meaning of crystallinity as applied to textile fibres.

All organic fibres, both natural and synthetic, consist of macromolecules having a length of the order of thousands of Å, hundreds or thousands of times greater than their average diameter. This property determines their tendency to become parallel by the effect of a longitudinal stretching, or to be associated in parallel bundles; however, only those polymers which are formed by chemically and sterically equal groups, repeat regularly and can crystallize. Linearity and flexibility of the single macromolecules, as well as the regularity of their structure, leading to the crystallinity of their aggregates, are factors which determine a number of very important mechanical properties, independently of the type of fibre (either artificial or synthetic).

Crystallinity in textile fibres has, however, a different meaning from the one known before the discovery of X-rays. It is not due to the presence of crystals visible to the naked eye or with the microscope. Crystals in textile fibres correspond to a regular arrangement within the substance, which can be compared to the condition found in metals, with the difference that it is limited to submicroscopic regions. The usual optical microscopes do not allow, in the case of linear polymers, to see single crystals, but only their aggregates.

While, in crystals of low-molecular-weight substances, each crystal contains a very great number of complete molecules, crystals of linear macromolecules generally contain only portions of molecules and each single macromolecule can be a part of various crystals. This property eliminates intercrystalline ruptures and contributes to the high mechanical resistance of oriented fibres.

In spite of the extremely small dimensions of crystals, which can be determined by X-ray diffraction, their presence exerts a decisive influence on the properties of textile fibres.

For instance, nylon and certain polyester fibres consist of highly crystalline substances and contain a high number of chains per section

and, therefore, they exhibit a high tensile strength. Cotton has a very high crystallinity; artificial cellulose fibres have a low crystallinity; wool has an even lower crystallinity. On the contrary, polyacrylonitrile and polyvinylic fibres are almost amorphous.

A comparison is made in Table 1 among the chain sections, crystallinity and tenacity of organic fibres. The high melting crystalline

TABLE 1. CRYSTALLINITY AND TENACITY OF FIBRES

	Crystallinity	*Section of the chain of crystals* Å²	*Tenacity g/denier*
Synthetic Fibres			
Isotactic polypropylene	70–85% [a]	33	6 –8 [a]
Technical-isotactic polypropylene	55–75% [a]	33	4·5–8 [a]
Nylon	55–70% [b]	17·6	4·5–8 [c]
Linear Polyethylene (low pressure)	65–85% [a]	18·2	2 –6 [a]
Polyethylene (high pressure)	40–60% [a]	18·2	1 –2·5 [c]
Polyvinylchloride	< 10% [a]	28·6	2·5–3·5 [a]
Cellulose Fibres			
Ramie	69–71% [b]	32·8	5 [c]
Cotton	69–70% [b]	32·8	2 –6 [c]
Rayon Viscose	37–40% [b]	32·8	1·8–4·5 [c]

[a] Our measurements.
[b] Stuart, *Der Physik der Hochpolymeren*, Vol. III, Springer-Verlag, Berlin (1955), p. 272.
[c] E.R. Koswell, *Textile Fibers*, Reinhold, New York (1953), p. 8.

fibres generally show a high resistance to viscous flow, whereas the non-crystalline fibres are already deformed irreversibly at temperatures near the glass transition temperature and below it the material becomes somehow fragile. This is why most non-crystalline synthetic fibres (e.g. the vinylic ones) do not withstand high temperatures.

The man-made fibres obtained from wood cellulose, cannot show a high crystallinity since the crystallinity of the starting cellulose itself is rather low; moreover, since this is an infusible material, it must undergo, in order to be spun, chemical transformation to make it soluble, but at the same time this reduces the ability of the material to crystallize.

On the other hand, before the discovery of the stereospecific anionic coordinated polymerizations, the possibility of obtaining macromolecules, with a highly regular structure (a prerequisite for crystallinity) and suitable to yield fibres, was limited to the use of a rather low number of raw materials or of intermediate low-molecular-weight products (monomers).

In order to obtain crystalline products, the previously known polymerization processes required highly symmetric monomers. The polycondensation processes required the use of unbranched monomers with terminal reactive groups.

As a result of this, a number of single raw materials, and in particular the most available monomers, could not be used for the synthetic production of textile fibres. The synthesis of diacids, diamines, lactams, glycols used for polyamidic and polyester fibres requires a series of complex chemical reactions and it runs into a high cost. In contrast with previous man-made crystalline synthetic fibres the natural textile fibres consist of asymmetric elements, which cannot be obtained by direct synthesis unless mixed with enantiomorphous forms.

Whereas in natural fibres the monomeric substances are optically active, those synthetic monomers obtained by man are usually optically inactive mixtures. Nature has disposed very regularly the asymmetric elements both in the synthesis of cellulose and in the synthesis of fibroin in such a way as to build linear crystallizable molecules.

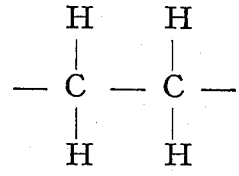
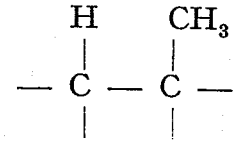
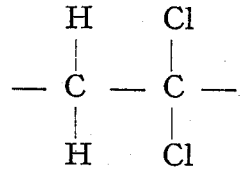
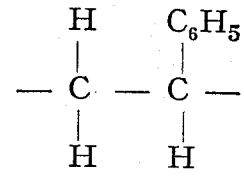
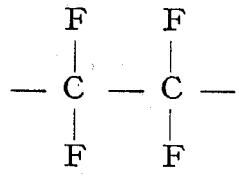
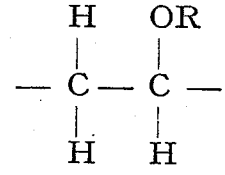
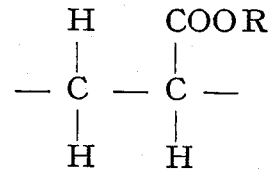
The discovery of stereospecific polymerization processes at the Polytechnic Institute of Milan, about five years ago, has permitted us to obtain linear macromolecules with an exceptional regularity of structure, using as monomers very simple raw materials.

Among these monomers there are some mono-olefinic hydrocarbons (such as propylene) which can be obtained from crude oil at a very low cost.[1]

These alpha-olefins generate asymmetric monomeric units and therefore they could not yield, before the discovery of the stereospecific polymerization processes, linear polymers having a high regularity of structure, and therefore crystallizable.

These new processes afford the polymerization of asymmetric monomers and allow the obtainment, with the aid of non stereospecific catalysts, of linear macromolecules with a disordered steric structure (elastic rubbers) or, with the aid of stereospecific catalysts, of linear macromolecules with a regular structure, able to crystallize to yield plastics and textiles with superior mechanical properties.

TABLE 2. OLEFINIC MONOMERS

Monomers (*)	*Symmetric monomeric units*	*Monomers (**)*	*Asymmetric monomeric units*
Ethylene		Propylene	
Vinylidenechloride		Styrene	
Perfluoroethylene		Vinylethers	
		Acrylates	

(*) Yield crystalline or crystallizable linear polymers by the usual polymerization processes.

(**) Yield crystalline polymers obtained only by stereospecific polymerization processes.

I had named "isotactic structure" the type of regular structure consisting of chain portions having monomeric units, with the same relative steric configuration. Fig. 19 of paper 24 shows polypropylene chains with ordered (isotactic) and disordered (atactic) structures.

Some non-stereospecific catalysts, used in anionic polymerizations, permit the formation of linear molecules also from ethylene. The great flexibility of the polyethylene chain explains its poor hardness and its low melting temperature (120–137°C), which certainly limits its use in textile fibres.

Higher olefins yield isotactic polymers only when stereospecific polymerization processes are used.

The chains in the crystalline, isotactic polymers assume a helix conformation. Such helices may exist in the dextro or levo form, and

their side groups can be directed either up or down. Chains of four types can co-exist in the crystals. The stereospecific polymerization processes, which represent an Italian discovery, afford the formation of essentially isotactic polymers from propylene. These polymers are already produced commercially and they are used as thermoplastic materials due to their easy processability, high hardness, high melting temperature, high mechanical and chemical resistance and lightness (Moplen).

TABLE 3.

Polymer	*Cost of the monomer in U.S.A., cents/lb (*)*	*Melting point of the polymer °C*
(Linear) polyethylene	5- 6	125-137
Isotactic polypropylene	3- 5	170-176
Isotactic polybutene	4- 5	130-140
Isotactic poly-4-methylpentene-1 ...	(**)	240-250
Isotactic polystyrene	13-14	230-240

(*) Cost forecast for large scale output.
(**) No reliable data are available on the production cost of the monomer on a commercial scale.

In Table 3 are given the prices of propylene and of other vinyl hydrocarbons in the United States.

In Europe the cost of monomers produced purposely from crude oil, is a little higher than that indicated above.

The application of isotactic polypropylene to the field of textiles has been the fruit of my own intuition during the discovery of this highly crystalline polymer. A few weeks after its discovery, at the Polytechnic Institute of Milan, the polymer with a molecular weight of some hundreds of thousands was produced in the form of monofilaments, oriented by stretching following extrusion.

Since then resistances of 70 kg/mm^2 have been obtained. Oriented filaments with a weight of 1/8 that of iron possessed the same resistance as steel.

It took about five years work, chiefly done at the Montecatini Laboratories at Terni, to set up a pilot plant production and to

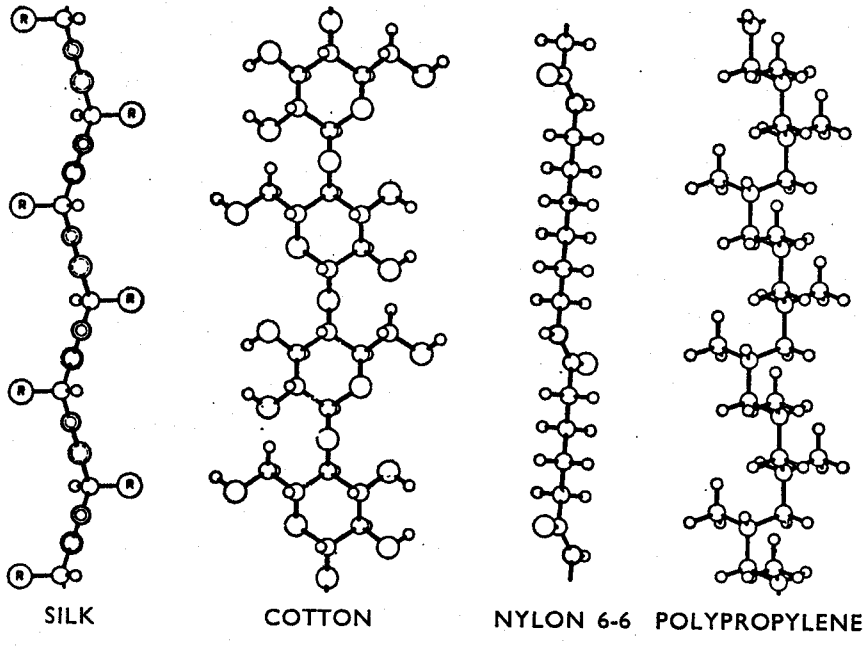


FIG. 1. Comparison among the chains of some natural and synthetic fibres.

achieve those processes which are now being applied on a large industrial scale.

Many chemists, physicists and engineers have contributed to these research problems, which over all have cost several billions of lire.

The time necessary to solve this problem (which, incidentally is much less than the time required by the Du Pont Co. for setting up the industrial production of nylon) was not too long, considering the difficulties met with due to the peculiar structure of the new polymers.

In the case of nylon, the choice of a given pure linear diacid with a given pure linear diamine, can produce only one type of macromolecular structure whose differences can be due to discrepancies in the average value and in the distribution of molecular weights.

In the case of alpha-olefins, using anionic co-ordinated catalysts which yield exclusively linear head-to-tail molecules, it is also possible to obtain products showing different properties depending on steric factors present in the structure. In the case of macromolecules with isotactic structure, the properties vary very markedly depending on whether the whole molecule possesses an isotactic regular chain or whether its structure is conditioned by chain segments of different lengths, which are the only ones able to crystallize.

It is of interest to point out that polymers obtained from the same

monomer can assume different properties depending on their steric structure. This finding allows one to produce, from the same raw material, products whose mechanical properties can vary at will, reaching or even surpassing in some cases the high tensile strength of nylon. It is also possible to obtain desirable elastic elongations, which can vary at will within broad limits, from a minimum value that can be compared to that of a cellulose fibre, to a maximum which is higher than that of wool. Furthermore, in some cases it is possible to produce polymers having properties that can be compared to those of a high-tenacity elastic rubber thread. It may seem difficult to produce a polymeric material having constant and perfectly reproducible properties among the many varieties of possible products; however, the problem has been brought under control.

TABLE 4.

Type of polypropylene	*Tensile strength g/d*	*Elastic elongation*	*Melting temperature °C*
Pure isotactic	5-8*	10- 20%	175-176
Technical isotactic	5-8*	15- 30%	170-175
Stereoblock	3-6	30- 50%	160-165
Stereoblock	2-4	50-100%	150-160

(*) Usual values of technical production, which can be increased to 10 g/d in special cases.

Whereas the various obtainable products were studied in the laboratory, the production in the pilot plants was directed first of all toward a type of polymer with constant properties, high crystallinity, high melting temperature, and easy to spin at high rates. This type of polymer shows the greatest practical importance, both for its production in the cotton and wool industries, and also for the making of continuous mono- and multifilaments, either smooth or curled.

One of the most important properties of crystalline polypropylene in its textile applications, is its low relative density, $\varrho = 0{\cdot}90$–$0{\cdot}91$, which is lower than that of water, and the lowest yet observed in the textile fibres known up to now.

Such a low density of the polymer influences the density of fibres and the apparent weight of fabrics. Since fabrics are generally sold in yards and not in pounds, this represents a factor of great practical importance.

Polypropylene fibres do not swell in the presence of water; therefore, their resistance is the same in dry or wet conditions.

The paraffinic nature of polypropylene determines its poor tendency to be dyed with colouring substances in aqueous solutions. The brilliant colour obtained by dyeing it in pulp is due to its own transparency.

This problem of dyeing fibres and fabrics was solved by means of chemical modifications of the polymeric chains so as to render them color-philic, or by grafting groups that can be dyed, or else by adding to polypropylene in the molten state, before its spinning, small amounts of other substances, soluble in it, which show affinities for colours. This last method appears particularly effective for polypropylene fibres owing to their high mechanical resistance. In fact, even in the most unfavourable hypothesis that such additions should not improve the mechanical resistance of the filament, but on the contrary diminish it proportionally to their weight percentage contained in the fibre, one finds that the addition of 10 or even of 20 per cent of such substances lowers the tensile strength of a fibre, which in their absence is, for instance, from 6 g/denier to values of 5·4 or of 4·8 g/denier, respectively. These values are, however, more than sufficient for practical application.

These systems have allowed us to obtain fibres or fabrics of polypropylene that can be dyed using the usual dyeing procedures. The dyeing in pulp is even cheaper, and it allows us to obtain quite easily a very wide range of stable brilliant hues.

The possibility of modifying at will the molecular weight and the steric composition, and therefore the crystallinity of the polymer, as mentioned above, permits one to obtain a variety of products with mechanical and elastic properties varying within wide limits.

The thermal treatments can markedly influence the properties of these polymers. Besides the highly crystalline polymer having a density of about 0·92 which provides fusible fibres at 170–175°C, which can thus be ironed in a similar way to most synthetic fibres, it is also possible from the same polymers to obtain, under certain conditions, products with a crystallinity of a different type with respect to the relative arrangement of the chains having a different direction of spiralization.

Whereas annealed crystalline polypropylene contains right- and left-handed helix chains regularly arranged, a different smectic crystalline modification, corresponding to a statistical disposition of the dextro and levo chains exists in quenched polypropylene (2). Its relative density is lower (0·86–0·88) and only a little higher than that of

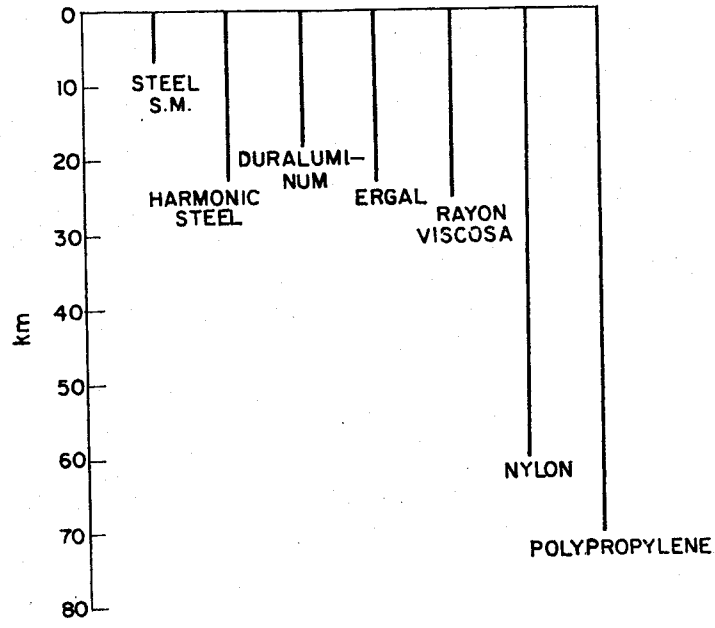


FIG. 2. Comparison between the maximum lengths capable of bearing the weight of threads of different materials.

amorphous polypropylene (0·85). Its refractive index is the same as that of amorphous polypropylene.

The products obtained from this smectic form are transparent even though crystalline. Usually, the crystalline polymers (e.g. low-pressure polyethylene) are opaque or translucent, because they contain crystalline and amorphous regions of different optical density. Such a property is very important and allows the production of polypropylene films with high mechanical properties and a high transparency due to a planar orientation of the crystals. In addition these films show a high flexibility or softness, contrary to the films obtained from other crystalline polymers (cellophane) or from non-crystalline and non-plasticized polymers (polyvinylchloride, polystyrene, etc.), which being used below their glass transition temperature, are either more rigid or more brittle.

With regard to polypropylene, contradictory opinions have been heard on the influence exerted by the presence of a glass transition on its properties at temperatures of about 0°C.

Such a transition is markedly observed only in amorphous products and at temperatures depending on the method used for the determination: −13°C (dilatometric method), +0 —15°C (certain dynamic methods). This transition, which increases the brittleness of the

TABLE 5.

Fibre	*Density g/cm³*
Saran (polyvinylidenechloride)	1·72
Cotton	1·50–1·55
Hemp, jute, flax	1·48–1·50
Raw silk	1·33–1·34
Wool	1·30–1·32
Terylene, Terital, Dacron	1·38–1·39
Movil (polyvinylchloride)	1·35–1·38
Nylon	1.14
Polypropylene (stable modification)	0·90–0·92
Polypropylene (smectic modification)	0·85–0·88

amorphous products, is, however, less marked in the highly crystalline and oriented products, even though it can be observed for the remarkable increase of the elastic modulus and of the tenacity of the fibre by cooling below 0°C.

The low costs of the propylene monomer and of its polymerization process, the ease of spinning and film-making from the melt, are some of the favourable factors which determine wide possibilities of application for the new products.

It is always risky to look into the future; however, I think I can state, without too much fear, that a cheaper organic fibre than polypropylene will hardly ever be synthesized.

It is possible to foresee, on the basis of the cost of the raw material and of the simplicity of the polymerization and spinning processes, that within a few years, when the production of polypropylene fibres will surpass the tens of thousand tons scale output per year, its cost will be markedly reduced and will become not only lower than that of any other synthetic fibre, but probably lower than the present cost of cotton. This will represent a significant contribution to the further development of the organic chemical industry, which will in turn exert considerable influence in the economic, social and even political fields. In fact it is possible to foresee that, by the end of this century, the world population will exceed 5–6 billions. Moreover, admitting that the standard of living will improve markedly, even for the poorest people, the agricultural areas to be employed for food production must necessarily increase considerably.

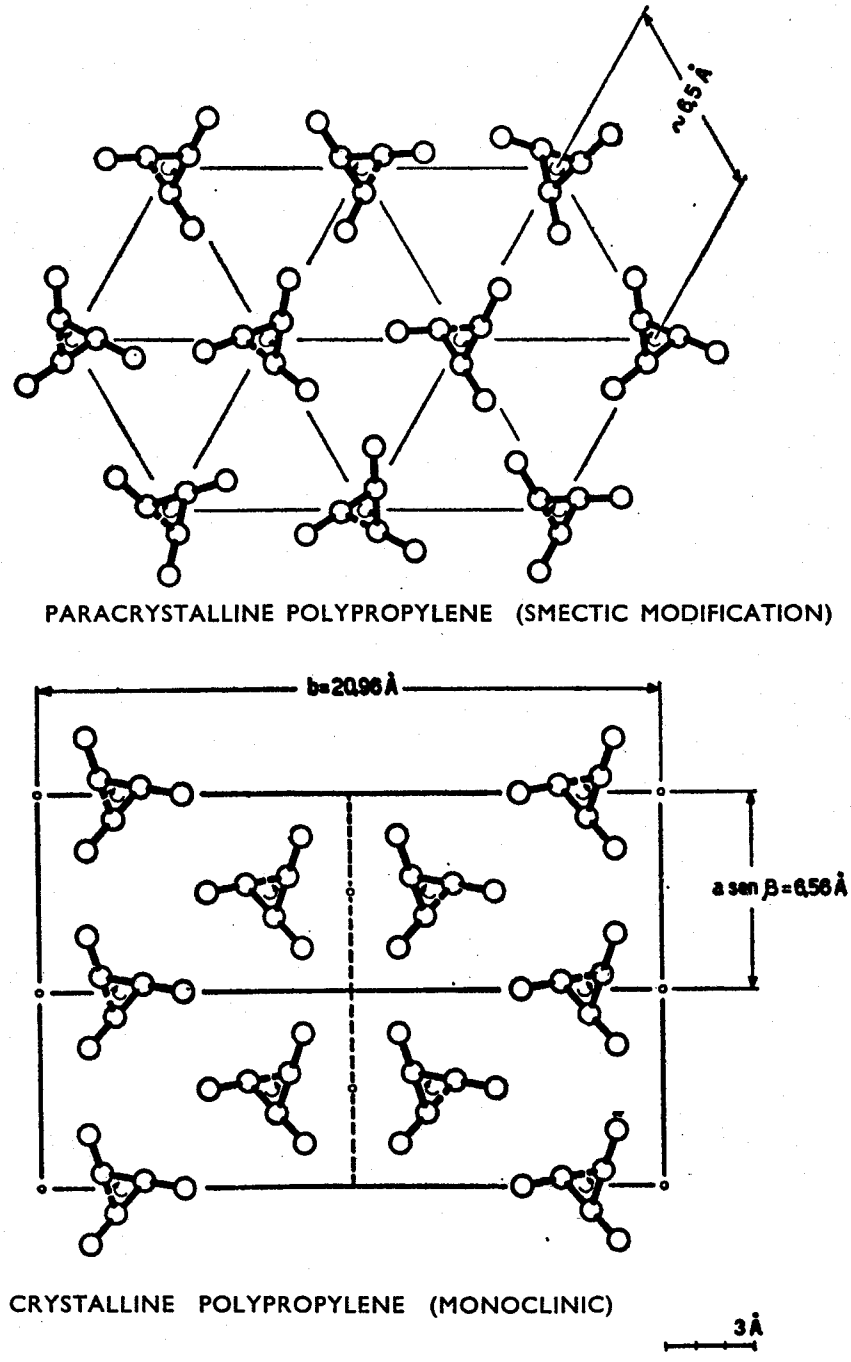


FIG. 3. Comparison between the end views of crystals of the stable modification of crystalline polypropylene and of its smectic modification.

This will be feasible only if a large–scale industrial production and a low cost of synthetic products will advantageously substitute some basic products (such as textiles, natural rubber, cellulose, wood, paper, etc.) which at present are derived from agricultural sources. The chemists' work could contribute, therefore, to the achievement of a higher standard of living and to a greater welfare which we wish for all the people in the world.

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THE INFLUENCE OF HYDROGEN ON COORDINATED ANIONIC POLYMERIZATION OF PROPYLENE AND ETHYLENE

by G. NATTA, G. MAZZANTI, P. LONGI and F. BERNARDINI

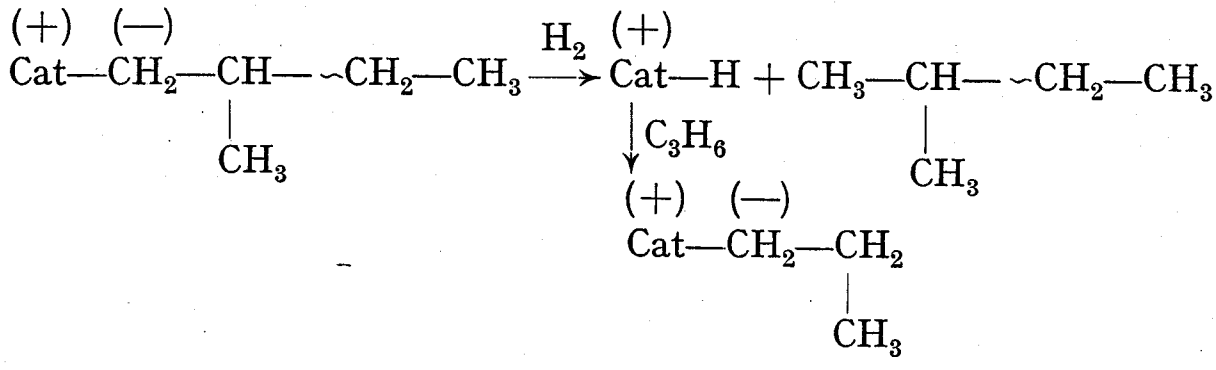
(22 Apr. 1959)
[*Chimica e Industria* **41**, 519 (1959)]

ABSTRACT

It has been observed that the presence of hydrogen during the polymerization of propylene, carried out with catalysts consisting of aluminum alkyls and titanium trichloride, exerts a considerable influence on both the rate of polymerization and the molecular weight of the polymer. On the other hand, by operating under suitable experimental conditions, the presence of hydrogen does not decrease the percentage of the isotactic polymer. It is also possible to minimize the hydrogenation reaction of propylene.

The decrease of the molecular weight, when operating at low pressures of monomer and hydrogen, depends only on the square root of the partial pressure of hydrogen.

The nature of the end groups and the overall polymerization rate concur with a kinetic interpretation, by which hydrogen does not chemically modify the catalytic system, but causes a hydrogenation of the bonds existing between catalyst and growing chains, according to the scheme:



The metal–hydride bonds formed on the catalyst, after its reaction with other monomer molecules, can regenerate the metal–carbon bonds, thus are promoted new polymeric chains.

On the basis of this hypothesis, the molecular weight of polypropylene obtained should depend on the partial pressure of hydrogen, related to the ratio:

$$\overline{PM} = \frac{1}{K_1 + K_2 \sqrt{P_{H_2}}}$$

where K_1 and K_2 are two constant values and P_{H_2} is the partial pressure of hydrogen used. In fact, the above ratio has been experimentally confirmed, thus proving the reliability of our hypothesis.

Even the I.R. study on the nature of the end groups of propylene macromolecules obtained in the presence of hydrogen has proved the hydrogenation hypothesis described above. In fact, isopropyl groups $-CH(CH_3)_2$, were found in samples of polypropylenes prepared in the absence of hydrogen.

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STEREOSPECIFIC POLYMERIZATION OF CONJUGATED DIOLEFINS. NOTE IV: PREPARATION OF SYNDIOTACTIC 1,2-POLYBUTADIENE

by G. NATTA, L. PORRI, G. ZANINI and L. FIORE

(29 Apr. 1959)

[*Chimica e Industria* **41**, 526 (1959)]

ABSTRACT

Some catalytic systems obtained by treating aluminum trialkyls with various transition metal compounds, such as alcoholates, acetylacetonates, carbonyl compounds, complexes with isonitriles or pyridine, permit the production of crystalline polybutadienes with 1,2-structure.

Two different crystalline polybutadienes with 1,2-structure were obtained and characterized, namely isotactic-1,2 and syndiotactic-1,2-polybutadiene.

This note describes the preparation of 1,2-syndiotactic polybutadiene with the aid of the catalytic system $Al(C_2H_5)_3$–Vanadium triacetylacetonate (VAc_3). This system, which is seemingly homogeneous, yields raw polymerization products, which consist of macromolecule mixture of different stereoisomeric composition. The raw products were fractionated by successive extractions with acetone (which dissolves the low molecular weight oily polymers) and with ether (which dissolves the amorphous or low-crystallinity polymers). The residue after the ether extraction (partially soluble in boiling benzene) consists of crystalline syndiotactic 1,2 polymers.

The $Al(C_2H_5)_3$–VAc_3 system is active at Al/V molar ratios higher than about 3; the highest activity (measured as amount of polymer

TABLE 1. POLYMERIZATION OF BUTADIENE WITH THE AID OF $Al(C_2H_5)_3 \cdot VAc_3$ AS CATALYST AT VARIOUS Al/V RATIOS. (VAc_3 0.5 g; BENZENE 80 cm^3; POLYMERIZATION TEMPERATURE 15°C; POLYMERIZATION TIME 16 hr)

No.	*Al/V*	*Butadiene g*[a]	*Polymer g*	*I. R. analysis*			*Fractionation*			
				trans-*1,4* %	cis-*1,4* %	*1,2* %	*Acetone extract* %[b]	*Ether extract* %[c]	*Benzene extract* %[d]	*Residue* %
1	3	30	2·6	12	9	78	—	99	1	—
2	3	30	0·5	10	11	79	—	99	1	—
3	3·5	30	3·2	8	12	80	—	94	6	—
4	3·5	30	4·1	3·5	10·5	81	—	96	4	—
5	4	30	12·8	6	16	78	22	71	7	—
6	4	30	13·2	5	14	81	21·5	67·5	9	2
7	5	30	12	4·5	13·5	81	23	62	12	3
8	6	30	10·2	4	16	80	24	51	20	5
9	8	30	9·3	5	10	85	20	44	33	3
10	10	30	9·3	4·5	7·5	87	23	37	34	6
11	10	50	12·1	4	12	84	21	39·5	21·5	18
12	10	50	11·6	3·5	11·5	85	21·5	37·5	13	28
13	15	30	8·6	4·5	12·5	83	23	36	38	3
14	20	30	8·5	3	13	84	20	41	16	23
15	30	30	8·7	3	11	86	22	37	32	9

a) From sulphone decomposition

b) I.R. analysis: *trans*-1,4 15–22 per cent; *cis*-1,4 10–13 per cent; 1,2 68–72 per cent. In runs 1–4 the product was extracted with ether at once, omitting the acetone extraction.

c) I.R. analysis: *trans*-1,4 3–7 per cent; *cis*-1,4 16–22 per cent; 1,2 75–80 per cent.
X-ray analysis: traces of crystallinity in the products obtained at Al/V ratios of about 3–5. Crystallinity (10–15 per cent) in the products obtained at higher ratios. Melting temperature $\sim$ 90°C. $[\eta]$ in toluene at 30°C, 0·8–1·2, 100 cm^3/g.

d) I.R. analysis: *trans*-1,4 2–4 per cent; *cis*-1,4 3–6; per cent; 1,2 90–95 per cent.
Crystallinity by X-rays (30–35 per cent). Melting temperature $\sim$ 156°C. $[\eta]$ in toluene at 30°C, 1·8–2, 100 cm^3/g (determined on the soluble part at 30°C).

obtained in a given length of time) occurs at an Al/V ratio of about 5. The percentage of ether non-extractable polymers increases with the Al/V ratio and reaches a maximum at ratios Al/V of about 10 (Table 1).

The catalyst aging leads to an increase of the highly crystalline fraction; at Al/V ratios of 10, with catalysts aged for 3 hr at room temperature, products containing about 60 per cent of ether non-extractable fraction are obtained. Aging, however, simultaneously causes a decrease of the amount of polymer obtained.

The purity of both the monomer and of $Al(C_2H_5)_3$ influences stereospecificity. The best results were obtained by using pure butadiene obtained by decomposition of sulphone, and $Al(C_2H_5)_3$ as much as possible free from $Al(C_2H_5)_2H$ and $Al(C_2H_5)_2(OC_2H_5)$.

When using catalysts prepared from $Al(C_2H_5)_3$ containing ^{14}C, ^{14}C was found in the polymer; it was also observed that the presence of ^{14}C does not depend, if not within narrow limits, on the transfer between $Al(C_2H_5)_3$ and the growing polymeric chain. The hypothesis is put forward that the catalytic complex obtained from $Al(C_2H_5)_3$ and VAc_3 contains a $V–C_2H_5$ bond or else a $–C_2H_5$ group bridge-bonded

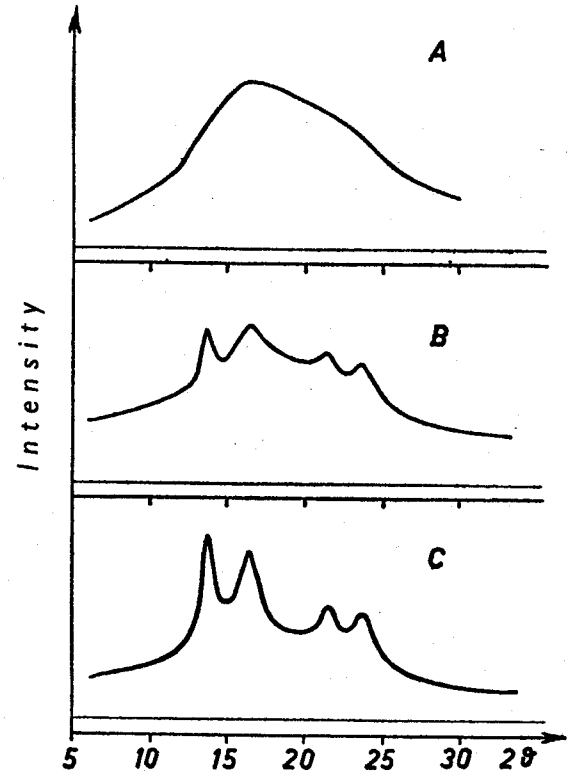


FIG. 1. X-ray spectra (Cu$K\alpha$), registered by Geiger counter, of 1,2-polybutadienes obtained with the catalyst system $Al(C_2H_5)_3$–VAc_3; (A) amorphous ether extract; (B) slightly crystalline ether extract; (C) benzene extract.

between an Al and a V atom. The 1,2 structure of the monomeric units should depend on how butadiene is co-ordinated to the transition metal, before inserting itself in the growing polymeric chain.

X-ray powder spectra of 1,2-polybutadienes obtained with the $AlEt_3$–VAc_3 catalyst system are reported in Fig. 1.

The crystallinity of syndiotactic-1,2 polybutadiene obtained with the aid of the $Al(C_2H_5)_3$–VAc_3 system is of about 10–15 per cent in the ether soluble fraction, of about 35 per cent in the boiling benzene soluble fraction, of 35–40 per cent in the residue after the benzene extraction.

It is possible to obtain a syndiotactic-1,2-polybutadiene having a higher degree of crystallinity with the aid of other catalytic systems, as will be described in other papers.

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VOLUMETRIC AND DILATOMETRIC PROPERTIES OF SOME OLEFIN POLYMERS

by F. DANUSSO, G. MORAGLIO, W. GHIGLIA, L. MOTTA and G. TALAMINI

(4 May 1959)

[*Chimica e Industria* **41**, 748 (1959)]

ABSTRACT

Specific volumes of samples of polyethylene possessing a high degree of linearity, and of samples of polypropylene, polybutene, and polystyrene with atactic, isotactic and isotactic stereoblock structures were determined over wide temperature ranges.

Experimental data show typical influences of the macromolecular structure on the volumetric and dilatometric properties and on the behaviour of the examined polymers, when they undergo phase and isophase transitions.

The dilatometric straight lines, which can be ascribed to the pure crystalline phase for each polymeric system, were calculated. This was done by extrapolating dilatometric curves of atactic and semicrystalline polymers towards low temperatures and then applying Kauzmann's postulate of the equality of the expansion coefficients of glass and pure crystalline phases.

Thus, besides experimental data, which can be directly obtained, other values of thermodynamic interest, which are also useful for technical calculations, have also been obtained. Table 1 reports the most salient data.

A method is also given, which provides the degree of crystallinity of the polymer samples studied by a measure of the specific volume. These determinations can be also obtained geometrically by the linear resolution of the nomographs of Fig . 1.

TABLE 1. VOLUMETRIC AND THERMODYNAMIC DATA OF THE EXAMINED POLYOLEFINS

	Polyethylene	*Polypropylene*	*Polybutene*	*Polystyrene*
T_m (the highest observed, in °C)	138	176	136	240
v at 30°C, amorphous	(1·17)	1·173	1·157	(0·93) [b]
v at 30°C, crystalline [a]	1·009	1·072	1·058	0·950 (glass) 0·898
$\left(\frac{\delta v}{\delta t}\right)_p \times 10^4$, amorphous	8·9	9·0	8·8	5·6) [b]
$\left(\frac{\delta v}{\delta t}\right)_p \times 10^4$, crystalline [a]	3·1	4·2	3·8	2·5 (glass) 2·5
$\frac{v_{am}-v_{cr}}{v_{cr}}$ at T_m	0·215	0·150	0·138	0·115 [c]
v at T_m, amorphous	1·270	1·305	1·250	1·060
v at T_m, crystalline [a]	1·045	1·135	1·100	0·950 [c]
T_{tr} (isophasic dilatometric) °C	—21 (—100 ÷ —130) [d]	—35	—45	160 [e] 80 ÷ 100
v_{am} at T_{tr}	(1·130) (1·05)	1·115	1·090	1·005 0·965

[a] Calculated values
[b] Values for the amorphous, non glassy state, obtained by extrapolation below the isophase transition.
[c] Values calculated by the hypothesis that the crystalline phase does not have a transition at 160°C (this fact has not been proved).
[d] Little marked transition by dilatometry; more marked by mechanical-dynamic methods.
[e] Less marked transition than that at lower temperatures.

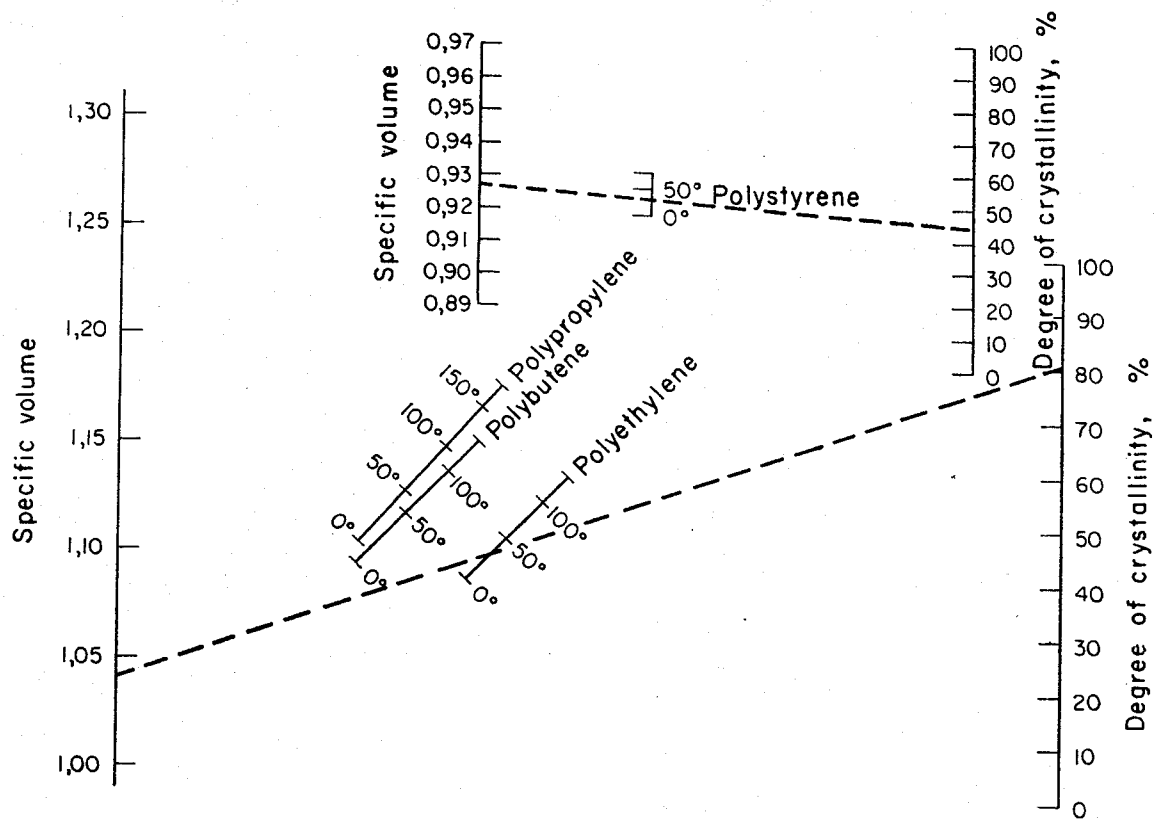


FIG. 1. Nomographs for the determination of the degree of crystallinity of polyethylenes, and isotactic polypropylenes, polybutenes and polystyrenes from specific volume and temperature in °C.

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THE COORDINATED ANIONIC POLYMERIZATION OF PROPYLENE TO ATACTIC AND STEREOBLOCK HIGH MOLECULAR WEIGHT POLYMERS. NOTE III: CHARACTERISTICS OF POLYPROPYLENE OBTAINED WITH THE CATALYTIC SYSTEM $VOCl_3$-$Al[CH_2CH(CH_3)_2]_3$

by I. PASQUON

(6 May 1959)

[*Chimica e Industria* **41**, 534 (1959)]

ABSTRACT

Samples of polypropylene obtained between —10° and 70°C with the aid of the catalytic system under consideration contain up to 58 per cent of atactic polymer, soluble in boiling ethyl ether, together with a stereoblock polymer fraction (about 20 per cent), soluble in boiling n-heptane. The remainder consists of n-heptane soluble polymer.

The most interesting results obtained from this work can be summarized as follows:

(a) The steric composition of the polymer depends slightly on the Al/V ratio, for ratios ranging from 1 to 4, but it depends on the method of preparation of the catalyst.

(b) The viscometric mean molecular weights of each separated polymer fraction are high; they are even higher than 200,000 for the ether extracts, and up to 500,000 for the n-heptane extracts.

They change little by varying the temperature within the considered range, (—10+70°C).

(c) The value of the molecular weights is conditioned by a chain transfer process, the rate of which is of the first order with respect to the monomer concentration, and it is also conditioned by at least another process; the rate of the latter process is a function of the catalyst concentration.

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A STUDY ON THE INVERSION OF STERIC CONFIGURATION IN THE STEREOSPECIFIC POLYMERIZATION OF PROPYLENE

by G. NATTA and I. PASQUON

(9 May 1959)

[*Rend. Accad. Naz. Lincei* (8) **26,** 617 (1959)]

ABSTRACT

In the coordinated-anionic polymerization of α-olefins, in spite of the use of stereospecific catalysts, each monomeric unit, at the moment of its addition to the growing chains, can assume sometimes an enantiomorphous steric configuration with respect to that of the monomeric unit which precedes it.

The influence exerted by the partial pressure of the olefin and by the concentration of the aluminum alkyl with respect to the above-mentioned phenomenon is studied in this paper. The polymerization of propylene with the highly stereospecific catalytic system, α-$TiCl_3$–$Al(C_2H_5)_2Cl$ is also studied. The polymers obtained have been characterized by their fractionation with boiling solvents and by the determination of crystallinity and melting temperature of each separated fraction.

Intrinsic viscosity measurements were performed on the different fractions. The following results were obtained:

(1) the percentage of extractable polymer with each solvent increases by decreasing the pressure. This variation is clearly observed only if one operates at low pressures, i.e. lower than atmospheric pressure.

(2) The melting temperature of the extracts obtained, as seen by the polarizing light microscope, does not practically change by varying the pressure of the polymerization.

(3) The crystallinity of the n-octane extract and of the residue to the extraction is practically independent of the polymerization pressure.

(4) The percentage of boiling n-octane extractable fraction increases by increasing the concentration of the aluminum alkyl introduced in the catalytic system.

These results show that the stereoregularity of the polymer obtained, (and therefore the $1/n = v_p/v_i$ ratio, where n = inversions found in the polymeric chain; v_i = overall rate of the inversion phenomena; v_p = propagation rate), decreases by decreasing the partial pressure of propylene and—even if limitedly—by increasing the concentration of the aluminum alkyl.

The experimental results obtained concur with the hypothesis that v_i can be expressed as the sum of terms which do not depend on one another:

$$v_i = v_o + v_{Al} + v_M$$

where v_o = rate of an inversion process as a function of temperature only.

v_{Al} = rate of an inversion process as a function of the concentration of $Al(C_2H_5)_2Cl$.

v_M = rate of an inversion process as a linear function of the pressure of olefin.

The results were interpreted on the basis that n assumes the same value for the different polymeric fractions separated by a given solvent, independently of the polymerization conditions.

The process of inversion of steric configuration of the monomeric units, the rate of which is independent of the partial pressure of the olefin, was attributed, in agreement with what has already been reported in previous papers, to a process of dissociation from the active centre of the chains, or of organometallic compounds which contain them, followed by a re-association to the catalyst, possibly to a different active centre. Assuming that the re-association takes place at random, with regard to the steric configuration of the catalytic complex, the monomeric units when they are added to themselves, after the re-association of each polymeric chain, have a 50 per cent probability to assume an enantiomorphous steric configuration with respect to that of the last monomeric unit added before its dissociation.

On the basis of this hypothesis the atactic and stereoblock polymers could be produced by active centres, which are easily dissociated;

whereas, the isotactic ones could be produced by centres which are hardly dissociated.

The influence of the concentration of the aluminum alkyl (which, however, is limited) on the frequency of the inversion phenomena, has been interpreted bearing in mind that this compound exchanges alkyls with the growing polymeric chains on the active centres.

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A RAPID DETERMINATION OF LITHIUM IN THE PRESENCE OF ALUMINUM

by L. GIUFFRÈ and F. M. CAPIZZI

(11 May 1959)

[*Annali Chimica* **49**, 1414 (1959)]

ABSTRACT

Considering the particular interest of some organometallic complexes containing lithium and aluminum, equally used as catalytic systems in stereospecific polymerizations, we studied and succeeded in setting up a rapid method of separation and determination of lithium in the presence of aluminum. This method can be applied to any Li/Al molar ratio. Two different operating approaches of the method are described with respect to the mentioned Li/Al ratio; one approach used for Li/Al ratio $\geqslant 3{\cdot}5$ is based on the direct treatment of the solution under consideration with an anionic exchange resin used in the form of a free base; the other one, for Li/Al ratio $<3{\cdot}5$, is based on treating the solution with an anionic exchange resin, which had been previously saturated with a complexing agent of the aluminum ion.

The exchange resin holds the aluminum quantitatively as an alternate ion in the former case, and as a complex in the latter; whereas, the lithium hydroxide, which is titrated acidimetrically, comes down in the elution.

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INFRARED ANALYSIS OF POLYBUTADIENES OBTAINED BY STEREOSPECIFIC SYNTHESIS

by D. Morero, A. Santambrogio, L. Porri and F. Ciampelli

(15 May 1959)

[*Chimica e Industria* **41**, 758 (1959)]

ABSTRACT

The production by stereospecific syntheses of highly pure *trans*–1,4, *cis*–1,4 and 1,2–polybutadienes has allowed us to set up a method of I.R. analysis, which determines the different types of unsaturation in polybutadienes of any composition.

The *trans*–1,4–polybutadiene units are characterized by a strong absorption band at 10·35μ, the *cis*–1,4 units by a band at 13·6μ and the 1,2 ones by a band at 10·97μ.

With polybutadienes consisting of *trans*–1,4, *cis*–1,4 and 1,2 units respectively, provided each composition had a purity higher than 98 per cent, it was possible, with a system of subsequent approximations, to determine the absorption coefficients at 10·35μ, 10·97μ and 13·6 μ reported in Table 1, for the three types of structures.

Table 1. Coefficients of Absorption for the I.R. Analysis of Polybutadienes

(in mg^{-1} cm^{-1} 10 ml)

	trans-*1,4*	*1,2*	cis-*1,4*
10·35 μ	$23{\cdot}3 \times 10^{-2}$	$0{\cdot}828 \times 10^{-2}$	$0{\cdot}609 \times 10^{-2}$
10·95–10·98μ	—	$26{\cdot}7 \times 10^{-2}$	$0{\cdot}107 \times 10^{-2}$
13·50–13·65μ	—	$0{\cdot}231 \times 10^{-2}$	$5{\cdot}73 \times 10^{-2}$

The positions of the two last bands are slightly variable. The measurements were performed at the peak of absorption but not at an exact wavelength.

The analyses were carried out in solutions of carbon disulphide. The optical densities were read in reference to the base line obtained by the placement in the apparatus (Perkin-Elmer 21) of a cell containing the solution and of the same cell containing only the solvent. By solution of the following system

$$D_{10.97} = (K_{1,2}^{10.97} \cdot P_{1,2} + K_{cis-1,4}^{10.97} P_{cis-1,4})\, S$$

$$D_{13.6} = (K_{1,2}^{13.6} \cdot P_{1,2} + K_{cis-1,4}^{13.6} P_{cis-1,4})\, S$$

where:

D_λ = optical density at λ wavelength

K_x^λ = absorption coefficient for the x component at the λ wavelength, expressed in the same units of Table 1

P_x = weight of the component x, in mg per 10 ml of solution

S = thickness of the small cell used, in cm

and of the following equation:

$$D_{10.35} = (K_{trans-1,4}^{10.35} P_{trans-1,4} + K_{cis-1,4}^{10.35} P_{cis-1,4} + K_{1,2}^{10.35} P_{1,2})\, S$$

The weights of the three different types of arrangement of polybutadiene present in 10 ml of solution are obtained.

Knowing P (weight in mg of polybutadiene dissolved in 10 ml of solution) one can obtain the absolute percentages of the three types of arrangement:

$$C\%_{trans-1,4} = P_{trans-1,4} \frac{100}{P}$$

$$C\%_{cis-1,4} = P_{cis-1,4} \frac{100}{P}$$

$$C\%_{1,2} = P_{1,2} \frac{100}{P}$$

By setting up these analyses we observed that isotactic and syndiotactic 1,2 polybutadienes, show the same absorption coefficients at the wavelengths that we used for this analysis.

Isotactic 1,2–polybutadiene, also in solution, can be qualitatively distinguished from syndiotactic 1,2–polybutadiene, since the latter

shows a band at 14·95μ, which the isotactic polymer shows at 14·40μ. Just because of the presence of these bands, which are characteristic of the 1,2 structures, we had to consider as inaccurate the methods used for the determination of *cis*–1,4 units which comprise the whole band region between 12 and 15μ.

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CROSS-LINKING DENSITY AND PHYSICAL PROPERTIES OF ELASTOMERS OBTAINED FROM ETHYLENE-PROPYLENE COPOLYMERS

by G. Crespi and M. Bruzzone

(22 May 1959)

[*Chimica e Industria*, **41**, 741 (1959)]

ABSTRACT

Some vulcanizates obtained from an ethylene–propylene copolymer, cross-linked using different amounts of dicumylperoxide, have been examined by the equilibrium stress–strain measurements on samples swollen in benzene. Thus, it was possible to calculate the cross–linking density of these samples and the yield with regard to the employed cross-linking agent. At high concentrations of this cross-linking agent, the yield of the cross-linking reaction decreases.

The equilibrium swelling data in benzene agree with the relative cross-linking densities, according to the Flory–Huggins formula; from these data it was possible to deduce the interaction constants between the copolymer and the solvent (benzene). Furthermore, a description is made of the effects of the density of cross-linking on some typical properties, such as the stress–strain and the rebound–temperature curves of the ethylene–propylene copolymer, vulcanized in the absence of reinforcing fillers.

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COPOLYMERIZATION OF ETHYLENE WITH ALIPHATIC α-OLEFINS. NOTE VI: COPOLYMERIZATION OF ETHYLENE WITH BUTENE-1

by G. NATTA, G. MAZZANTI, A. VALVASSORI and G. PAJARO

(26 May 1959)

[*Chimica e Industria* **41**, 764 (1959)]

ABSTRACT

It has been possible to prepare, under suitable experimental conditions, using catalysts consisting of vanadium halides and trialkyl aluminum, linear, high-molecular-weight ethylene-butene-1 copolymers, which were free from amorphous homopolymers.

In this communication we report on the experimental conditions, which we used to prepare ethylene-butene-1 copolymers, and the methods employed to characterize them. The results reported here were obtained with two different catalytic systems prepared from VCl_4 and $Al(C_6H_{13})_3$ and from VCl_3 and $Al(C_6H_{13})_3$.

These systems were chosen from several possible ones, and could be considered as typical examples of two classes of catalysts for the ethylene-α-olefin polymerization differing in their degree of stereospecificity.

The composition of the copolymers is independent of the following factors: concentration of the catalyst, time elapsed from its preparation and its use, molar ratio of the two reagents present in the catalyst and period of the polymerization run.

The composition of the copolymers changes considerably by varying the composition of the starting monomer mixture.

The system adopted for establishing whether the products obtained were truly copolymers of ethylene–butene-1, was based on a comparison between the results obtained from the fractionation of samples of copolymers with boiling solvents and from that of two homopolymers obtained under the same conditions. Further proofs that the different fractions consist actually of copolymers, were given by X-rays and I.R. spectra.

We determined reactivity ratios on the basis of runs performed with monomer mixtures having different composition (see Table 1).

TABLE 1. REACTIVITY RATIOS OF THE ETHYLENE-PROPYLENE AND ETHYLENE-BUTENE-1 COPOLYMERIZATIONS WITH CATALYSTS PREPARED FROM $Al(C_6H_{13})_3$ AND VANADIUM CHLORIDES

Catalyst	*Ethylene-Propylene Copolymerization*		*Ethylene-Butene-1 Copolymerization*	
	$r_{C_2H_4}$	$r_{C_3H_6}$	$r_{C_2H_4}$	$r_{C_4H_8}$
$VCl_4+Al(C_6H_{13})_3$	7·08	0·088	29·60	0·019
$VCl_3+Al(C_6H_{13})_3$	5·61	0·145	26·96	0·043

The reactivity ratios of the ethylene–propylene copolymerization are less different from one another than those of the ethylene–butene-1 copolymerization using the same catalytic system.

The decrease of reactivity observed when passing from ethylene to propylene and to butene-1, agrees with the decrease of the polymerization rate observed in the preparation of the homopolymers with the same catalytic systems.

The lower reactivity of propylene and butene with respect to that of ethylene, should agree with what can be foreseen for a copolymerization occurring with an anionic mechanism. The difference of reactivity existing between propylene and butene-1 could be attributed to the influence of steric factors or conditions depending on the adsorption of monomers on the surface of the catalyst.

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ORGANOMETALLIC COMPLEXES OBTAINED BY THE REDUCTION OF HYDROCARBON SOLUTIONS OF TITANIUM HALIDES WITH ALUMINUM

by G. NATTA, G. MAZZANTI and G. F. PREGAGLIA

(29 May 1959)

[*Gazz. Chim. It.* **89**, 2065 (1959)]

ABSTRACT

By reacting $TiCl_4$ with aluminum, aluminum chloride and benzene at 80°C, a violet, crystallizable complex is rapidly formed, to which we have assigned the empirical formula: $Al_2TiCl_8(C_6H_5)$. This complex is active only in the polymerization of ethylene. By its air oxidation, good yields of phenol are formed. Lewis base type compounds react with this complex by fixing a molecule of $AlCl_3$ to them followed by the formation of a crystalline brown complex which precipitates out from the solution. Propylene in the presence of this latter complex yields a crystalline product in which there are present phenyl nuclei, as is shown by its I.R. spectrum.

H. Martin and F. Vohwinkel (Chem. Ber. **94**, 2416 (1961)) have assigned the formula $Al_2TiCl_8(C_6H_5)$ to the violet complex obtained in the Friedel–Crafts reduction reaction of $TiCl_4$; benzene is indeed so reactive that it is oxidized by air to phenol.

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ELASTIC AND UNELASTIC BEHAVIOUR OF SOME ISOTACTIC POLYMERS

by G. NATTA, M. BACCAREDDA and E. BUTTA

(May 1959)

[*Chimica e Industria* **41**, 737 (1959)]

ABSTRACT

The dynamic mechanical properties of linear polymers of alpha-olefins (polypropylene, polybutene, polystyrene) containing crystalline fractions with different isotactic steric purity, have been determined.

The transitions determined by means of the positions of singular points on the curve of the sound velocity and of the damping factor as a function of the temperature, have values which depend on the content of amorphous polymer and on the steric purity of the crystalline polymer.

Fairly high values of the damping factor in a wide temperature range are observed only by examining products with a high content of non-crystalline fractions.

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CRYSTALLINE SYNTHETIC HIGH POLYMERS WITH A STERICALLY REGULAR STRUCTURE

by G. NATTA

(7 Aug. 1959)

[*Nuovo Cimento*, Suppl. **15**, (10) 3 (1960)]

INTRODUCTION*

The discovery of stereospecific polymerization processes leading to new linear high polymers of vinylic and diolefinic hydrocarbons having a regular structure, also with regard to the steric configuration of the monomeric units, probably represents the most important event in the pure and applied macromolecular chemistry, during these last 20 years.

Even if it is a fairly recent discovery (the first patents on the subject were filed in June 1954[1] and the first scientific communication was presented in December 1954[2] before the Accademia dei Lincei) nevertheless its influence was considerable and roused a wide international movement of research, to which thousands of chemists devoted themselves in university and industrial research laboratories. This research brought the discovery of a great number of new stereo-ordered polymers.

The importance of these new processes clearly appears, considering that with the old processes a great number of simple monomers, able to give asymmetric monomeric units by polymerization, could only be

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* This paper was published as introduction to a series of papers (from paper 136 to paper 145) belonging to a special issue (Suppl. Vol. 15) of *Nuovo Cimento*.

polymerized to products having an irregular structure due to the random distribution along the chain of isomeric monomeric units with different steric configurations. As a result of chemical and steric structure irregularities, the macromolecules presented, in the solid state, lack of crystallinity and of suitable mechanical properties and therefore there were only a few possibilities of valuable applications.[3]

Even before the discovery of the stereospecific polymerization processes, different types of synthetic and natural macromolecules with sterically regular structures were known. Some of these macromolecules are thoroughly related to many phenomena of the organic life.

In the field of linear macromolecules, some crystalline natural products (i.e. cellulose, silk, etc.) show sterically regular structures, because they contain asymmetric carbon atoms, but only one of the two possible enantiomorphous forms is present. Thus the steric structure regularity of those polymers is due to a regularity already existing in the monomers that contain asymmetric carbon atoms. The monomers of those natural products exhibit optical activity; in fact they rotate the plane of the polarized light; therefore the steric regularity of the corresponding polymers is not determined by the polymerization process which does not modify the steric structure of the monomeric units.

The new stereospecific polymerization processes recently discovered give the possibility of obtaining sterically regular polymers (which contain asymmetric carbon atoms) also starting from monomers that, actually, do not have asymmetric carbon atoms, owing to the fact that the asymmetric carbon atoms are formed only during the polymerization reaction. They give the possibility of realizing a synthesis which can be defined as asymmetric in respect to the monomeric units of a single macromolecule with a sterically regular structure[3]. The crystallizability of the macromolecules of this kind is due to the presence, at least for long sections of the main chain, of asymmetric carbon atoms having the same steric configuration.

Other examples of natural polymers with steric regularity (which imply the so-called geometrical asymmetries and not the optical ones) are given by natural rubber and guttapercha: both isoprene polymers with 1–4 arrangement, the former being almost completely ($\sim$97 per cent) formed of *cis* units, the latter of *trans* ones. The poor elastic properties of all synthetic rubbers known before 1954 in comparison with those of natural rubber, depended on the chemists inability to produce diolefin polymers having a high steric purity in the *cis*-1,4 arrangement.

The new processes of stereospecific synthesis allowed the U.S. chemists to produce a sterically regular *cis*-1,4 isoprene polymer very similar to natural rubber[4] and the Italian ones to synthesize for the first time the *trans*-1,4 polyisoprene[5] and all the stereoisomeric polymers[6] (isotactic–1,2, syndiotactic–1,2, *trans*–1,4, *cis*–1,4) of butadiene (a diolefin less expensive than isoprene). The synthetic rubbers produced by these processes, with *cis*–1,4 structure and a very high steric purity, have, as does natural rubber, high elasticity, low hysteresis and high tensile strength also in vulcanizates without reinforcing fillers.[7]

Physico-chemical methods (in particular the interpretation of the X-ray, electron diffraction and I.R. spectra) mostly contributed to the discovery of the new stereoregular polymers and to their characterization; they also helped to determine the internal structure of the polymeric chains and of their crystalline aggregates, to distinguish polymers with different types of arrangement and of steric order and to determine the degree of steric purity.

On the specific results in the field of crystallinity obtained by these methods we have published only preliminary papers till now, which were sufficient to recognize and distinguish the new types of macromolecules. We did not publish the whole set of works because we were to devote most of our time to the study of catalysts, of the polymerization processes and of the other properties of the new polymers. Just recently we have had the possibility of reviewing the various experimental results collected during these years of research.

I therefore accepted the kind proposal of Prof. *Polvani* who, last year, invited me to publish in this Journal some significant parts of our research in the macromolecular field, limiting them to the above-mentioned field of the polymeric structures in the crystalline state.

Considering the character of this review, I do not describe the nature and mechanism of the chemical processes of stereospecific polymerization developed to synthesize linear head-to-tail polymers, where monomeric units with a certain type of steric structure are orderly disposed. This introduction is followed by ten papers. The first paper describes our original observations on the principles determining the chain conformation of the linear high polymers in crystals. We proved the remarkable usefulness of these principles in the interpretation of the structures of the new isotactic polymers and, recently, also in determining the structure of syndiotactic alpha-olefin polymers and other di-isotactic ones we have synthesized. The crystalline structure of some stereo-ordered polymers is described in the following 7 papers.

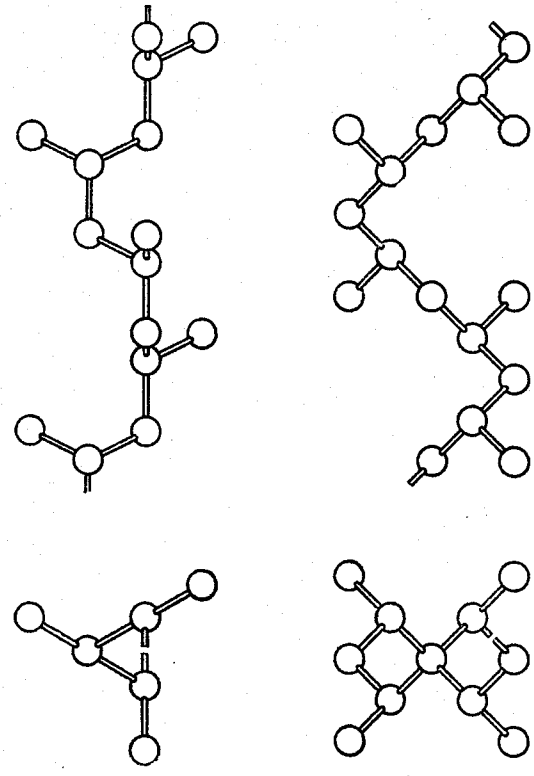


FIG. 1. Conformations found in the crystals of the chains of isotactic (left) and syndiotactic (right) polypropylenes.

The two last papers on I.R. spectroscopy complete the study of the crystallinity by methods which are more suitable and sensitive than X-rays for the determination of limited degrees of order.

To point out the importance of crystallinity in the macromolecular field, I shortly summarize the difference found in the mechanical properties of stereo-ordered polymers compared with those of polymers having a complete or partial steric disorder.

In the polymers of alpha-olefins, which are remarkably important because of the low cost of monomers (some of them are by-products of the petroleum industry), two types of steric orders are possible: the "*isotactic*" and the "*syndiotactic*" ones.

An isotactic structure is characterized by the fact that the monomeric units (which may exist in two enantiomorphous forms that cannot be superposed, one being the mirror image of the other) follow each other along the chain, at least for long chain portions, with the same steric configuration.[8] In a syndiotactic structure, on the contrary, enantiomorphous monomeric units follow each other alternately.[9] Figure 1 shows the chains of isotactic[10] and syndiotactic polypropylenes recently obtained in the crystalline state.[11]

In the atactic polymers there is no order in the succession of the enantiomorphous monomeric units, and this is the reason for the lack of crystallinity.

Properties, differing considerably from those of stereo-ordered macromolecules (isotactic or syndiotactic) and from those of sterically disordered atactic macromolecules, can be found in products with a degree of an intermediate order, which allows only a very little part of the polymeric chains to crystallize.

We called "stereoblock", the polymers formed of chain sections of different steric composition, which present a low degree of crystallinity.[12]

As examples, we report some properties of high molecular weight (>50,000) linear polypropylenes of different steric composition. The isotactic sterically pure polymers have a melting point of about 175°C; in the non-oriented state they can be interesting as thermoplastic materials with elastic moduli of 150–200 kg/mm², maximum tensile strength of about 4 kg/mm² and ultimate elongation of 400–700 per cent. In the oriented state they give transparent films with a resistance to tensile stress in two orthogonal directions of about 20 kg/mm².

Oriented fibres exhibit elastic moduli of 300–360 kg/mm² and resistance to tensile stress of 60–70 kg/mm². Their lightness (density of 0·91 instead of 1·50 of cotton and of 1·14 of nylon), excellent mechanical characteristics, low cost and high insulating properties, make these products very interesting in the field of synthetic textile fibres.[13]

Atactic polypropylenes, on the contrary, are amorphous; if they are subjected to prolonged stresses, they show high viscous creeps; in the vulcanized state they behave as elastomers. The inconvenience of the high elastic hysteresis of atactic polypropylenes can be reduced, introducing, as we did, by copolymerization, more flexible ethylene monomeric units in the polypropylene chain; as a result, the amorphous ethylene-propylene copolymers represent interesting synthetic rubbers, which are cheaper and more durable than natural rubber.[14]

The influence exerted by crystallinity on the properties of diolefin polymers is very important. As regards stereo-ordered butadiene polymers, isotactic and syndiotactic polymers with 1-2 structure, are crystalline and have high melting temperatures (respectively 125°C, 155°C). They are hard materials with a high elastic modulus and they are thermoplastic if cross-linking is absent.

The corresponding atactic polymer is a rubber which shows high elastic elongations, low moduli and relatively high elastic hysteresis

because the presence of vinyl side groups introduces a certain hindrance to the free rotation of the C—C bonds of the main chains.

The polymers with 1-4 structure have been prepared in two sterically ordered forms: *cis*[5] and *trans*[6] respectively. The *trans* form of polybutadiene has a high melting temperature (148°C) and only if crystallinity is hindered either by an increase in temperature or by different systems of plasticization or by vulcanization, it behaves as an elastomer: it gives hard rubber-like products having a fairly high elastic modulus.

The *cis*–1,4 polybutadienes with a high steric purity crystallize at room temperature under stretching (as natural rubber and *cis*—1,4 synthetic polyisoprene),while the previously known synthetic rubbers did not crystallize. The initial elastic modulus is low, but crystallinity, produced by orientation of macromolecules under stretching, causes an increase in the elastic modulus, with the increase of the elastic deformation, and furthermore gives a very high value of the ultimate tensile strength.[15]

Contrary to natural rubber, sterically pure *cis*–1,4 polybutadiene shows low hysteresis even at very low temperatures, and high resistance to abrasion.

The technological information we have given in this short introduction, has been reported with the purpose of pointing out the importance of the steric order on crystallinity and on the mechanical properties, and in particular on the elastic properties of the new polymers. Fuller details are reported in the original works. They can make anybody realize the enormous interest which was introduced by the discovery of stereospecific polymerization processes in the field of plastics, of synthetic fibres and of elastic rubbers.

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GENERAL CONSIDERATIONS ON THE STRUCTURE OF CRYSTALLINE POLYHYDROCARBONS*

by G. NATTA and P. CORRADINI

(26 June 1959)

[*Nuovo Cimento*, Suppl. **15**, (10) 9 (1960)]

Owing to the discovery of stereospecific polymerization processes effected in our Institute, we have been able to determine, in the last few years, the crystal structure of a great number of new polymers. In this paper we will discuss the general principles, leading to the determination of the shape and mode of packing of macromolecules in the crystals.[1]

1. STEREOISOMERISM IN HEAD-TO-TAIL ALIPHATIC LINEAR POLYMERS

Before explaining the principles and discussing, in accordance with them, the crystal structure of some macromolecular compounds, we would like to emphasize the importance of stereoisomeric phenomena in order to determine the capability of the polymers to crystallize.

There are different types of stereoisomerism in organic chemistry, generally distinguished into two classes:

(1) geometrical stereoisomerism, whenever the same chemical formula may correspond to intrinsically different geometrical configurations (e.g. in compounds containing a double bond, or in cyclic saturated compounds);

(2) optical stereoisomerism, whenever a molecule cannot assume, by free rotations around single bonds, the enantiomorphous configuration

* A preliminary communication on this subject was presented at the meeting of the A.C.S. (S. Francisco, April 1958).

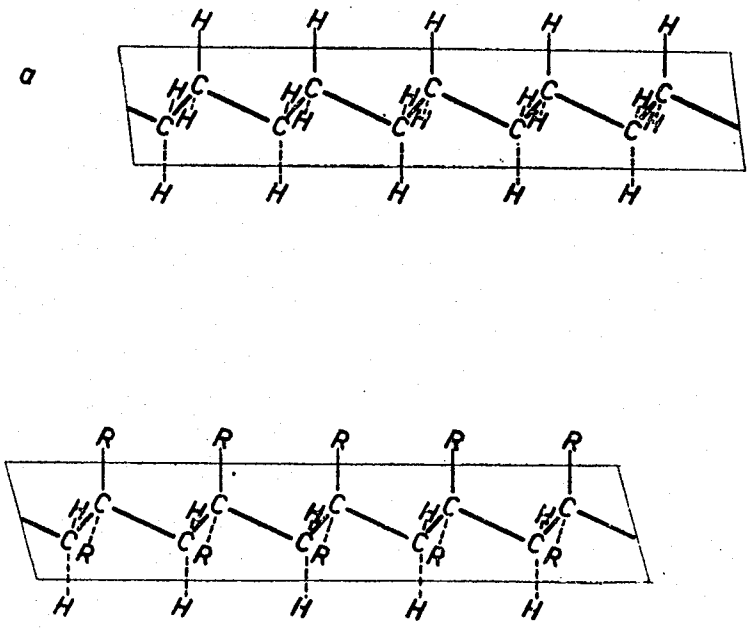


FIG. 1. A head-to-tail succession of (*a*) ethylenic (—CH_2—CH_2—) or (*b*) vinylidenic (—CH_2—CR_2—) monomeric units may be realized in one way only (main chain arbitrarily stretched on a plane.)

(this is in most cases due to the presence of carbon atoms linked to four different substituents[2]).

These two cases are both important in macromolecular chemistry.

Since the definition of crystal implies a three-dimensional order, in order that a polymer be crystallizable, a regularity in the succession of configurations of its monomeric units is necessarily required. A crystalline polymer can be obtained, in fact, only when all monomeric units belonging to a long chain segment show the same configuration, or when enantiomorphous configurations follow each other orderly. On the contrary, amorphous polymers are obtained when different stereoisomeric configurations of the same monomeric unit, e.g. *cis* and *trans*, or those "left" and "right" handed, follow each other disorderly. The stereospecific polymerization processes, first carried out in our Institute, permitted us to obtain head-to-tail linear polymers of alpha-olefins and di-olefins arranged according to regular successions of monomeric units, having equivalent steric configurations. These polymers are generally characterized by a high degree of crystallinity.

Before their discovery only a relatively limited number of crystalline synthetic hydrocarbon polymers were known.

Those obtained by poly-addition generally derived from monomers, such as ethylene or some vinylidenic monomers containing at least two symmetry planes in their molecules (isobutylene, vinylidene-chloride).

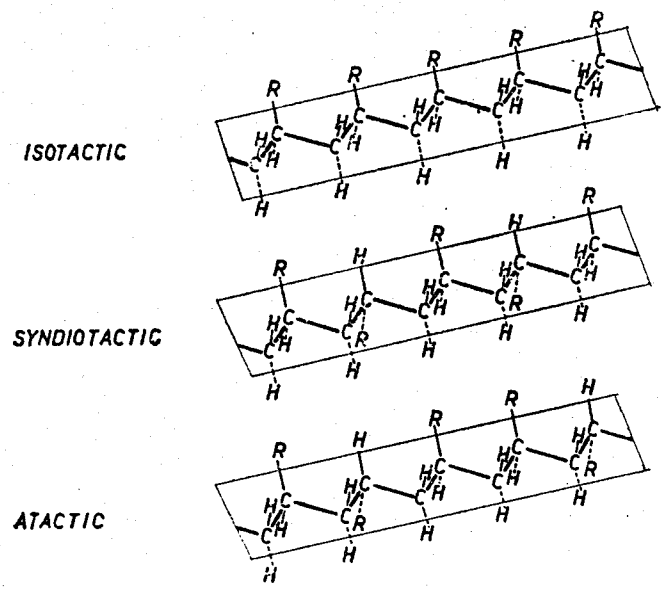


FIG. 2. Various types of possible head-to-tail successions of vinylic (—CH_2CHR—) monomeric units: isotactic, syndiotactic, atactic (random) (main chain arbitrarily stretched on a plane).

When these symmetrical molecules undergo a polymerization process, only one type of head-to-tail linking along may occur, as shown in Fig. 1. On the contrary, alpha-olefins and di-olefins may give rise to various types of stereoisomeric modes of the main chain; actually all synthetic polymers of alpha-olefins and di-olefins, prepared before the discovery of stereospecific catalysis, were amorphous. Figure 2 shows molecules of stereoisomeric vinyl polymers with the chain arbitrarily settled on a plane: the isotactic[3] polymers in which successive head-to-tail monomeric units show the same steric configuration; syndiotactic polymers[4], in which successive head-to-tail monomeric units show alternately opposite steric configurations; atactic polymers in which successive head-to-tail monomeric units, having different configurations, are randomly distributed along the chain.

In the field of di-olefin polymers other stereoisomeric phenomena of geometrical type appear: polyisoprene regular stereoisomers with 1,4–arrangement occur in nature; natural rubber has nearly a complete *cis* structure (~97 per cent), guttapercha has a *trans* structure. Other new stereoisomers of diolefins with 1,2–arrangement, which do not exist in nature, have been synthesized in our Laboratory in the last five years.

The configurations of the four possible regular stereoisomers of polybutadiene, whose structure was studied by us, are shown in Fig. 3.[5] Stereoisomeric phenomena are of interest in the field of polymers; in fact the most interesting physical and technological properties

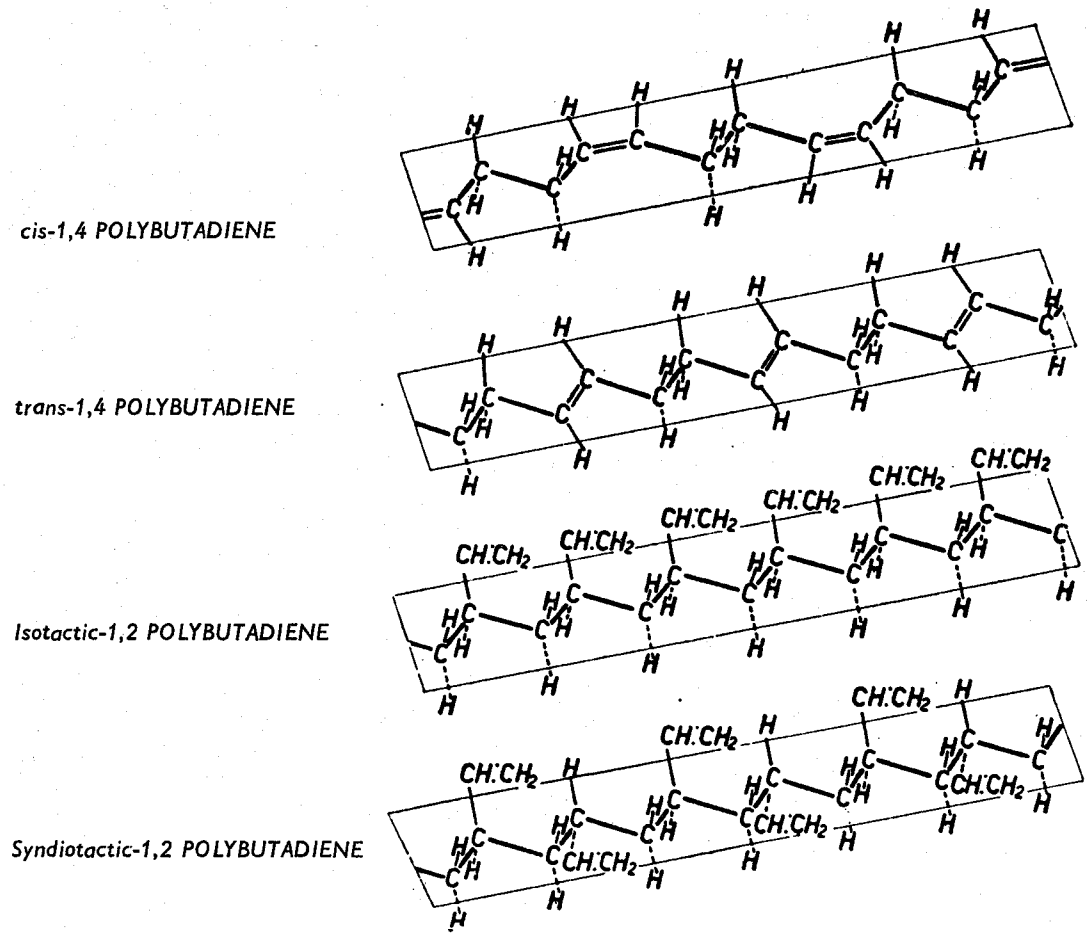


FIG. 3. Regular successions of stereoisomeric butadiene monomeric units: *cis*–1,4, *trans*–1,4, isotactic 1,2, syndiotactic 1,2 (main chain arbitrarily stretched on a plane).

of isotactic polymers of alpha-olefins and of some new stereoisomers of polydiolefins, in the field of plastics and of textile fibers, are due to the ability of these polymers to crystallize.[6] Atactic polymers of alpha-olefins cannot crystallize and possess completely different properties. Their practical interest is confined to very high molecular weight products that give a particular type of elastomers.

The most characteristic features connected with crystallinity, such as the conformation of the chain in the crystalline state, the relative positions of the chains in the crystal, the degree of freedom of rotation of lateral groups, the rate of crystallization, the size, distribution and orientation of the crystals and so on, determine the most interesting technical properties of these polymers, i.e. hardness, mechanical properties such as modulus, ultimate tensile strength and elasticity, melting temperature range, moulding properties and the possibility of giving high tenacity fibers.

In this paper we shall examine the conditions adopted to make the polymer crystallizable and the shape and mode of packing it will attain in the crystalline state.

2. SHAPE AND MODE OF PACKING OF MACROMOLECULAR CHAINS IN THE CRYSTALS

As we have already seen, regularity in the succession of monomeric units is the first requisite for a linear polymer to be crystallizable. As the definition of crystal implies three-dimensional order, a possible lack of order along the chain prevents in general any possibility of crystallization. It is in practice observed that:

(1) In linear crystalline polymers the axis of the macromolecule runs parallel to a crystallographic axis of the crystal. Moreover, in all known structures all the monomeric units have been found to occupy geometrically equivalent positions with regard to this axis* (*equivalence postulate*).

(2) The conformation of the chain in a crystal approaches that of minimum potential energy, which should be assumed by an *isolated* chain oriented along an axis, with the restrictions contained in the equivalence postulate. This means that lateral packing contacts (between neighbouring chains) generally play a secondary role in determining the conformation of the chain in comparison with the internal chain contacts. Thus, lateral packing contacts cause only slight deviations of the chain form from the one foreseeable only on the basis of the above considerations.

(3) The chains approach parallel to each other at intermolecular distances similar to those realized in low molecular weight compounds, to fill possibly any hole between themselves. With this restriction, all possible symmetry elements of the isolated chain are maintained in the lattice. That is, equivalent atoms of different monomeric units along an axis tend to assume equivalent positions in regard to the atoms of neighbouring chains.

Let us discuss systematically the consequences of these statements in the crystal structure of polymers.

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* This is a sufficient but not a necessary condition, to ensure order along the chain. Since this condition appears to be most frequently verified, it may be taken as a work postulate.

2.1. *Equivalence postulate*

According to the equivalence postulate, all the monomeric units which form a macromolecular chain occupy equivalent positions along an axis in the crystalline state.

In turn, a condition to be fulfilled by a crystallizable polymer, is that its monomeric units have defined configurations, as required, in order that they may occupy equivalent positions along an axis. Let us call *isoclined* two monomeric units, whose equivalent atoms have the same z coordinates after a suitable translation of the origin along the chain axis z; *anticlined*, two monomeric units whose equivalent atoms have the same z coordinates after a suitable translation of the origin accompanied by a reversal of direction of the z-axis.

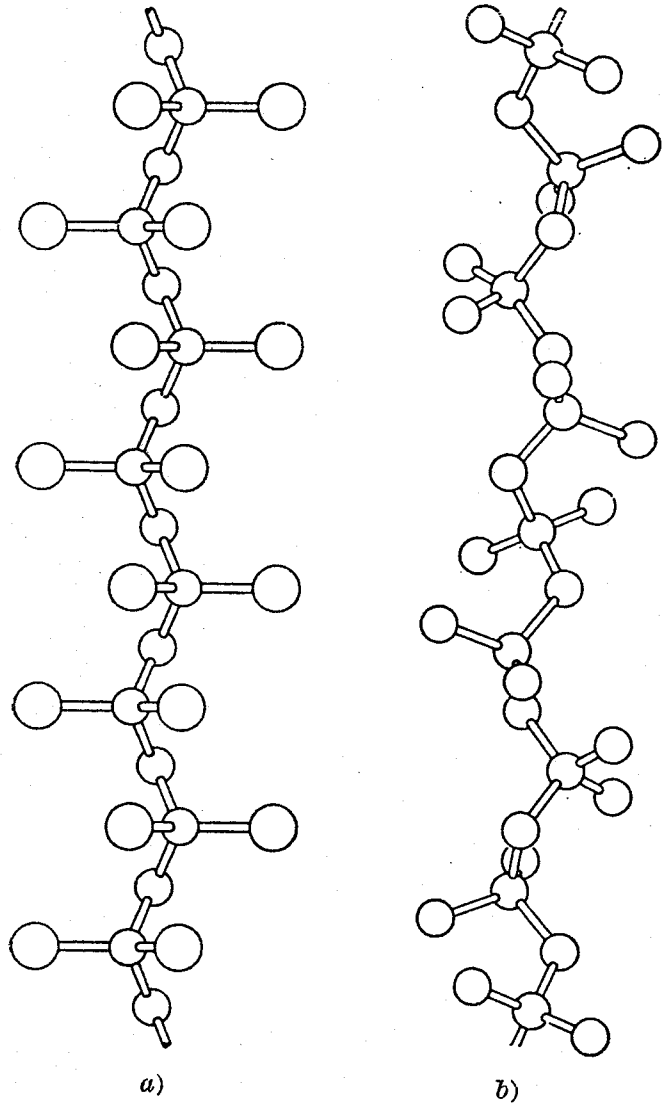


FIG. 4. Model of the assumed structure of (left) polyvinylidene chloride (glide-plane type) as compared with the one found by A. Liquori[42] for (right) polyisobutylene (helix type).

Repetition of equivalent monomeric units may be obtained along an axis in the following ways:

(1) Repetition of isoclined isomorphous equivalent units: through the operation of a translation c/p along z, accompanied by a rotation $2\pi(P/p)$ in a plane perpendicular to z. A helix is thus generated which contains p monomeric units and P pitches within the period c (helix type succession).

(2) Repetition of isoclined alternately enantiomorphous equivalent units: through the operation of a translation $c/2$, accompanied by a reflection in a plane containing the axis of the chain (glide-plane type succession).

(3) Repetition of isomorphous alternately anticlined equivalent units: along a helix associated with twofold axes perpendicular to z.

(4) Repetition of enantiomorphous anticlined equivalent units: through a translation along z associated with a symmetry plane perpendicular to z or a symmetry centre.

All head-to-tail crystallizable polymers, in which the two possible chain directions are intrinsically non-equivalent (for instance, a polyamide $(-(CH_2)_m-NH-CO-)_n$ or 1,4 polyisoprene$(-CH_2-CH=\underset{\displaystyle CH_3}{\overset{|}{C}}-CH_2-)_n$) must be built up in the crystal of *isoclined* equivalent units. Hence, only the helix and the glide-plane type structures are possible. In particular, a polyamide containing asymmetric carbon atoms, such as a crystalline protein, must necessarily have a helix type chain structure.

All the four types of regular repetitions, described by us, are possible for head-to-tail vinyl polymers. In fact, for these polymers, the two possible chain directions can be considered intrinsically equivalent: however, we must distinguish two intrinsically different (that is stereoisomeric) types of regular successions. Isotactic polymers are the vinyl polymers able *per se* to assume a helix type structure (or, possibly, the structure type 4). Syndiotactic polymers are the vinyl polymers able *per se* to assume a glide-plane type structure (or, possibly, the structure type 3).

As we shall see later, from the point of view of the equivalence postulate only, other polymers may be expected to crystallize in both the helix or the glide-plane type structure, without any intrinsic difference in stereoisomeric type (Fig. 4) (polyisobutylene, helix type; polyvinylidene chloride, probably glide-plane type). This happens

when the *monomeric unit* (for instance —CH_2—CR_2—), by free rotations around single bonds, may assume a conformation that can be superposed on its mirror image.

The general rules, above outlined, require, for their practical application to the study of new structures, a knowledge of the conformation that the chain is likely to assume in the crystalline state. We should expect that the conformation of the portion of chain, which takes part in a crystalline zone, is the one which nearly corresponds to a minimum of potential energy for the molecule in free conditions (e.g. in the melting or in ideal solution) under the restrictions imposed by the equivalence postulate.

The actual conformation of the chain has in turn a great influence in determining the possible modes of packing of the chains in the crystal, and on some physical properties of the polymer, such as the temperature and entropy of fusion.

2.2. *Shape of the macromolecule in the crystal state*

Stable conformations of a chain should in principle satisfy, as happens for low molecular weight compounds, the following conditions:

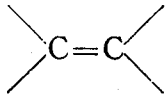
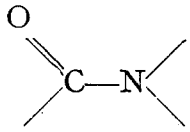
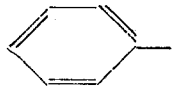
(1) Bond length conditions.[7]
(2) Bond angle conditions.[8]
(3) Planarity of certain groups of atoms.[9]
(4) Staggered carbon–carbon bonds.
(5) As appropriate as possible Van der Waals distances between non-bonded atoms within the chain.

A compromise between these 5 conditions is generally achieved in actual structures, as we shall see later in more detail.

There is no need to illustrate the first three items: a discussion is only needed for the two last ones.

(1) Principle of staggered bonds. The fourth point was emphasized for the first time by *Pitzer* and coll.[10] with regard to low molecular weight hydrocarbons, such as butane. He showed, on the basis of thermodynamical calculations, that the *trans* conformation of the butane chain was more stable than the *gauche* conformation, both conformations however lying in a minimum of potential energy. *Cis* conformations of the butane chain are, on the contrary, thermodynamically unstable. *C. W. Bunn* was the first to apply[11] these assumptions to the conformation of polymeric chains, and we could

TABLE 1. SIGNIFICANT ATOMIC DISTANCES AND BOND ANGLES OBSERVED IN POLYMERS EXAMINED IN THIS AND IN OTHER PAPERS OF THIS SERIES.

C—C	1·54 Å
C=C	1·32 Å
C—C (benzene ring)	1·40 Å
C—C—C	110°–116°
C=C—C	120°–125°
C—C—C (benzene ring)	120°
	all bonds in one plane
	all bonds in one plane
	all bonds in one plane

confirm them in a great number of cases. Because of its importance, the fourth item needs a detailed discussion.

If one considers two carbon atoms C_1 and C_2, joined by a single bond, the positions of minimum energy of the other bonds coming out from C_1 and C_2 are those outlined in Fig. 5. This is probably due to repulsions between localized bonding electron pairs.[12] The application of this principle alone is not sufficient to find out which conformation will be assumed by a linear saturated chain. The number of possible stable

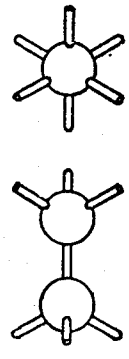


FIG. 5. Positions of minimum energy of the valence bonds of two tetrahedral singly linked carbon atoms (side and end views).

conformations is however limited by the equivalence postulate and by condition 5 of this paragraph, which implies that carbon–carbon bonds tend to be farther off than C–H bonds, favouring the *trans* conformation. Thus we arrive, for an unbranched crystallizable paraffin, at a

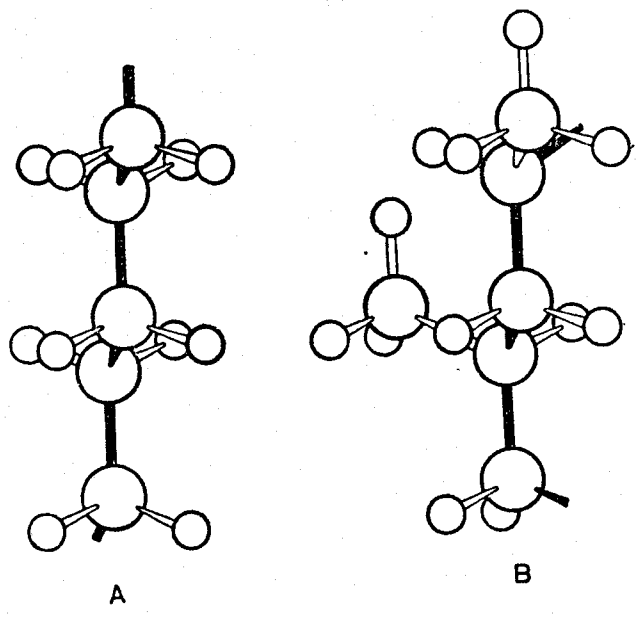


FIG. 6. Elements of polymer chains: Polyethylene (*A*). Polypropylene (*B*).

planar zigzag structure of the whole chain. The presence of *lateral* methyl or more bulky groups, may lead to a *gauche* conformation of the chain, which is the reason for the threefold helisc form assumed by the molecules of isotactic polymers. Evidently a comfortable accomodation of bulky side groups is not compatible with the maintenance of a planar zigzag chain for isotactic polymers. As examples, in Fig. 6 the structures of chain elements of polyethylene and polypropylene are shown. In Fig. 7 a model of the chain of poly-alpha-butylene is compared with a model of the staggered structure of diamond.

If a double bond comes out from a carbon atom, it must be considered, with regard to the orientating effect on the other single bonds, as lying in a plane normal to that containing the two remaining single bonds. The π-electron concentration in this perpendicular plane probably influences the direction to be assumed by the remaining bonds of successive carbon atoms. It has been indeed emphasized that the most probable distribution of electrons in a double bond is the one in which two electron pairs lie in opposite sides of the plane defined by the other four bonds.[13]

The resulting effect is that the single bonds adjacent to the double bond are in staggered positions, while the double bond is not (Fig. 8). As a consequence of this, a portion of chain containing four carbon atoms and a central double bond is planar, but the successive carbon atoms tend to be no longer in the same plane (Fig. 9). This tendency explains, as we shall see later, in particular cases, the conformation

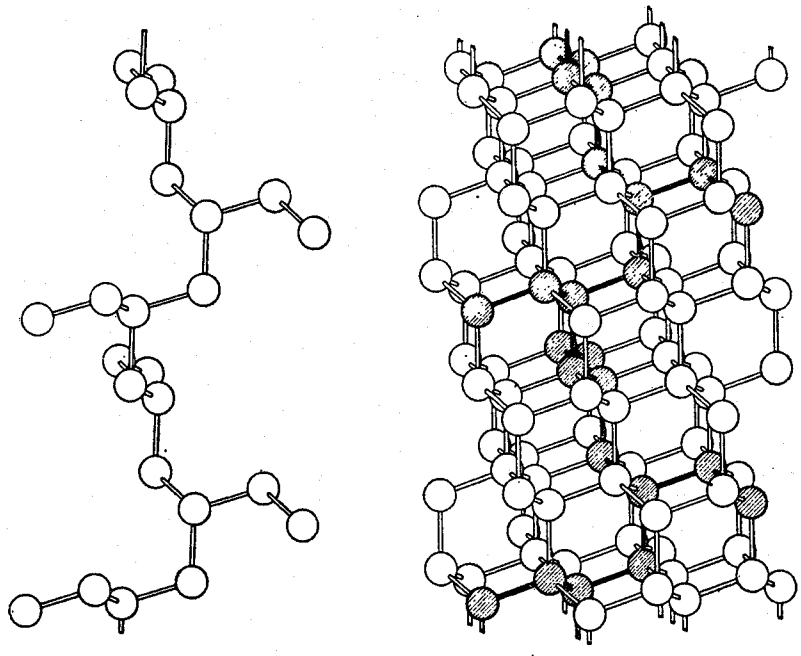


FIG. 7. Model of the poly-alpha-butylene macromolecule: carbon atoms are staggered as in the diamond lattice.

assumed by the monomeric units in all four crystalline polybutadiene stereoisomers (Fig. 10).

(2) Van der Waals' contacts. As we have already seen, Van der Waals repulsions, noted as the fifth point in this section, are extremely important in determining the form of the chains, when large atoms in comparison with hydrogen, or lateral chains are bonded to an aliphatic chain.

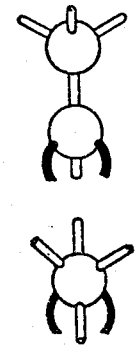


FIG. 8. Positions of minimum energy of the single bonds of a carbon atom singly linked to a double-bonded one (side and end views).

Indeed, an approach of two atoms not directly bonded at a distance below the one in agreement with Van der Waals' forces leads to a large increase in potential energy, which opposes this approach.

Qualitatively correct Van der Waals' distances between two atoms

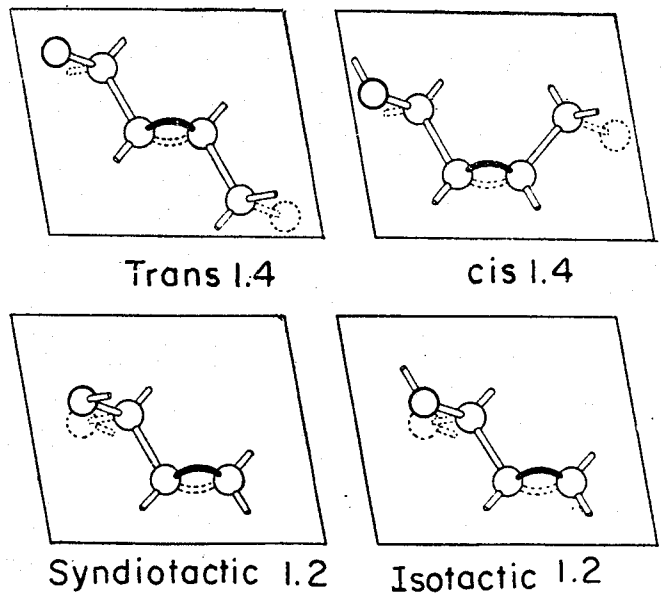


FIG. 9. Conformation of carbon-carbon bonds adjacent to double bonds, as found in crystalline polybutadiene isomers.

may be calculated on the basis of the additivity of Van der Waals' covalent radii, when electrostatic interactions of the type involved in hydrogen bridges play no part.[14] Approximately, Van der Waals' radii are 0·8 Å greater than the corresponding covalent radii. However, they cannot be precisely defined, because only in a rough approx-

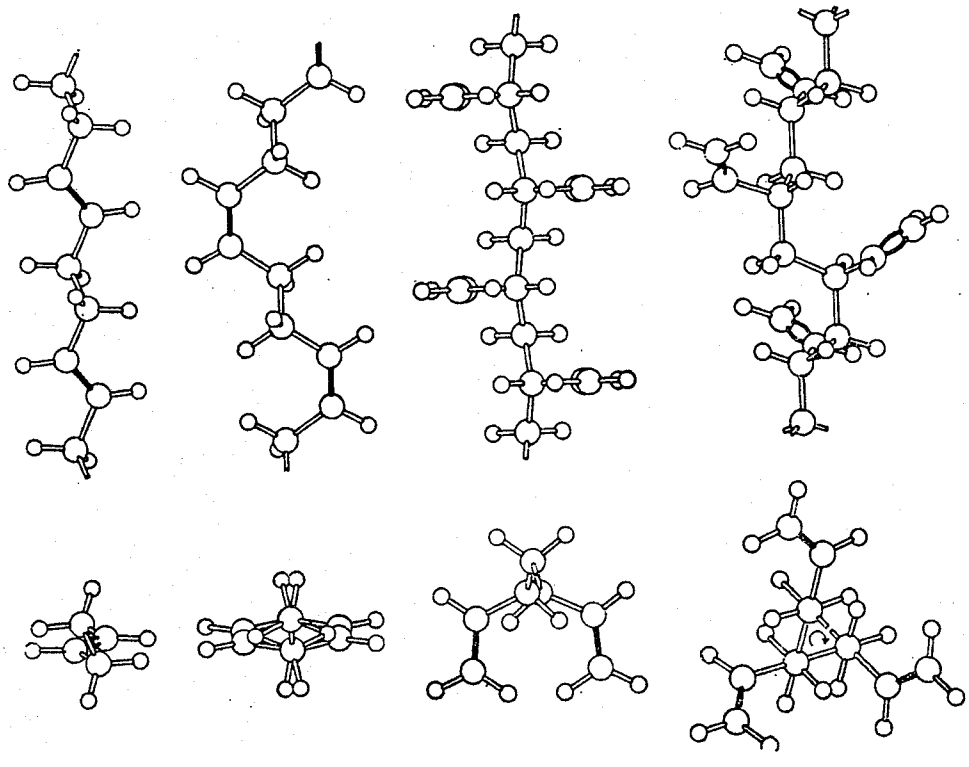


FIG. 10. Chain conformations of the four crystalline polybutadiene stereoisomers as determined in our Institute.

imation may atoms be considered spherically shaped; therefore they depend a great deal on the relative positions of the atoms and on the shape of the electron clouds.

The determination of the most probable shape of the macromolecule involves reconciliation of the five rules outlined above with the equivalence postulate to approach a minimum of potential energy. In many instances indeed, these five rules cannot rigorously hold together, especially when substituents of large dimensions are present along the chain. For instance, the lower heat of polymerization of isobutylene, as compared to that of ethylene, should be attributed, partially at least, to the greater energy content of the C_nH_{2n} chain of polyisobutylene, in comparison with polyethylene, caused by the deformation of the bond sequence due to steric hindrance (as two CH_3 groups are joined to every two carbon atoms along the chain).

As a consequence of the minimum energy postulate, while rules 1 and 3 are always holding, in some instances we may expect:

(1) A deformation of bond angles exceeding the normal values (e.g. more than 110° for C—C—C angle).

(2) A modification of the form of the main chain contrasting the principle of staggered bonds.

(3) A greater approach of certain atoms in the chain, at slightly less distances than the normal Van der Waals' ones.

In general the above-mentioned deformations of the various types of chains take place simultaneously, but in different degrees, in order to approach a minimum of potential energy. For the prediction of the most stable conformations, the engineering principles used in the study of elastic structure deformations might be applied.[15]

Consequences of such deformations, which will be discussed more deeply later on, are, for instance, the non-planarity of the zigzag chain of syndiotactic 1,2 polybutadiene, the deformation of bond angles in polypropylene, the four-fold instead of three-fold helix structure of poly-3-methylbutene.

The above outlined principles, which regard only interactions between atoms in the same chain, are of general character and should be sufficient to establish the preferred conformations of small portions of chains also in the free state.

Also, in most cases and especially for hydrocarbon polymers, they allow us together with the equivalence postulate, to predict the conformation to be assumed by a single chain in the crystalline state. As we have already noted, however, the need of filling the space uniformly may cause slight modifications in the form of the chain from the one foreseeable as that of minimum energy in the free state.

2.3. *Mode of packing of the chains*

The order in three dimensions of polymer chains to give a crystal may be realized only by a parallel orderly association of the chains, with contacts between atoms of different chains not exceeding the Van der Waals' contacts established for low molecular weight compounds (see Table 2).

TABLE 2. VAN DER WAALS CONTACTS OBSERVED IN POLYMERS EXAMINED IN THIS AND IN OTHER PAPERS OF THIS SERIES.

CH_3— —CH_3	4.0—4.3 Å
C_{ar}— —C_{ar} (benzene ring)	3.5—3.8 Å
CH_2— —CH_3	4.0—4.3 Å
H— —H	2.4—2.7 Å

When, as frequently occurs, both up and down molecules are represented in the unit cell, the space-group is such as to allow the presence in the lattice of anticlined chains in equivalent positions. When from a given monomeric unit equivalent right and left-handed helices are likely to be built up (for example from a monomer not containing asymmetric carbon atoms, like propylene) both are often represented in the crystal lattice, and the space-group is such as to allow the presence of enantiomorphous chains in equivalent positions; however, it may occur that, when bulky side groups are present along the chain, a suitably close packing can be obtained only in space groups in which uniquely isoclined or uniquely isomorphous helices are accomodated.

For instance, whereas in the structure of poly-α-butylene both up and down molecules may be accommodated, only isoclined molecules are present in the closely related structure of poly-*o*-fluoro-styrene.[16] There is increasing evidence that in some cases, i.e. in the case of isotactic poly-t-butylacrylate, only isomorphous helices can be accommodated in the same crystal[17] so that a separation of optical antipodes occurs on crystallization from the melt, when it contains both

right- and left-handed helices. In other cases, isomorphous helices provide a good space filling only through a superspiralization, as in some proteins.[18]

It frequently occurs that nearly isosteric (e.g. with a similar steric bulkiness) equivalent chains (e.g. enantiomorphous isoclined, or isomorphous anticlined, or enantiomorphous anticlined) may vicariate themselves in the same lattice site. This phenomenon has been observed for the first time by *Nyburg* in natural rubber, in the crystal lattice of which, a statistical substitution of mirrored chains is possible.[19]

We have observed it in isotactic polymers,[20] and found evidence for its existence also in guttapercha and polychloroprene.[21]

Generally, in the packing, the polymer molecules tend to maintain, partially at least, the symmetry of the chain. For instance, in the structure of polymers whose chains are of the glide-plane type, the glide-plane is usually maintained in the lattice. This fact occurs in natural rubber, as well as in polyvinylchloride, syndiotactic—1,2 and *cis*—1,4 polybutadiene and rubber hydrochloride.[22] The threefold helix symmetry of the chain of poly-α-butene, polystyrene and poly-*o*-fluoro-styrene, as well as the fourfold helix symmetry of the chain of poly-α-vinylnaphthalene and poly-*o*-methylstyrene, are maintained in the respective crystal lattices.[23]

In the parallel association of chains to provide polymer crystals, we often recognize ordered layers of macromolecules on planes; and we may imagine that the crystal is formed by the parallel or antiparallel association of them. These planes are defined by the chain axis and by one of the smallest crystallographic translations equatorial to the fiber axis. The values of both translations defining these planes are scarcely affected by thermal movements, so that thermal expansion occurs almost completely in a direction perpendicular to these planes.[24]

We shall call them, whenever recognizable, "principal planes". They contain in general, as was mentioned above, two crystallographic axes: the fiber axis and what we shall call the "principal equatorial axis". It is very likely that the polymer crystals may grow at their best along this axis, because we generally find it in the growing direction of the spherulites; this can be concluded from the known structure of spherulites of polythene, polypropylene, and nylon.[25]

With these background principles we shall now discuss in a more detailed way the structure of some crystalline polymers which have been studied by us.

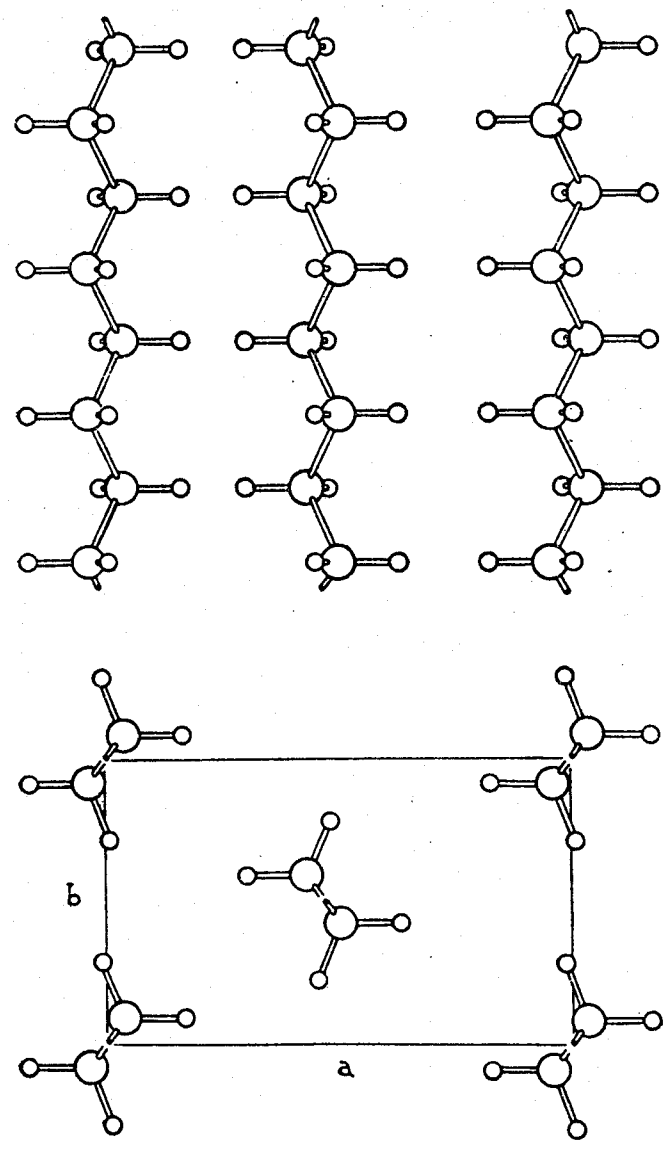


FIG. 11. Model of the crystal structure of polymethylene.

3. THE STRUCTURE OF SOME CRYSTALLINE POLYHYDROCARBONS

3.1. *Polymethylene*

Polymethylene, that is the polymer obtained by catalytic decomposition of diazomethane, is the simplest completely linear hydrocarbon polymer. Its structure is the same as that proposed by *Bunn* for the crystalline part of I.C.I. polyethylene.[26] The zigzag structure of the chain has already been discussed in this paper, in connection with the equivalence postulate and minimum energy considerations: equivalent isomorphous —CH_2— groups repeat themselves along a two-fold helix. The nearly cylindrical molecules fit themselves in a quasi hexagonal array (Fig. 11).

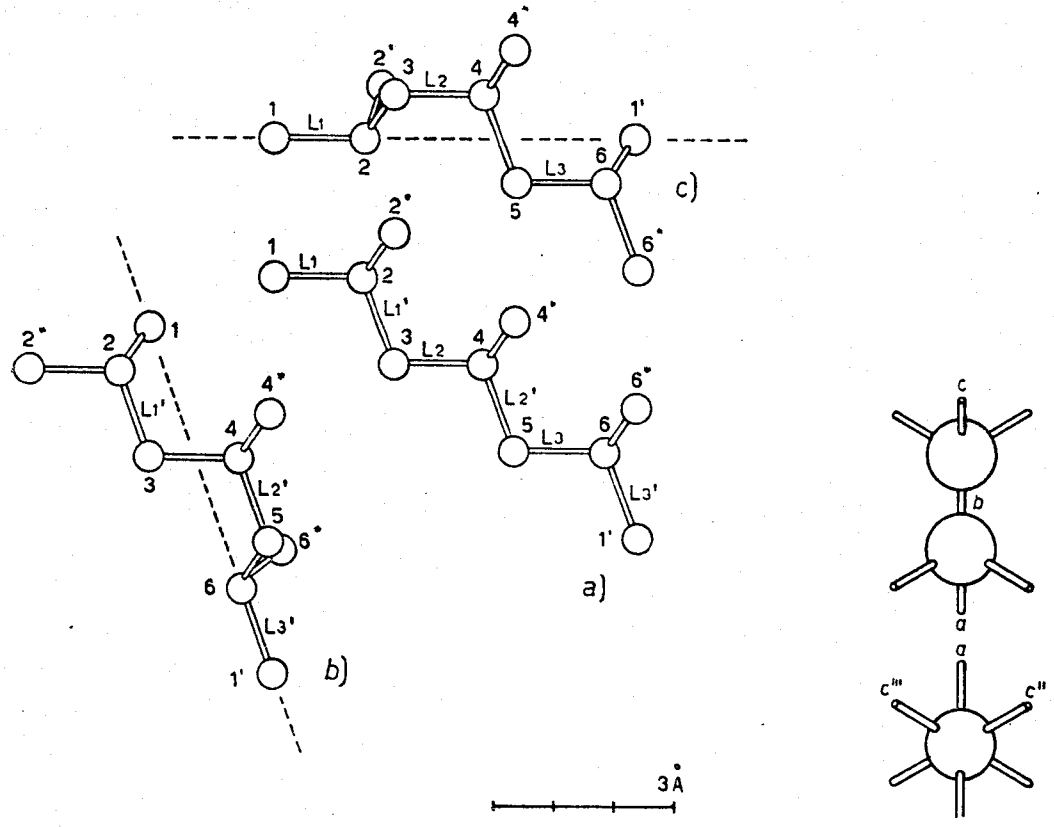


FIG. 12. Actual conformation of isotactic polypropylene chain as derived from the planar chain structure.

3.2. *Isotactic polymers*

Isotactic polymers are the *cis* stereoisomers of the vinyl head-to-tail polymers, as we have already quoted in Section 1. The bulky dimensions of side groups do not allow for these polymers a planar chain conformation. A planar structure is indeed impossible, because the distance of 2·5 Å (if we consider for example polypropylene), which should come out between the nuclei of two carbon atoms of successive methyl groups, is such that certain hydrogen atoms of the methyl groups would result too near to each other, in contrast with minimum energy requirements.[26] The nature of the strain may be easily understood when we consider that the large resonance energy of polyacetylene, which has a planar structure and is crystalline, is destroyed in polypropine, whose chain structure is non-planar, with a net loss, according to our calculations, of about 10 kcal per monomeric unit (something like happens with benzene and cyclo-octatetraene).[27, 28]

A suitable accommodation of the methyl groups may be achieved in a helix type structure, imposed by the equivalence postulate, and in accordance with the principle of staggered bonds, only when the successive monomeric units are arranged along a three-fold helix.

This structure may be easily obtained from the planar one, drawn in Fig. 12,a) by effecting rotations of 120° around L_1, L_2, L_3 bonds or around L'_1, L'_2, L'_3, bonds respectively clockwise or anticlockwise; thus a left- (c) or a right-handed (b) helix is generated. The methyl separation achieved in this way is comfortable (>4 Å) and the staggered bonds principle is respected. As the planar configuration is strongly hindered from a thermodynamic point of view, no interconversion of enantiomorphous helices appears to be likely at low temperatures, and we may consider left- and right-handed helices as optical stereoisomers.

Optical activity is prevented by the presence of an equal quantity of the two forms.

When built up with normal bond lengths (1·54 Å) and angles (109° 28′), the isotactic threefold helix should have an identity period of 6·2 Å; actually for polypropylene an identity period as large as 6·5 Å has been observed. A slight enlargement of C—C—C angles along the chain appears to be the reason for this fact, owing to a more comfortable accommodation of Van der Waals' contacts between the hydrogen atoms of the chain. The bulkiness of side groups, and more precisely, the steric bulkiness of side groups in proximity of the chain is, on the contrary, the reason why 3-methyl substituted polyolefins have a four-fold helix structure in the crystalline state, and 4-methyl substituted ones a 3·5-fold helix structure. The staggered bonds principle is no longer strictly respected, but valence angles along the chain tend to approach the normal ones again, so that very low differences in energy should be present between a three-fold and a four-fold helix[29] (Fig. 13).

Thus, for instance, it has been observed that poly-α-butene is crystallizable in both forms, the four-fold one however being the less stable.[30] It has been concluded, from the fact that this form is the first appearing on crystallization from the melt, that in the liquid state by small energy intakes there is a certain degree of freedom around single bonds in the chain, in the sense of a slight despiralization of the chain.

It is interesting to note that the four-fold helix poly-α-butene crystals are suddenly transformed into the three-fold helix ones by drawing, or by pressing and, more slowly, on standing at room temperature.

Other chain structures slightly modified from those above mentioned may also appear in crystalline isotactic polymers. For

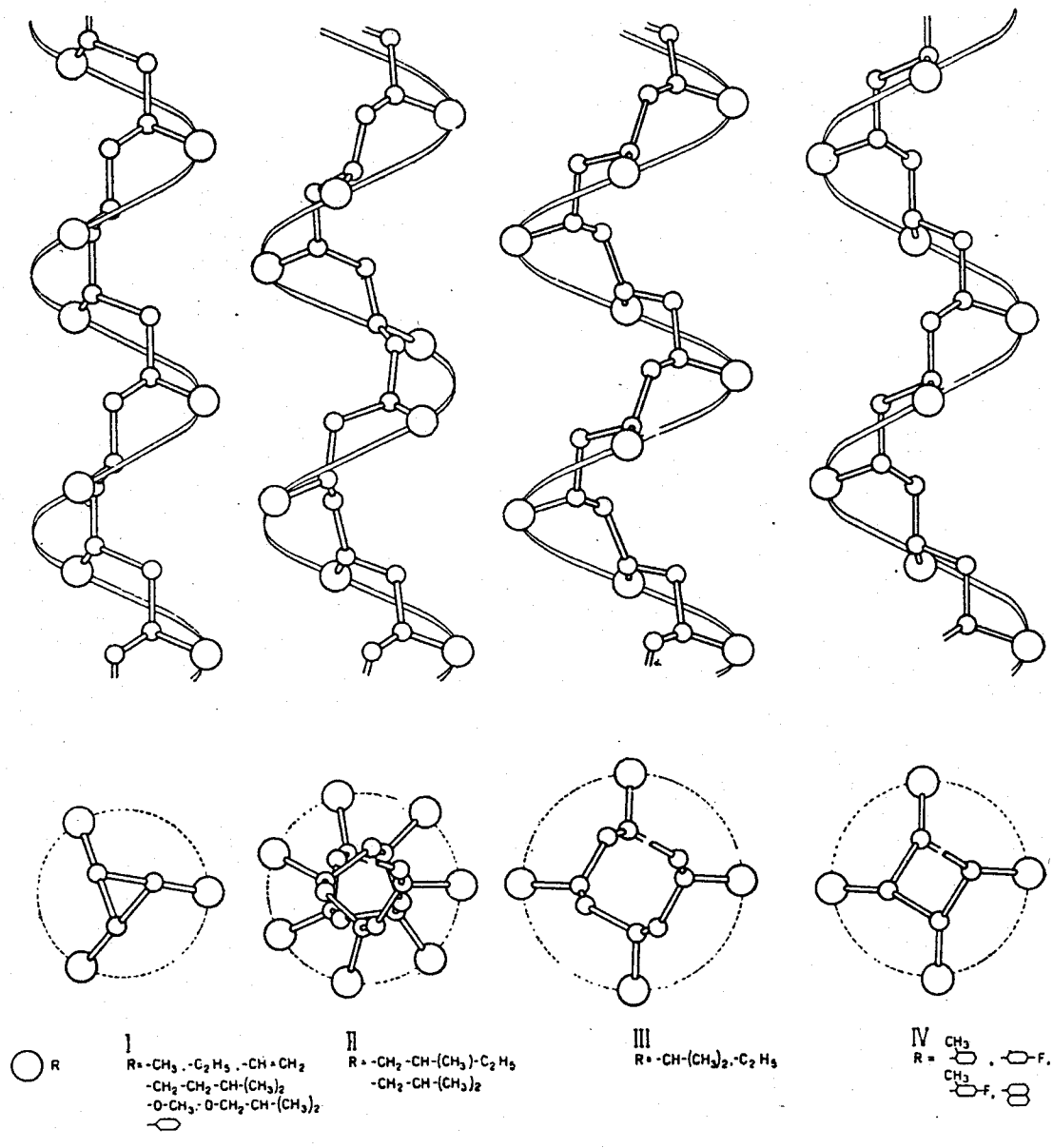


FIG. 13. Models of helicoidal chains found for different isotactic polymers.

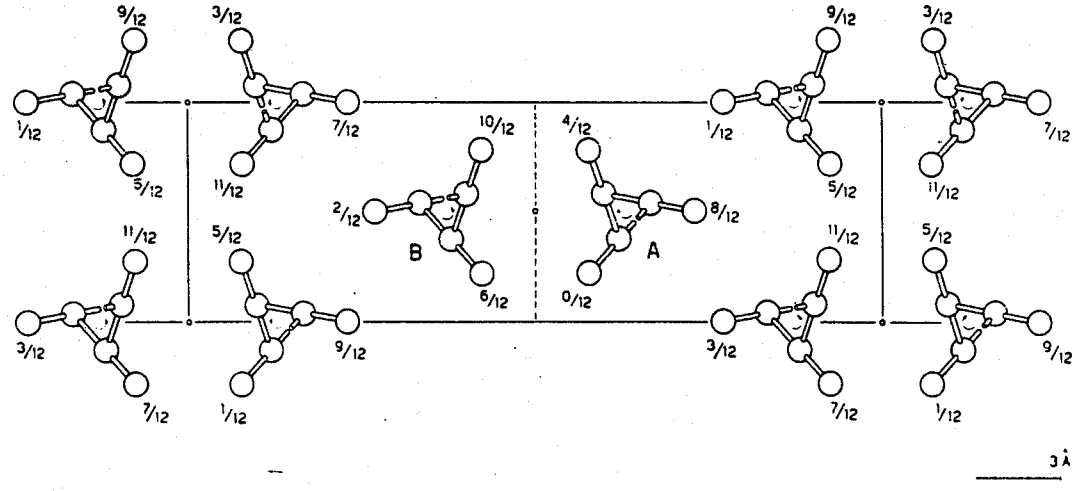


FIG. 14. Mode of packing of polypropylene chains in the crystal.

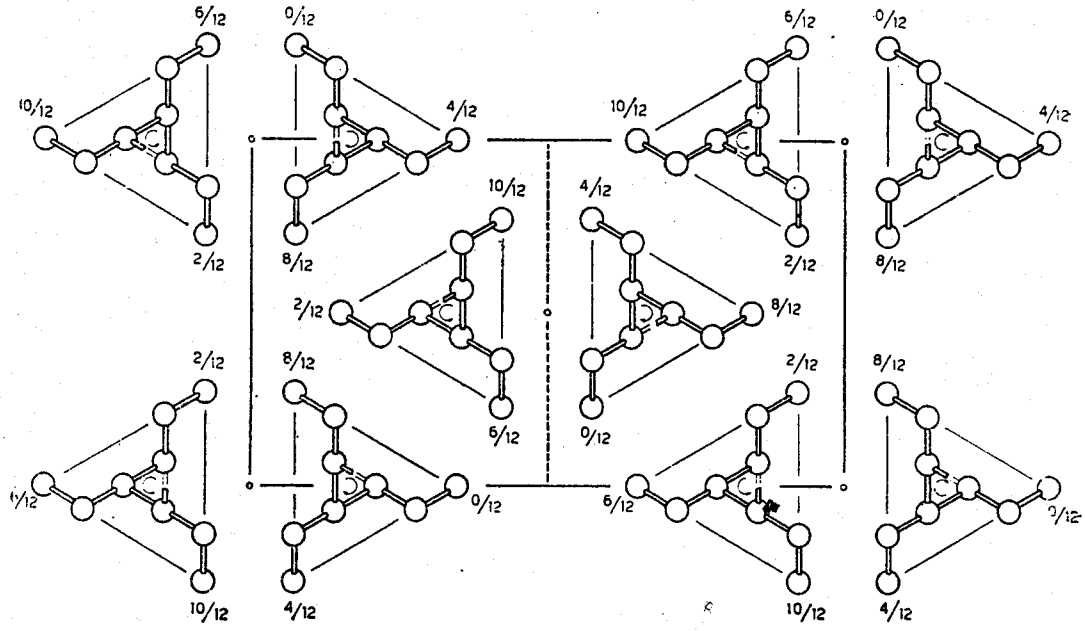


FIG. 15. Mode of packing of poly-α-butene chains in the crystal.

example, poly-*o*-methylstyrene has a four-fold helix chain structure different from the one described for aliphatic polyolefins (Fig. 13), whereas poly-*m*-methylstyrene has a 3·67-fold helix chain structure (11 monomeric units in three pitches along the identity period). Quite complicated chain structures, which have not yet been completely examined, have been observed for other substituted polystyrenes. The reason for such a variety of different forms is to be found in the packing requirements, both within the chain itself and also among different chains, the side groups of substituted polystyrenes being very stiff and bulky. The determination of the complete crystal structure of polypropylene and poly-α-butene effected by us[31] permits a discussion on the mode of packing of the chains of these isotactic polymers in crystals (Figs. 14, 15).

On considering the packing requirements explained in Section 1, the lattice of an isotactic polymer should possibly accommodate enantiomorphous chains in equal quantity, presumably through operations of symmetry of the space group.

According to the requirements just explained, it is actually found that, in all these polymers, enantiomorphous chains face each other in pairs, a close packing being realized through the operation of a glide-plane with translation parallel to the fiber axis. Moreover, anticlined isomorphous chains of the isotactic polymers of propylene and α-butene are nearly isosteric, when we refer to the bulkiness of side groups (Fig. 16) and, as long as intermolecular contacts are realized

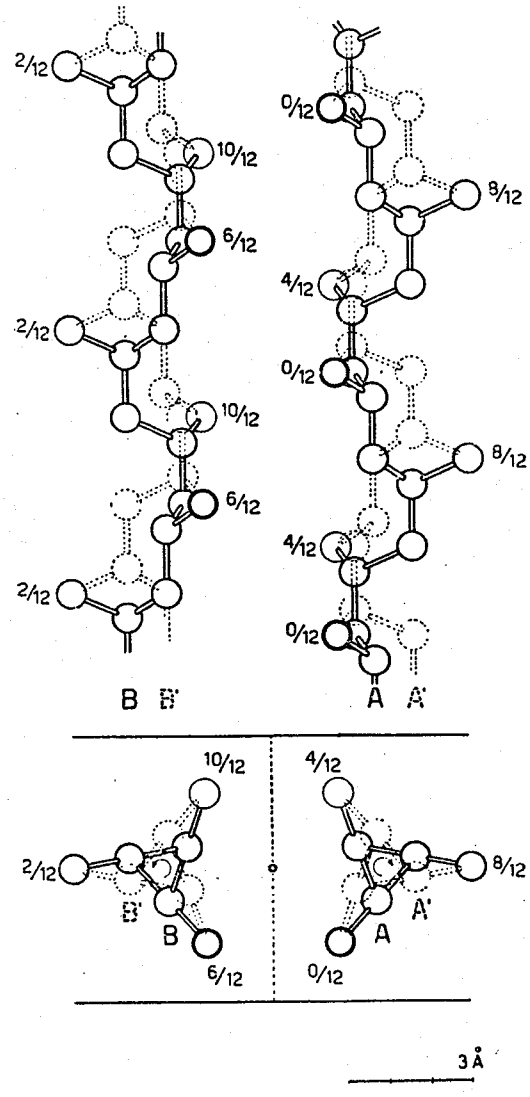


FIG. 16. Model showing isosterism of anticlined isomorphous chains of polypropylene in a crystal.

almost uniquely by these side groups, anticlined isomorphous chains may in principle vicariate in the same lattice site. In fact it is thought that each crystal of these polymers is composed of very small blocks of anticlined crystallites built up of isoclined chains, so that diffraction phenomena may be more easily interpreted supposing that anticlined isomorphous chains may statistically vicariate in each site of the crystal.

Poly-α-butene (and the closely related isotactic poly-1,2-butadiene) are able to maintain the complete symmetry of the chain, so that three glide planes making angles of 120° among themselves and related by a three-fold screw axis are easily recognizable in the rhombohedral structure of these polymers.

A too loose mode of packing should result when a similar structure is supposed to be likely also for polypropylene.

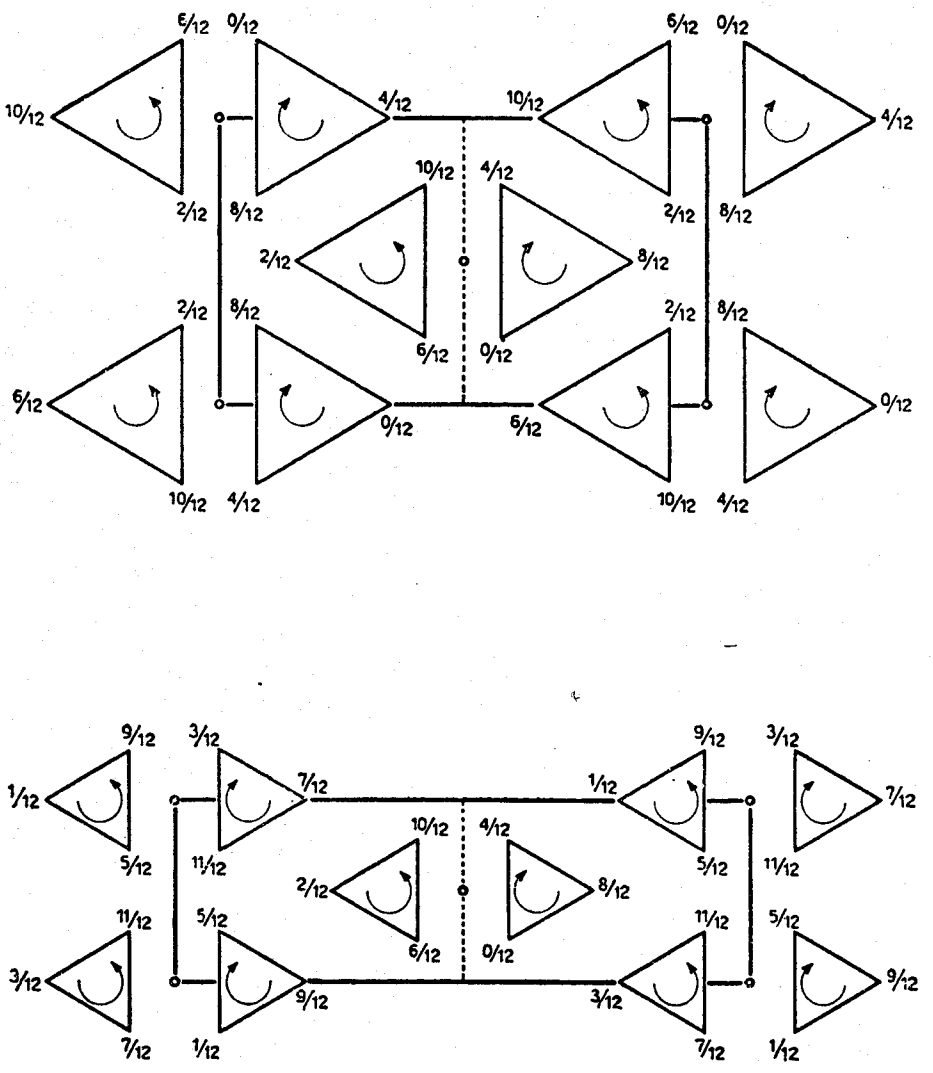


FIG. 17. Comparison between the mode of packing of polypropylene and poly-α-butene in the crystal state.

The glide plane, through which two enantiomorphous facing chains are related, turns out to be, in this case, a principal plane. Evidence that the *a-c* plane is a principal plane in polypropylene is found in the close-packing along this plane of the side groups of two enantiomorphous symmetry related chains (Fig. 17) and hence in the shortness of the *a*-axis, in its parallel orientation along the radii of spherulites and in its very low thermal expansion, as compared to the one taking place along the *b*-axis.

The mode of packing of four-fold helix poly-α-vinylnaphthalene and poly-*o*-methylstyrene is also obtained through the operation of glide planes between enantiomorphous chains, as may be to seen in Fig. 18.

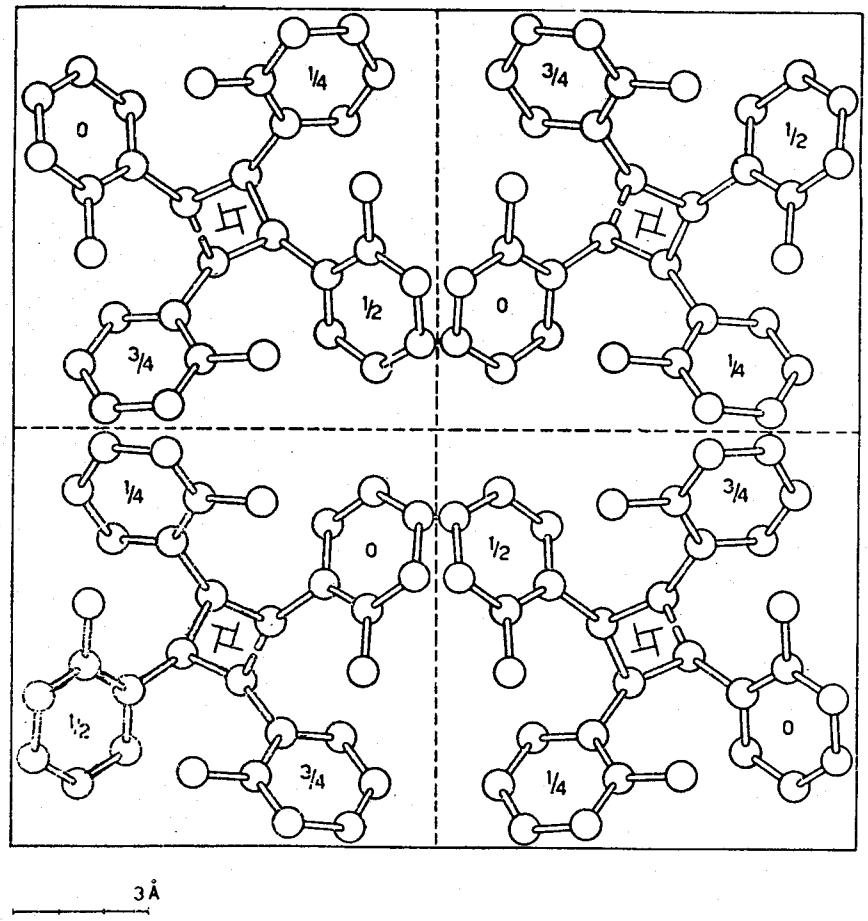


FIG. 18. Model of packing of poly-ortho-methylstyrene chains in the crystal.

3.3. *Syndiotactic polymers*

Syndiotactic polymers may be defined as *trans* stereoisomers of the vinyl head-to-tail polymers.

Their chain structure, according to the equivalence postulate, may be of the glide-plane type, repetition being achieved along the fiber axis every two (*σὺν δύο*) monomeric units, or their chain may follow a helix associated with perpendicular twofold axes.*

Now it is known that two polymers possess a syndiotactic chain structure: polyvinylchloride and one of the two crystalline stereoisomers of 1,2-polybutadiene.[32]

The bulkiness of the side groups of these two polymers does not hinder, as was the case of isotactic polymers, a planar or nearly planar conformation of the chain. Only with regard to polybutadiene a

* *Note added in proof.* This is the type of chain recently found by the AA. for syndiotactic polypropylene. The model is shown in Fig. 1 of the introductory paper of this series.

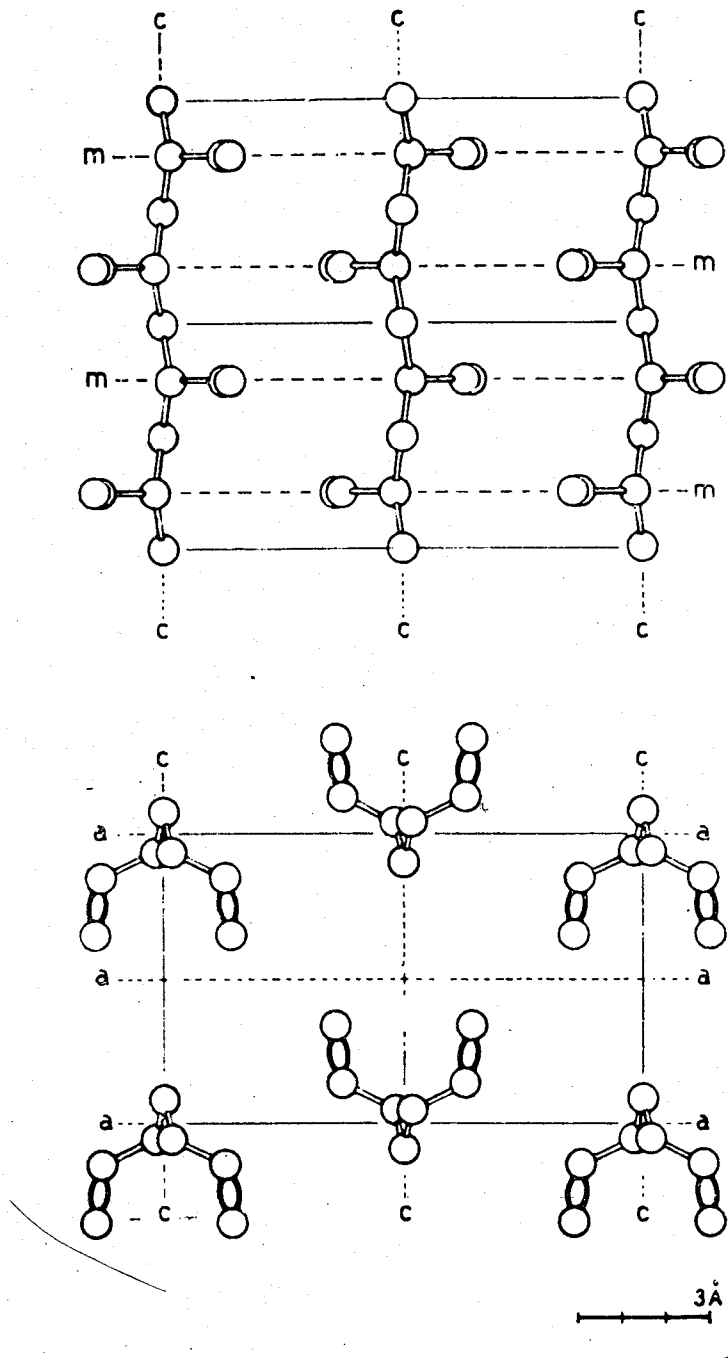


FIG. 19. Model of packing of syndiotactic—1,2 polybutadiene in the crystal.

slight deviation from a completely zigzag planar structure of the chain has been supposed (but not thoroughly confirmed) due to steric repulsions between successive side vinyl groups, the perpendicular orientation of which in regard to the chain axis obeys the principle of staggered bonds (Fig. 19, see also Fig. 9). In every case it is easy to observe that no distinction is needed between up and down molecules, and only one type of chain can be placed in the lattice.

The glide plane is maintained in the unit cell of these polymers. The molecules pack closely in layers along this plane. The crystal is

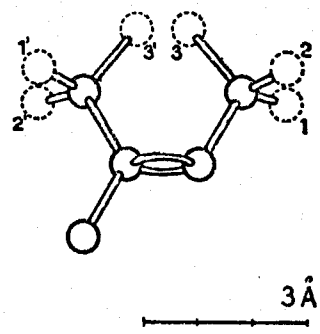


FIG. 20. Possible conformations of *cis*—1,4 isoprene unit satisfying the principle of staggered bonds.

built up of many antiparallel layers that pack at their best between themselves.

The thermal expansion occurs almost completely in syndiotactic 1,2–polybutadiene in a direction perpendicular to the glide-plane, according to the phenomena connected with the supposed existence of a principal plane of packing.

3.4. *Crystalline* 1,4–*Polydienes*

Under the heading of isotactic and syndiotactic polymers we have dealt with the known structure of 1,2 stereoisomeric polydienes. In this chapter we shall deal with the known structures of crystalline 1,4–polydienes. The synthesis of all four crystalline stereoisomers of polybutadiene and the study of their structure effected in the Institute of Industrial Chemistry of the Polytechnic of Milan, enables us to have a clearer idea of stereoisomeric phenomena in the field of polydienes.

(*a*) *Cis*–1,4 *polydienes*. — Natural rubber is the regular head-to-tail polymer built up of *cis*–1,4 isoprene units. Its chain structure may be expected uniquely in one of the two types of successions, the glide-plane and the helix-type succession. However, it is impossible, on the basis of the equivalence postulate only, to establish which of the two forms will be actually chosen by the macromolecules on crystallization, as they would not correspond to intrinsic differences in the chain configuration.

Actually a glide-plane non-planar structure is found for the chain of crystalline *cis*–1,4 polyisoprene.[33] Indeed on the basis of minimum energy considerations we should expect that:

(1) the five atoms of each monomeric unit are situated in a plane;

(2) the direction of the CH_2—CH_2 bond, in accordance with the

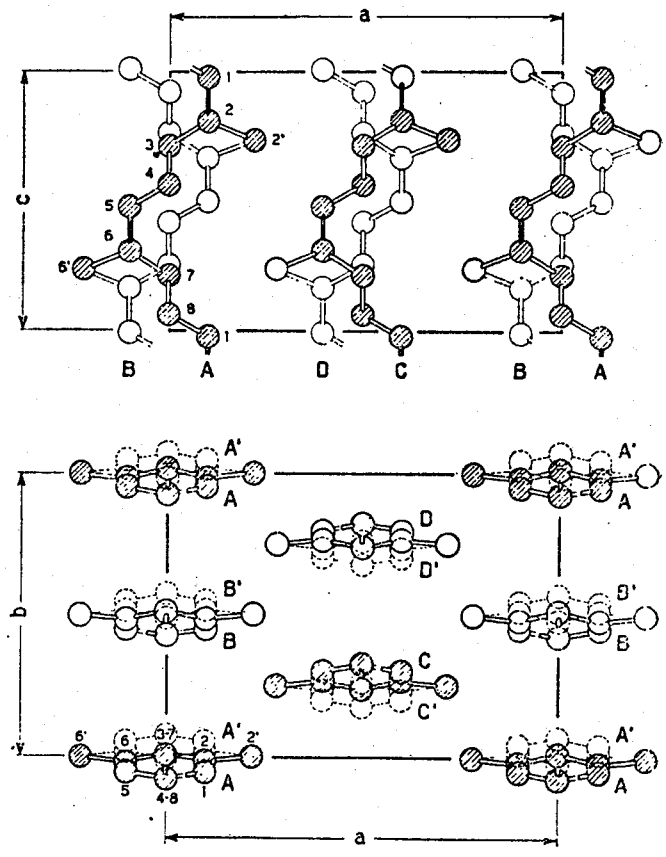


FIG. 21. Model of the structure of *cis*—1,4 polyisoprene.

principle of the staggered bonds, should assume any of the three positions outlined in Fig. 20. Positions 3 and 3′ must be discarded because of excessively short Van der Waals' contacts between atoms of the same chain;

(3) the directions of the two CH_2—CH_2 bonds on the two sides of the isoprene unit should be in opposite and parallel directions: i.e. the enantiomorphous conformations 1–1′ and 2–2′ are most likely to be realized;

(4) repetition of a monomeric unit with such a conformation, may be achieved in a helix type or in a glide-plane type succession, the first possibility being discarded because of unsuitable contacts between the methyl group and some chain carbon atoms.

The glide-plane is maintained in the lattice, according to a common feature occurring in many studied polymers, so that a close packing of molecules is expected along this plane: also, alternatively up and down molecules should be represented along this plane.

As the contacts lateral to the principal plane thus realized are due only to methyl groups, we find that, in the actual structure, successive parallel or antiparallel principal planes (*bc*) are able to pack themselves at random. It is possible to see from Fig. 21 that a layer of molecules

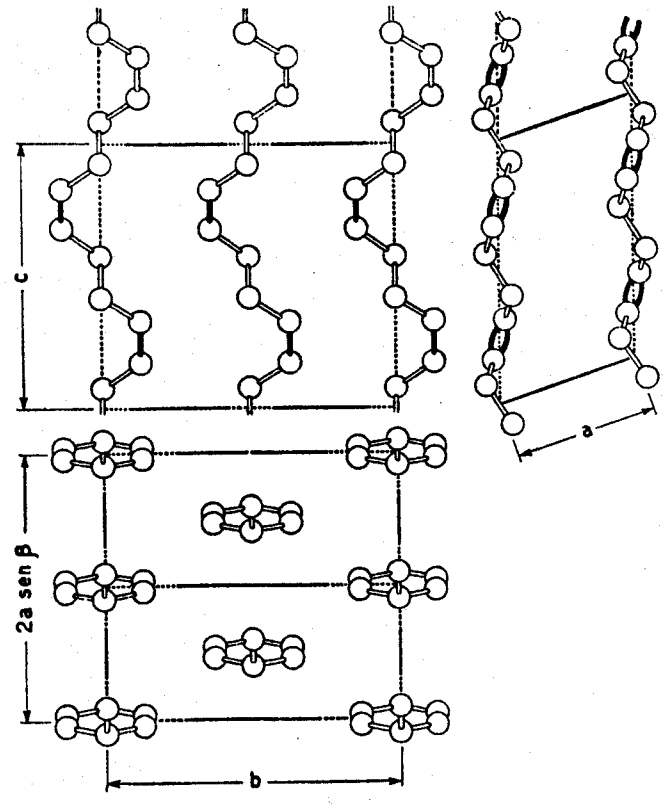


FIG. 22. Model of the structure of *cis*–1,4 polybutadiene.

such as A—B—A—B can be followed equally well by a layer such as C—D—C—D or C′—D′—C′—D′—.

Perhaps, we may explain the low melting entropy of rubber in comparison with that of guttapercha, by supposing that, in the molten state, not only a certain degree of parallelism between the chains is maintained, but also that the flexible ribbon-shaped molecules tend to maintain some kind of parallel association of the ribbons.

A great similarity of structure is to be expected between[34] *cis*–1,4 polybutadiene and *cis*–1,4 polyisoprene. Actually similar conformations of the chains were found by us, where enantiomorphous monomeric units repeat along a glide plane. However, no more distinction is needed in *cis*–1,4 polybutadiene as compared with *cis*–1,4 polyisoprene between up and down molecules; in addition, an identity period is found that is slightly longer than the one foreseeable on the basis of the staggered bonds principle; this fact is probably due to repulsions between hydrogen atoms of two CH_2 groups, in opposite position with regard to the double bond, which tend to lengthen the chain: these repulsions could not be eliminated in the case of polyisoprene because of the steric hindrance provided by the methyl group (Fig. 22).

The glide-plane may be also considered as a principal plane in poly-

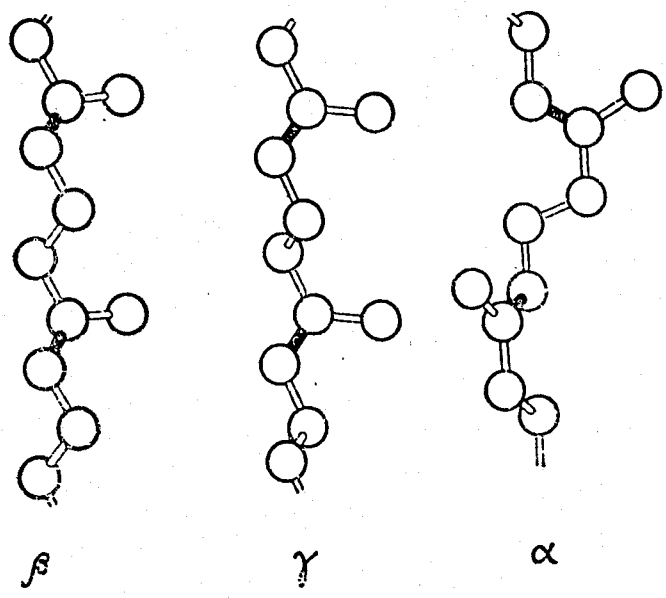


FIG. 23. Models of the chain of guttapercha (*trans*—1,4 polyisoprene) in different crystalline modifications

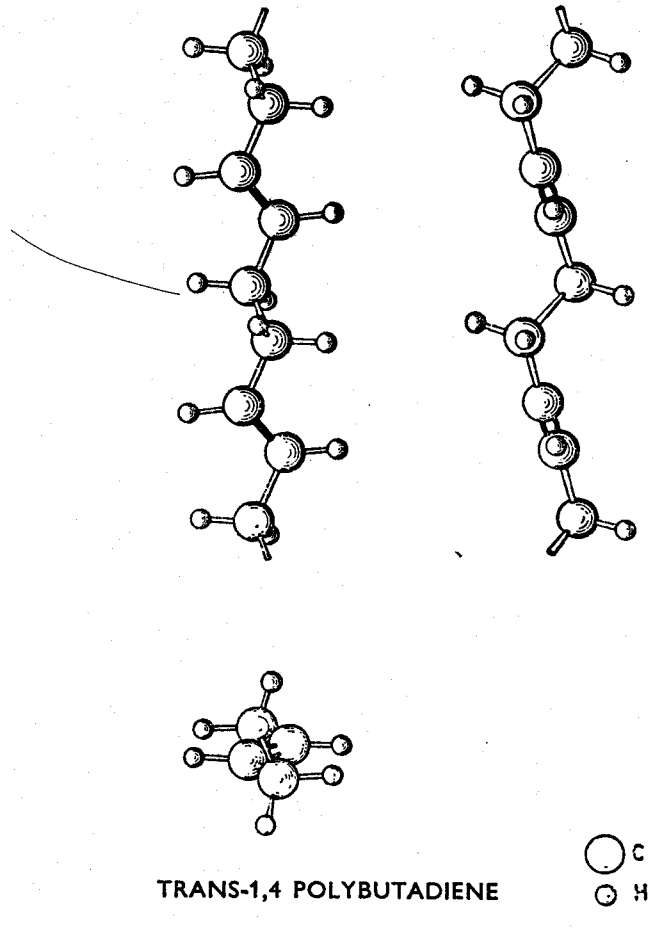


FIG. 24. Model of the chain of *trans*—1,4 polybutadiene.

butadiene, and determines a mode of packing of the macromolecules in the crystalline state, which is very similar to, but simpler than that realized in the structure of polyisoprene. In fact, there is no more need for accommodation of up and down molecules, nor for statistical distribution of successive antiparallel or parallel layers of molecules developed on the principal plane, owing to the absence of side groups.

(*b*) *Trans*–1,4 *polydienes*. The structure of guttapercha, the *trans*–1,4 head-to-tail stereoisomer of polyisoprene, was thoroughly studied for the first time by *C. W. Bunn*[35], who assessed the principal features of the structure of one of the three crystalline forms in which this polymer may occur (β form).

Some strangeness in the chain structure was eliminated by *Jeffrey*[36], by supposing and then proving that the five atoms of each isoprene unit must be in a plane.

As a matter of fact, successive *trans* isoprene units may repeat, according to the principle of staggered bonds, in various ways without any great difference in regard to steric hindrances; depending on this fact, different identity periods have been found for the three different crystalline forms in which guttapercha may occur; and yet, however, there is no complete agreement as to the form of the chains, reported by different authors.

In accordance with the equivalence and minimum energy postulate, we tentatively proposed the three forms shown in Fig. 23, whose calculated identity periods are in accordance with literature data.[37]

A chain structure similar to the one of β-guttapercha is possessed by *trans*–1,4 polybutadiene, which, according to our studies, can also appear in different forms as guttapercha does[38].

This polymer shows in its crystal state at room temperature, a chain structure (with an identity period $c = 4{\cdot}92$Å) very similar to that of β-guttapercha (Fig. 24). The almost cylindrical shape of its molecules favours a mode of chain packing in a pseudo-hexagonal array with $a = 4.54$ Å. At about 65 °C a first order transition in the solid state takes place. The structure of the high temperature phase corresponds to a mode of packing in which the chains, always remaining parallel to each other, should be more free to move and rotate along the chain axes. The phase change is accompanied by a lowering of the density of more than 9 per cent. The low density phase possesses a pseudohexagonal array with $a = 4{\cdot}88$ Å, $c = 4{\cdot}68$ Å. In a drawn fiber this transformation gives rise to a sudden reversible contractile

process, which is obviously analogous to the one taking place in living muscles.

The dimensional change along the fiber axis corresponds to the change of the *c*-dimension (about 5 per cent). We believe this is the first time that a similar phenomenon has been observed in synthetic fibers, related to a first order crystal–crystal transition.

4. OTHER NOTABLE STRUCTURES

The principles discussed in this paper with regard to hydrocarbons may be also applied to other notable structures of non-hydrocarbon polymers; thus, we report some examples to demonstrate the general validity of the principles previously discussed.

Nylons. The form of the chain of nylon is nearly planar in accordance with the principle of staggered bonds.[39] Hydrogen bonds are formed among different molecules in the same plane in which the chain is contained ; successively these planes pack themselves at their best. Along these planes the growing direction of spherulites is found.

At the melting point[41] we should expect rupture of the lattice chiefly in a direction normal to this plane. It seems plausible that thermal oscillations should occur chiefly around CH_2—CO and NH—CH_2 bonds, owing to the lower energy barriers to the rotation around these bonds than around the other chain bonds. Therefore, different deviations from the planar chain conformation should occur for nylon 6 and nylon 66 (Fig. 25), resulting in a lower packing efficiency, and therefore in a lower melting point for the former. More generally, nylons containing odd sequences of CH_2 groups should be expected to melt at a lower temperature than those containing even sequences.

There is some evidence that a slight deviation from the completely planar form is present in nylon 66 and nylon 6 even at room temperature. The fact, which has not yet been explained, that nylons have a lower heat and entropy of fusion than polyolefins or polyethers, supports our assumption that hydrogen bonds are statistically maintained on layers also in the melt.

Teflon. Teflon is the polymer of tetrafluoroethylene. According to the principle of staggered bonds the best form of the chain should be the planar one; but, owing to repulsions between fluorine atoms, a slight spiralization of the chain occurs, giving rise to a helix along a pitch of which 13 CF_2 units repeat themselves[41].

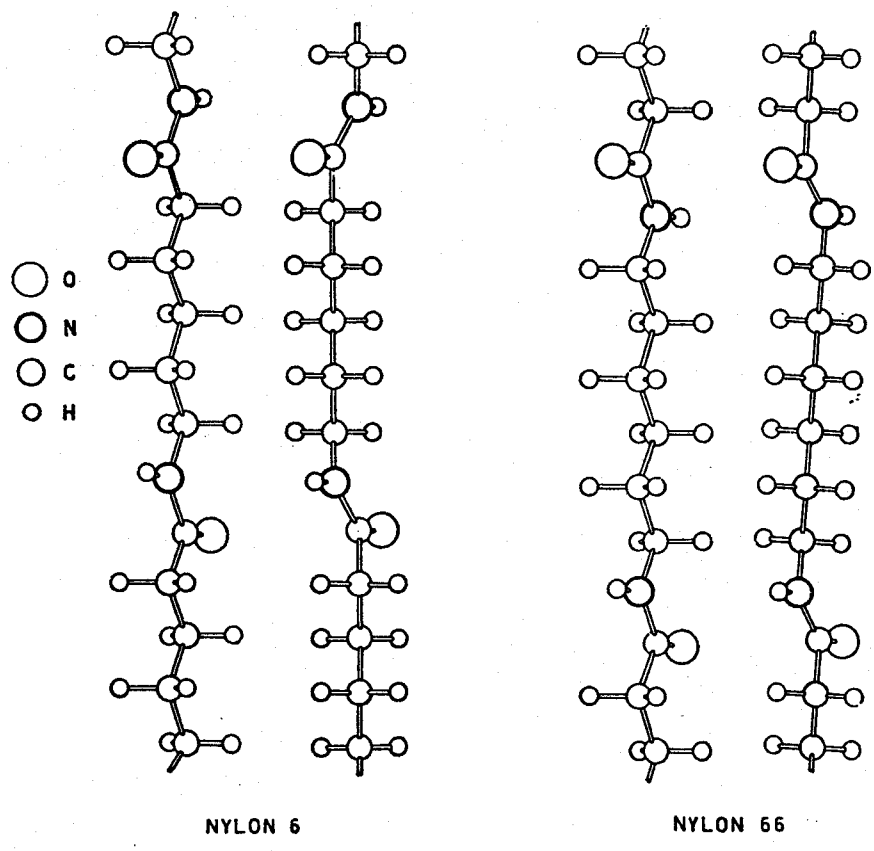


FIG. 25. Possible models of the chains of nylon 6 and nylon 66 slightly deviating from planarity in a thermal vibration.

The chains have an almost cylindrical bulkiness, so that they pack in a pseudo hexagonal array.

Polyisobutene[42], *polyvinylidene chloride*[43]. The complete crystal structures of these polymers are not known; but the form of their chains is supposed to be of the glide plane type for polyvinylidene chloride, and, according to *Liquori*, of the helix type for polyisobutene; this may be deduced from the length of the fiber axis and from the principal features of their X ray spectra. The deviation of their chain from staggered structures is certainly due to the great steric bulkiness of the side groups (see Fig. 4).

Polypropylene oxide[44]. This polymer, which was studied by us, is of some interest because the monomer contains asymmetric carbon atoms. In fact a helix structure has been found, in accordance with the equivalence postulate, satisfying the minimum energy requirements. When starting from the racemic monomer, a crystalline polymer is obtained only with the aid of stereospecific catalysts, which permit the growth of chains only from isomorphous monomeric units (Fig. 26).

Polyvinylalcohol[45]. This polymer, notwithstanding the irregular suc-

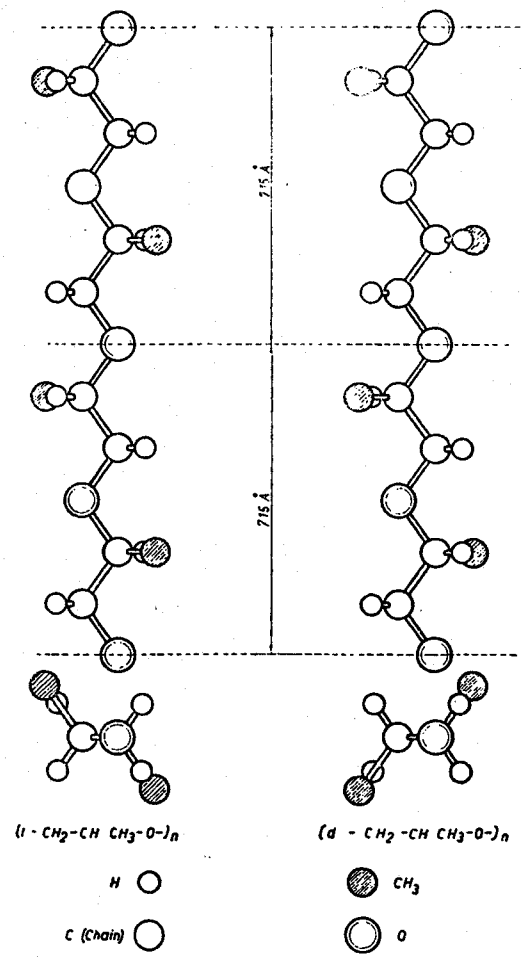


FIG. 26. Model of the chain of *d*- and *l*- polypropylene oxide.

cession of hydroxyl groups, is able to crystallize. Actually, the chain form is similar to that of polyethylene, the OH groups being of a sufficiently small size (in comparison to the H atoms) to be placed also in a *cis* succession. In the crystal structure, the molecules face in pairs, so that a random distribution of hydrogen bonds between them is possible, according to the position of the hydroxyl groups.

Proteins[46]. Depending on whether hydrogen bonds are formed between different chains or in the same chain, two different kinds of helix type structures are possible for the chain: 2-fold helix structures (Fig. 27) (the packing being determined by hydrogen bonds on opposite sides of the chain along a principal plane) or more-fold helix structures with the plane of the amide group parallel to the chain axis so as to form intramolecular hydrogen bonds within the chain (Fig. 28).

Polysaccharides[47, 48]. Cellulose may be considered as the 1,4 polymer of α-glucose; α-glucose residues follow each other in a 2-fold helicoidal path, without strain, satisfying the principle of staggered bonds.

A 2-fold helix path is no longer possible for the chain of starch,

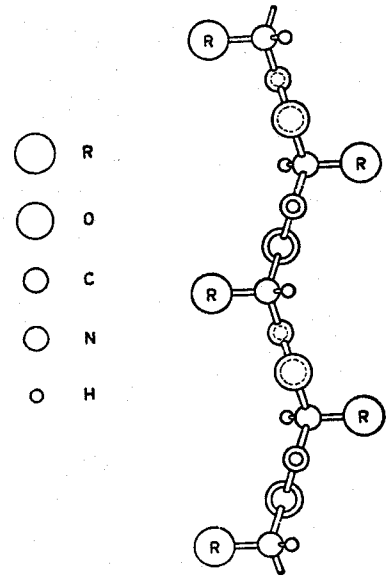


FIG. 27. Model of the chain of β Keratin type proteins.

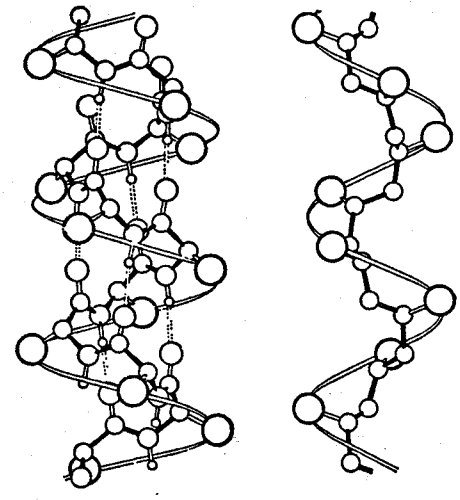


FIG. 28. Model of the chain of α Keratin type proteins (left), compared with the chain of a 3,5 helix isotactic polymer (right).

built up of β-glucose residues. It has a three-fold helix structure, and close similarity may be found between the chain structures of these two polymers and, respectively, the 2-fold helix structure of polyethylene (all *trans* bonds) and the 3-fold helix structure of polypropylene (alternatively *trans* and *gauche* bonds) (Fig. 29).

The packing of the chains of polysaccharides mostly depends on the formation of strong intermolecular hydrogen bonds.

The uniqueness of helix-type structures for the chain of crystalline proteins and polysaccharides follows directly from the equivalence postulate, as the corresponding monomeric units contain asymmetric carbon atoms.

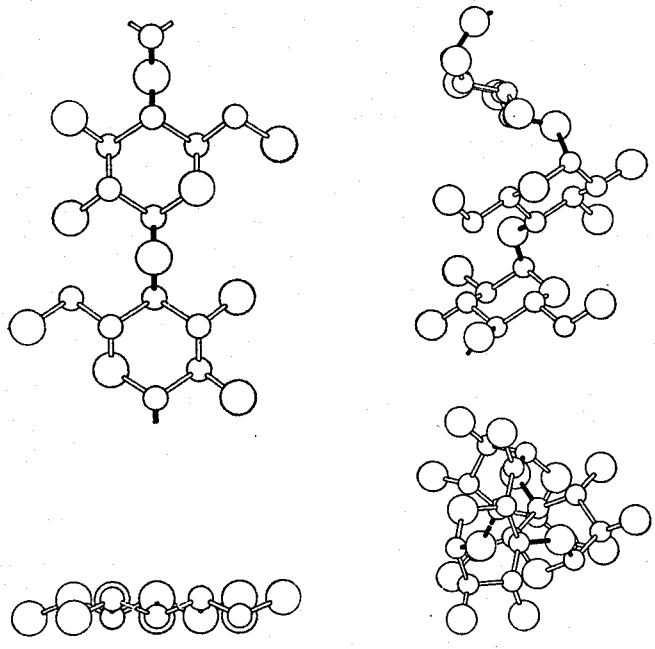


FIG. 29. Comparison between the chain of cellulose (left) and of starch (right). The pyranic ring is rigid. The black drawn bonds, joining the rigid rings through an ethereal oxygen atom, follow one to another like polymethylene (cellulose) and polypropylene (starch) bonds.

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STRUCTURE AND PROPERTIES OF ISOTACTIC POLYPROPYLENE

by G. NATTA and P. CORRADINI

(26 June 1959)

[*Nuovo Cimento*, Suppl. **15**, (10) 40 (1960)]

ABSTRACT

The crystal structure of isotactic polypropylene and its chemical-physical properties are described here. The polymer crystallizes in the *Cc* space group with the following constants of the unit cell:

$$a = 6{\cdot}65 \pm 0{\cdot}05 \text{ Å}; \; b = 20{\cdot}96 \pm 0{\cdot}15 \text{ Å}; \; c = 6{\cdot}50 \pm 0{\cdot}05 \text{ Å}$$
$$\beta = 99°20' \pm 1°.$$

The chain conformation is a threefold helix with internal rotation angles $\sigma_1 = 180$, $\sigma_2 = 60$ ($\sigma_1 = 300$, $\sigma_2 = 180$) for the right- and left-handed helices respectively, and valency angles of 114° (Fig. 1) between the carbon atoms in the chain.

The agreement between the calculated and observed structure factors is very good. Figure 2 shows the mode of packing found, for which each distance between atoms belonging to different molecules is higher than ~ 4 Å; the corresponding projection of the electron density, which allowed us to determine the atomic coordinates within $\pm 0{\cdot}05$ Å is reported in Fig. 3.

Finally, the possibility of a statistical vicariance is discussed, in view of the foreseeable existence of chains, isomorphous anticlined between themselves, without remarkably altering the packing (Fig. 4). The micrograph of a highly crystalline film of isotactic polypropylene completely spherulitized is reported in Fig. 5.

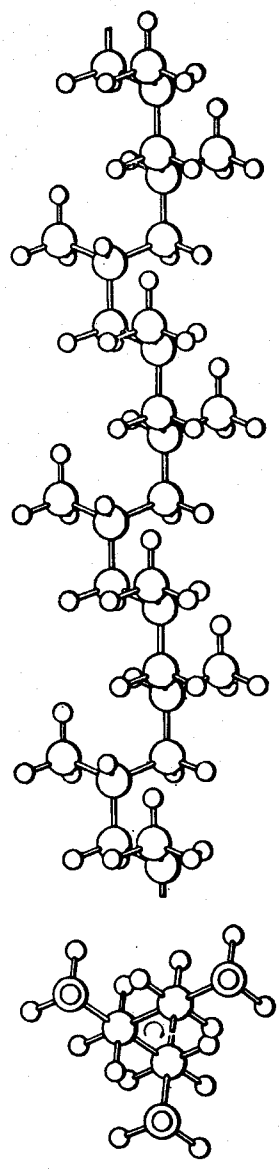


FIG. 1. Conformation of a macromolecule of polypropylene (side and end views).

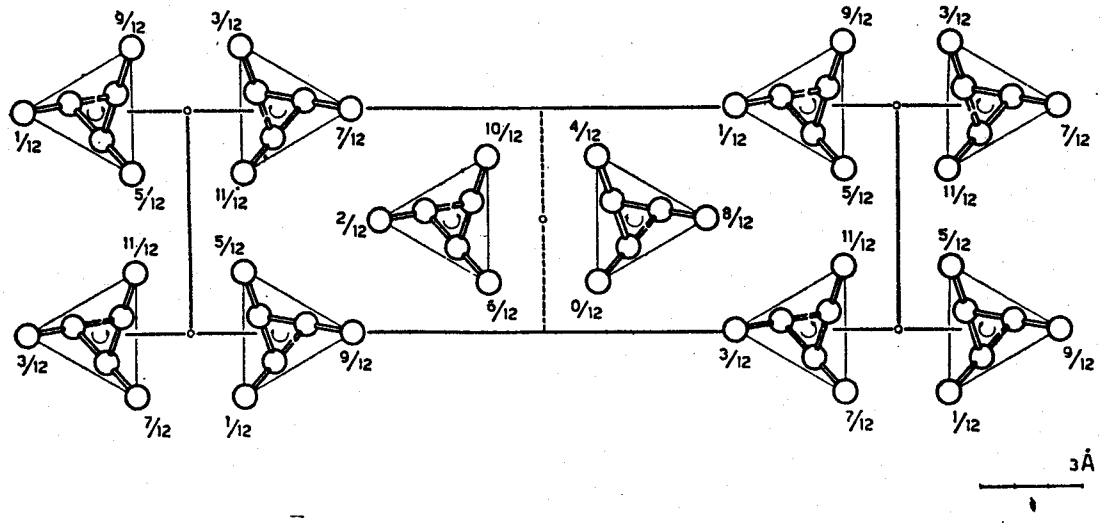


FIG. 2. Projection on (001) of the structure of polypropylene for the *Cc* space group.

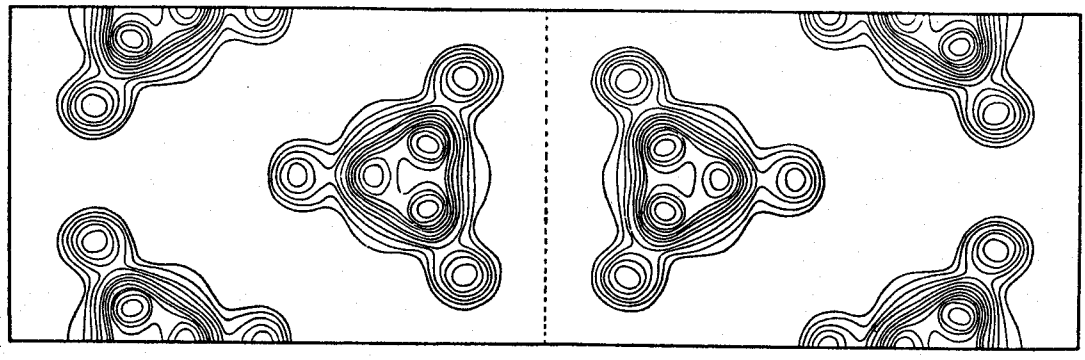


FIG. 3. Electron density projection on (001) of polypropylene calculated according to the $C2/c$ space group. Contours are drawn every 0·5e/Å². The first line corresponds to the 2e/Å² level.

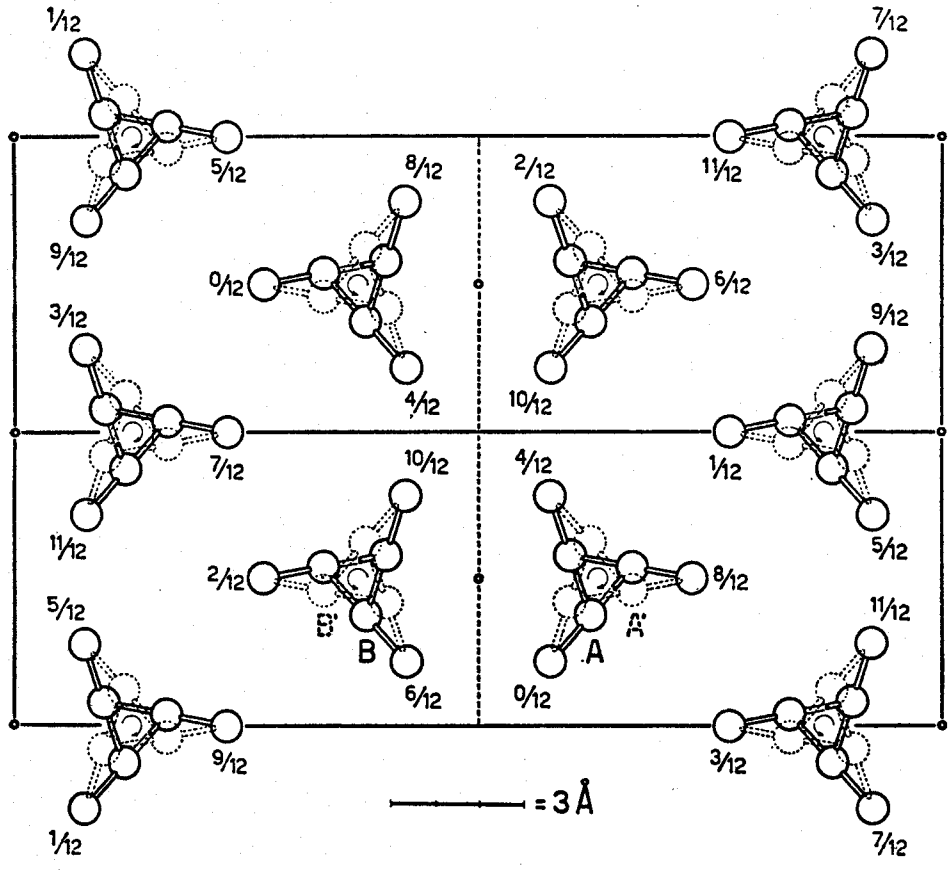


FIG. 4. Projection on (001) of the structure of polypropylene for the $C2/c$ space group.

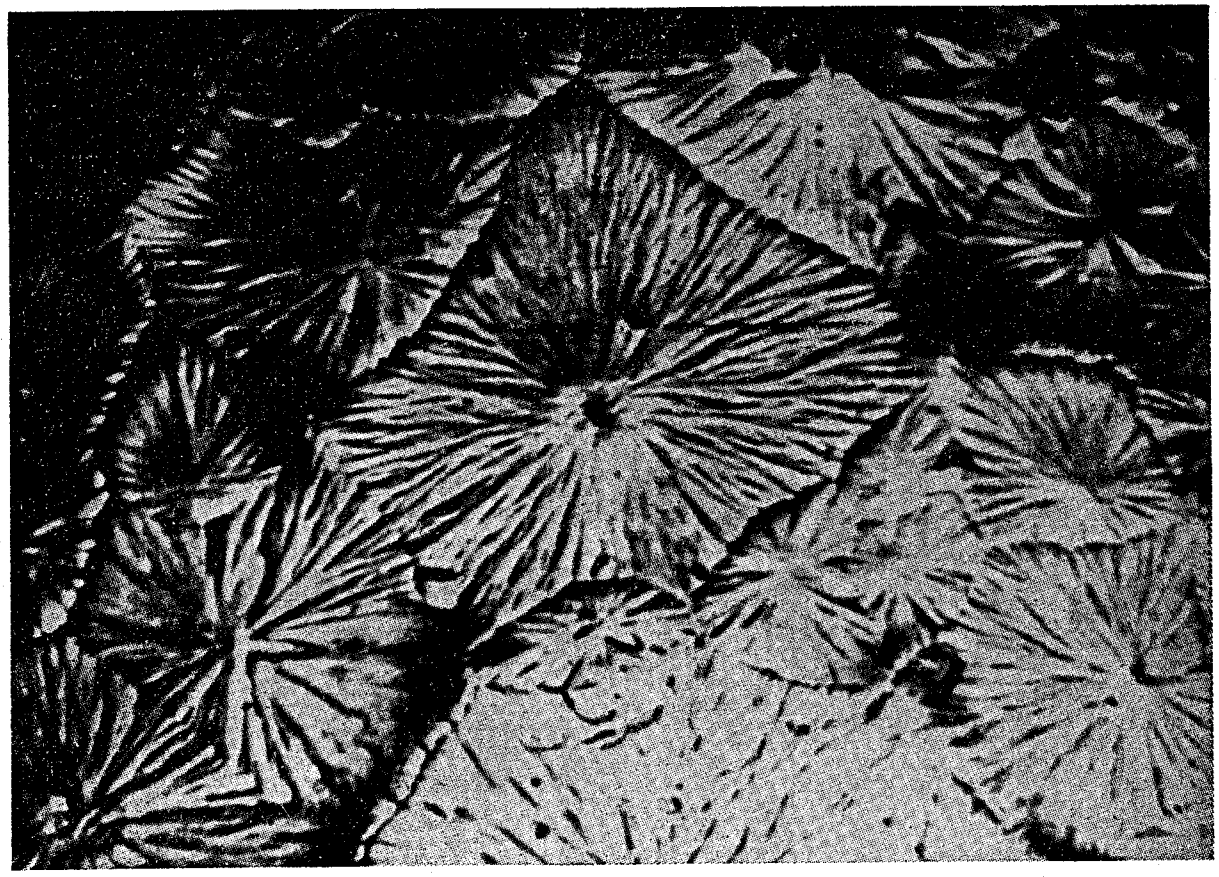


Fig 5. Photomicrograph showing spherulites in polypropylene.

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CRYSTAL STRUCTURE OF ISOTACTIC POLY-α-BUTENE

by G. NATTA, P. CORRADINI and I. W. BASSI

(26 June 1959)

[*Nuovo Cimento*, Suppl. **15**, (10) 52 (1960)]

ABSTRACT

The crystal structure of the most stable crystalline modification of isotactic poly-α-butene was examined by X-ray diffraction spectra of oriented samples. The unit cell is rhombohedral and its constants, referred to hexagonal axes, are:

$$a = 17{\cdot}7 \pm 0{\cdot}1 \text{ Å}, \quad c = 6{\cdot}50 \pm 0{\cdot}05 \text{ Å (chain axis)}$$

Space group $R3c$ or $R\bar{3}c$, $Z = 18$.

The monomeric units repeat themselves along a threefold helix and the principle of staggered bonds is strictly obeyed by all the atoms of the macromolecule (Fig. 1).

By using structure factor graphs and double oriented specimens it has been possible to determine the space position of the independent structural unit. A good improvement in the atomic coordinates has been achieved by a Fourier projection on (001). The reliability index R reaches good values for both $R3c$ and $R\bar{3}c$ space groups; the contribution of hydrogen atoms cannot be neglected. Both $R3c$ and $R\bar{3}c$ space groups demand that left-handed and right-handed macromolecules be present in the unit cell. An interesting phenomenon of statistical vicariance is noticeable between isomorphous anticlined macromolecules. Each macromolecule is surrounded by three enantiomorphous macromolecules. By taking into consideration the packing conditions imposed by the $R\bar{3}c$ space group as well as our calculations, one may

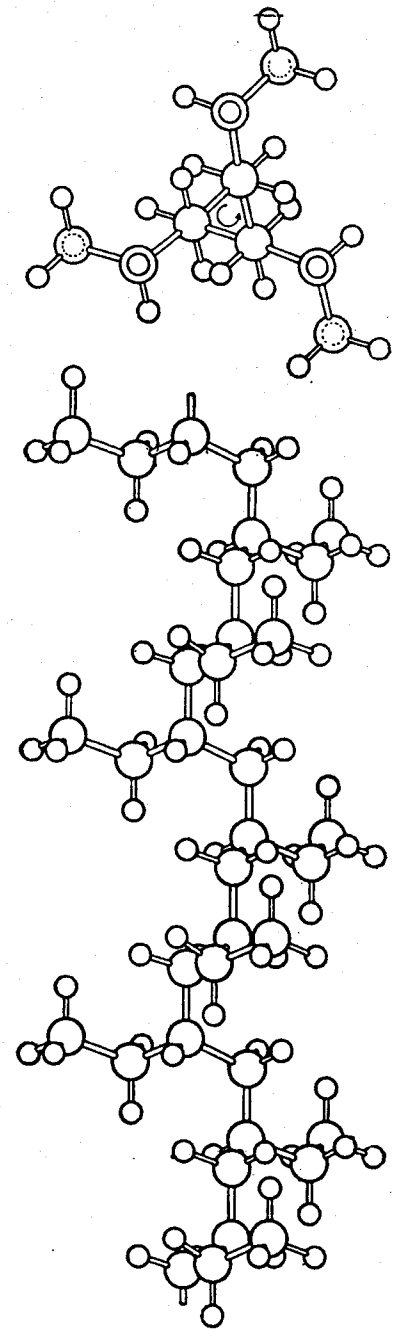


FIG. 1. The actual conformation of poly-α-butene macromolecule in the crystalline state (side and end views).

suppose that each macromolecule could be substituted by the isomorphous anticlined one; the space coordinates of the carbon atoms of the CH_3 groups are the same for the A-A′ and B-B′ anticlined macromolecules (Fig. 2). The six threefold screw axes present in the unit cell thus lose some of their polar character.

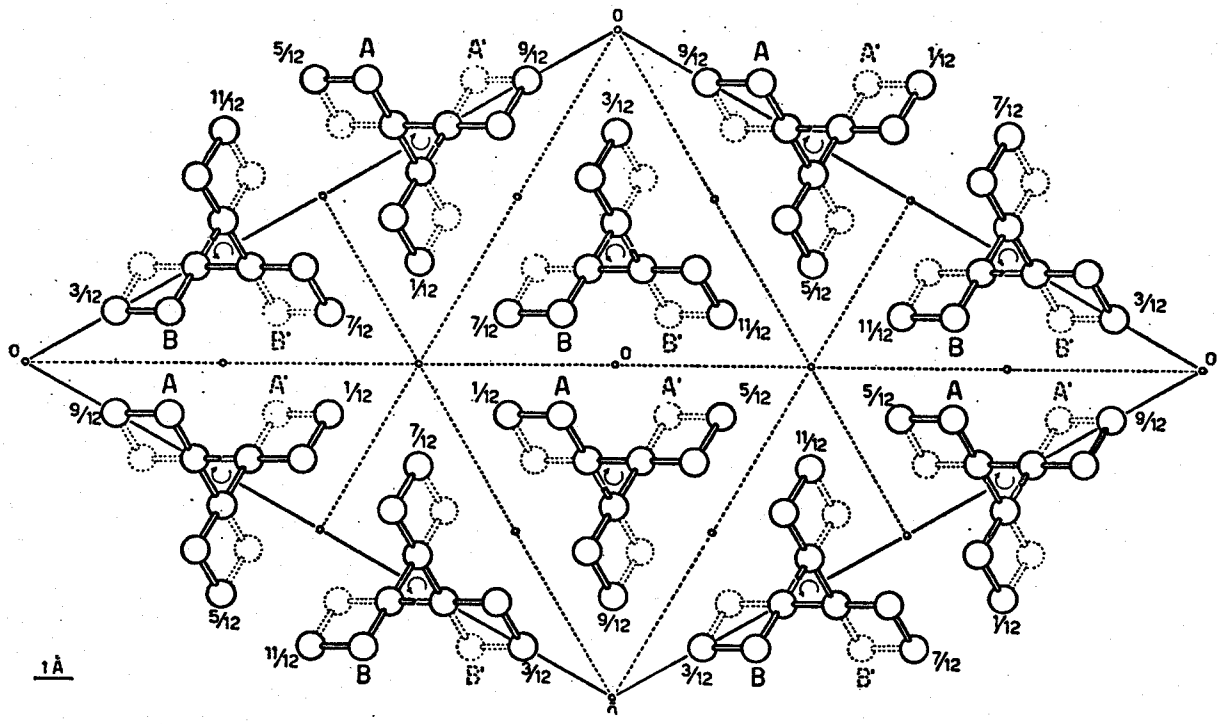


FIG. 2. Projection of the structure of poly-α-butene on (001) for the $R3c$ space group.

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CRYSTAL STRUCTURE OF ISOTACTIC POLYSTYRENE

by G. NATTA, P. CORRADINI and I. W. BASSI

(26 June 1959)

[*Nuovo Cimento*, Suppl. **15**, (10) 68 (1960)]

ABSTRACT

The crystal structure of isotactic polystyrene is described in this paper. The unit cell as determined from the X-ray diffraction spectra of oriented samples is rhombohedral, and its constants referred to hexagonal axes are:

$a = 21{\cdot}9 \pm 0{\cdot}1$ Å, $c = 6{\cdot}65 \pm 0{\cdot}05$ Å (chain axis)

$Z = 18$; space group $R3c$ or $R\bar{3}c$.

The macromolecular conformation shows a threefold helix symmetry (Fig. 1). The crystal structure of isotactic polystyrene has been determined with the aid of structure factor graphs and taking into account the intermolecular Van der Waals' distances. The calculations of structure factors have been performed for both $R\bar{3}c$ and $R3c$ space groups. An improvement of the atomic coordinates has been achieved by a Fourier projection on (001). The agreement between calculated and observed structure factors is satisfactory for both space groups. The contribution of the hydrogen atoms to the structure factors has also been considered. In the unit cell of isotactic polystyrene, as we have observed in the case of isotactic polymers of propylene and butene–1, equal amounts of left-handed and right-handed macromolecules are present.

According to our calculations a statistical vicariance may be possible between isomorphous anticlined A-A′ or B-B′ macromolecules (Fig. 2).

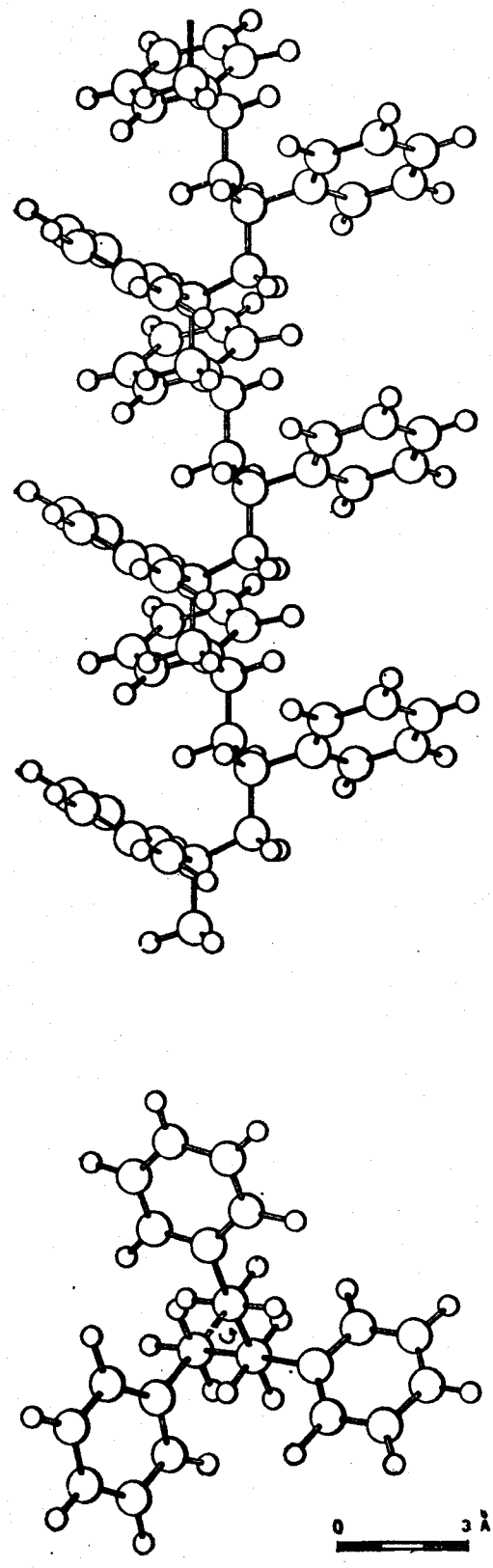


FIG. 1. Conformation of the isotactic polystyrene macromolecule in the crystal state (side and end views).

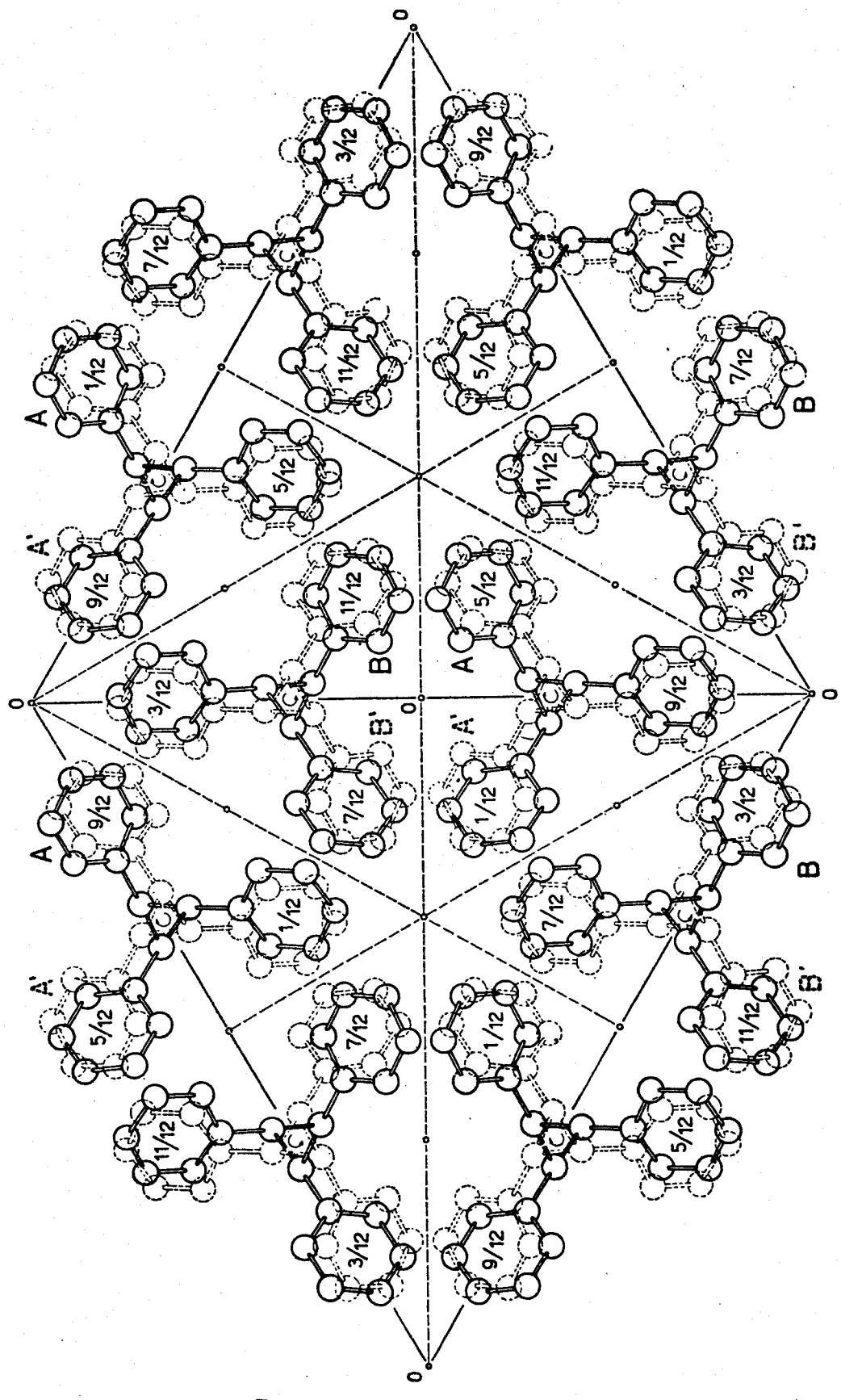


FIG. 2. Projection on (001) of isotactic polystyrene structure according to the $R\bar{3}c$ space group. (For this space group, a statistical vicariance may exist around the same threefold screw axis of isomorphous anticlined macromolecules.)

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CRYSTAL STRUCTURE OF POLY-*O*-FLUOROSTYRENE

by G. NATTA, P. CORRADINI and I. W. BASSI

(26 June 1959)

[*Nuovo Cimento*, Suppl. **15**, (10) 83 (1960)]

ABSTRACT

The X-ray diffraction spectra obtained from oriented fibres of poly-*o*-fluorostyrene are very similar to those obtained from fibres of isotactic polystyrene. The diffraction spectra are interpreted on the basis of a rhombohedral unit cell; its constants, referred to hexagonal axes, are:

$a = 22{\cdot}15 \pm 0{\cdot}10$ Å, $c = 6{\cdot}63 \pm 0{\cdot}05$ Å (chain axis)

$Z = 18$; space group $R3c$ or $R\bar{3}c$.

The shape of the macromolecule is that of a threefold helix (Fig. 1). The macromolecule has been constructed on the basis of the known structure of isotactic polystyrene. There are two ortho non-equivalent positions for the fluorine atom; a choice between them is possible on the basis of intramolecular Van der Waals' distances. The atomic coordinates of the independent structural unit have been determined by trial and error methods. The agreement between the calculated and observed structure factors is satisfactory only for the non-centrosymmetric $R3c$ space group. An improvement of the atomic coordinates has been achieved by means of a Fourier projection on (001). The packing conditions of $R3c$ space group demand that equal amounts of left-handed and right-handed macromolecules be present in the crystallites (Fig. 2).

The six threefold screw axes contained in the unit cell have the same polar direction. Contrary to what happens for the crystallites of iso-

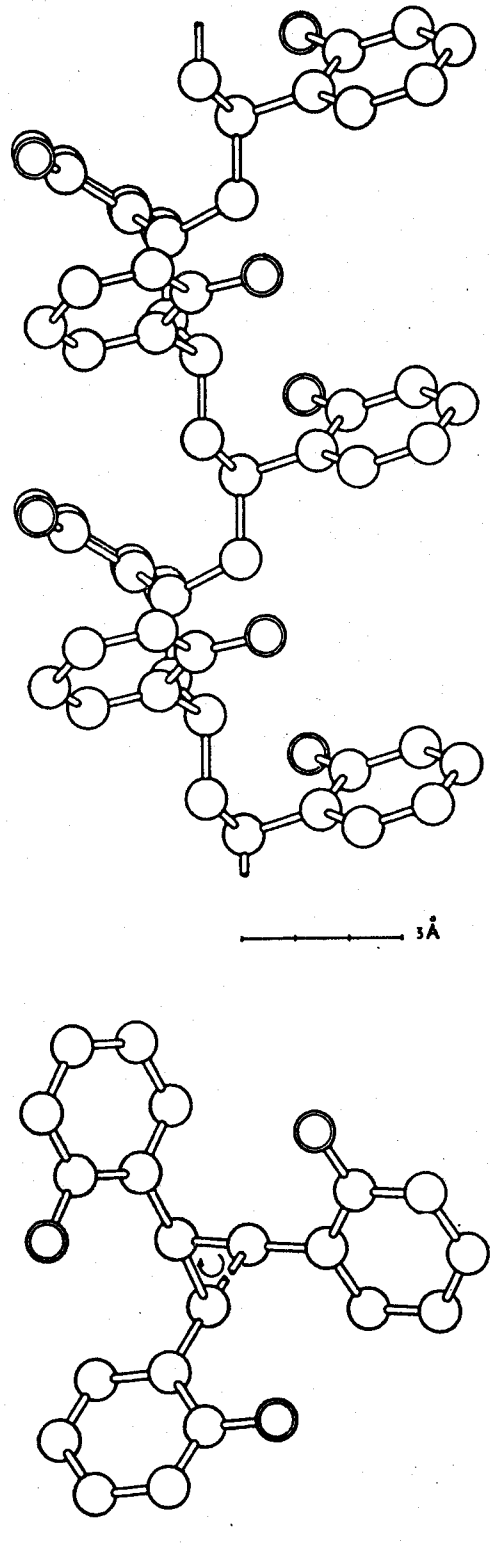


FIG. 1. Conformation of the poly-*o*-fluorostyrene macromolecule (side and end views).

tactic polystyrene and poly-α-butene, the statistical vicariance between the anticlined isomorphous macromolecules is not present in the crystallites of isotactic poly-*o*-fluorostyrene.

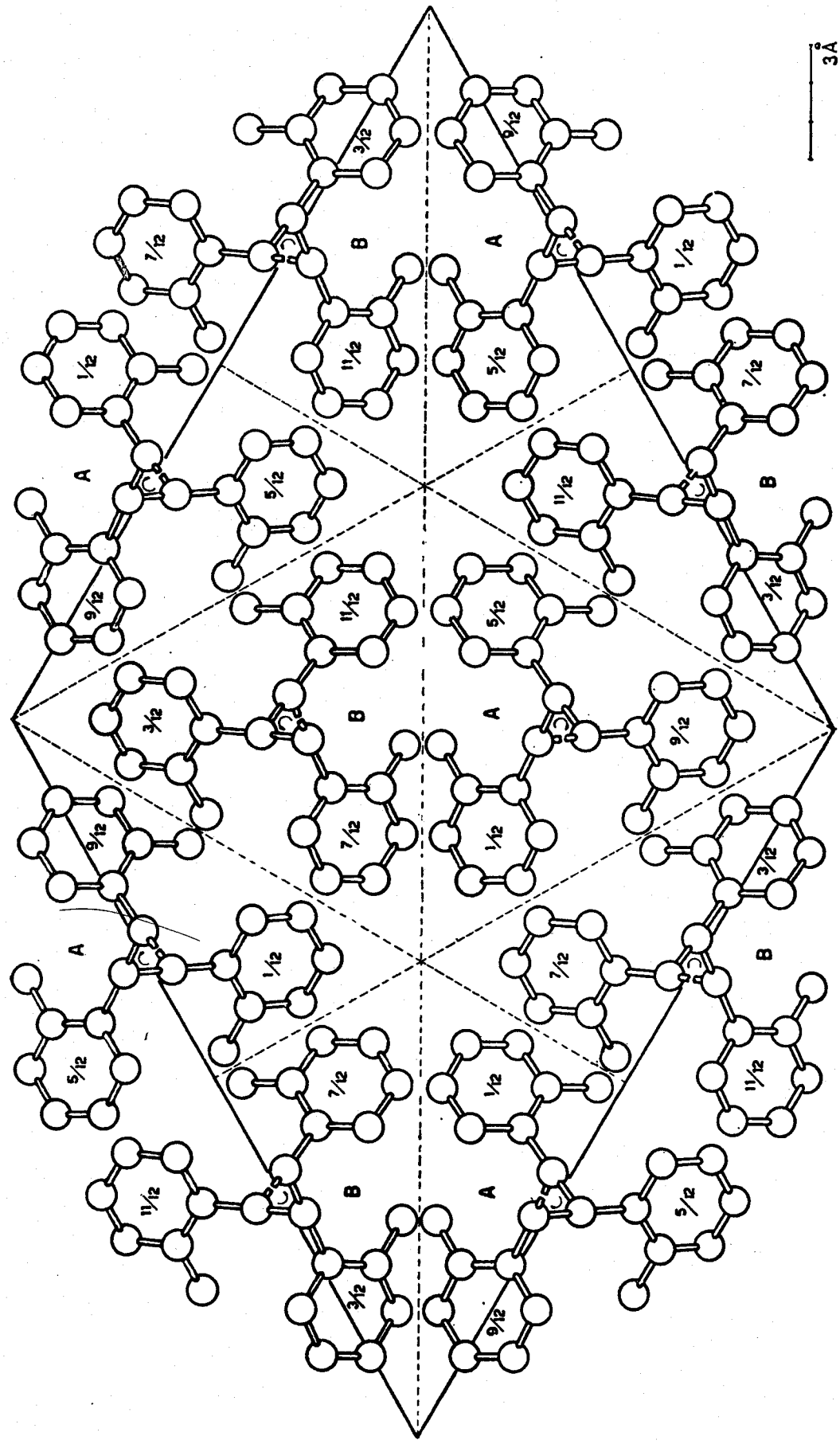


FIG. 2. Projection on (001) of the unit cell content of poly-*o*-fluorostyrene (*R*3*c* space group).

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CRYSTAL STRUCTURE OF POLY-*O*-METHYLSTYRENE

by P. CORRADINI and P. GANIS

(26 June 1959)

[*Nuovo Cimento*, Suppl. **15**, (10) 96 (1960)]

ABSTRACT

The chain structure and the crystal structure of isotactic poly-*o*-methylstyrene are reported here. The chain shows a four-fold symmetry (Fig. 1) with an identity period of 8·10 Å, the unit cell is tetragonal ($I4_1cd$) with axes $a=b=19{\cdot}01$ Å and $c=8{\cdot}10\pm0{\cdot}05$ Å.

There are two ortho non-equivalent sites for the methyl group; a choice between them is possible on the basis of intramolecular contact distances. The mode of packing of isotactic poly-*o*-methylstyrene macromolecules has been determined taking into account the achievement of the best intermolecular Van der Waals' distances.

For the final structure model, all approaches are higher than 3·8 Å, and the agreement between calculated and observed structure factors is very good.

Each right-handed helix is surrounded by four left-handed helices, thus giving rise to a packing that is very similar to that found for poly-*o*-fluorostyrene (Fig. 2).

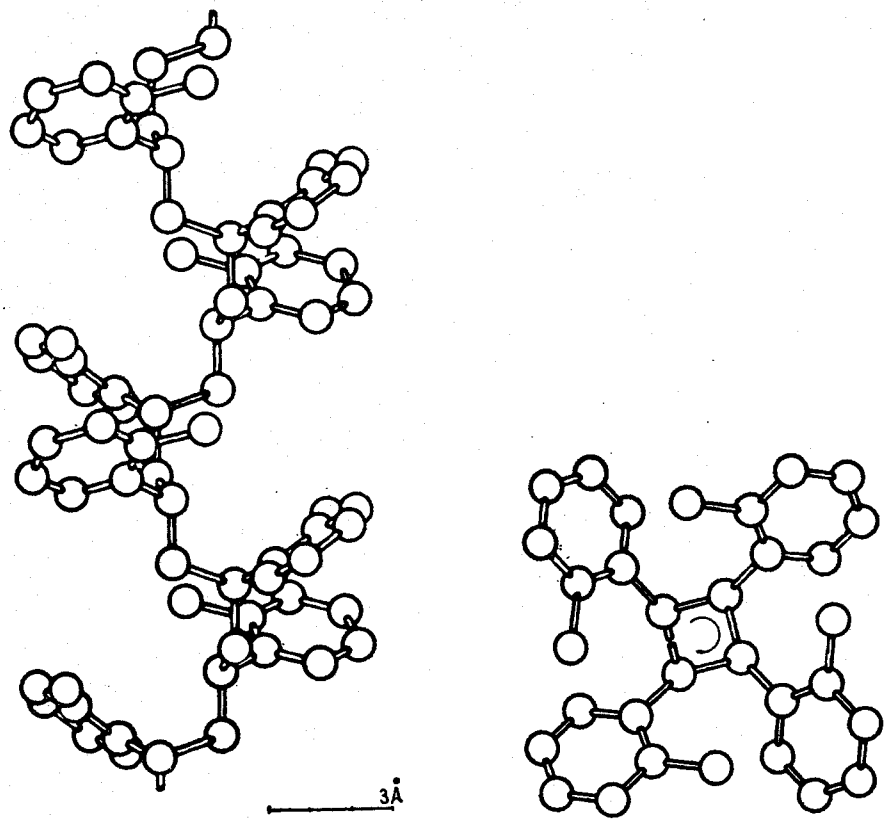


FIG. 1. Conformation of the poly-*o*-methylstyrene macromolecule in the crysta state (side and end views).

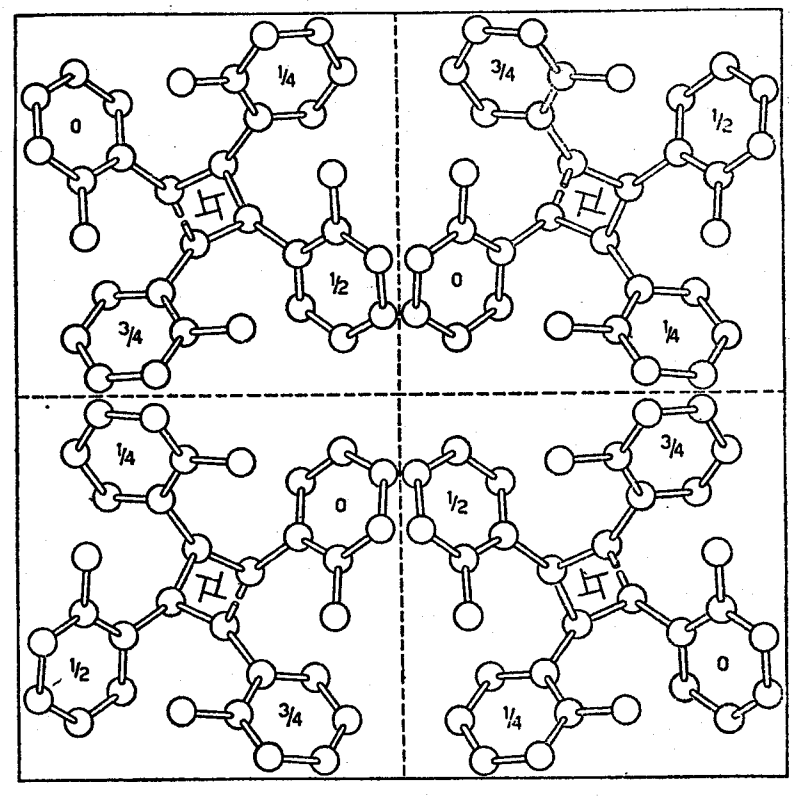


FIG. 2. Model of the structure of poly-*o*-methylstyrene on (001).

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CRYSTAL STRUCTURE OF POLY-α-VINYLNAPHTHALENE

by P. CORRADINI and P. GANIS

(26 June 1959)

[*Nuovo Cimento*, Suppl. **15**, (10) 104 (1960)]

ABSTRACT

A helix conformation with a fourfold symmetry (Fig. 1) and a tetragonal unit cell with axes $a = b = 21{\cdot}20 \pm 0{\cdot}10$ Å and $c = 9{\cdot}10 \pm 0{\cdot}05$ Å (space group $I4_1cd$) has been found for isotactic poly-α-vinylnaphthalene.

The mode of packing is analogous to that of poly-*o*-methylstyrene (Fig. 2); in this model all the Van der Waals' contacts between carbon atoms belonging to different molecules are quite satisfactory and the agreement between calculated and observed structure factors is very good.

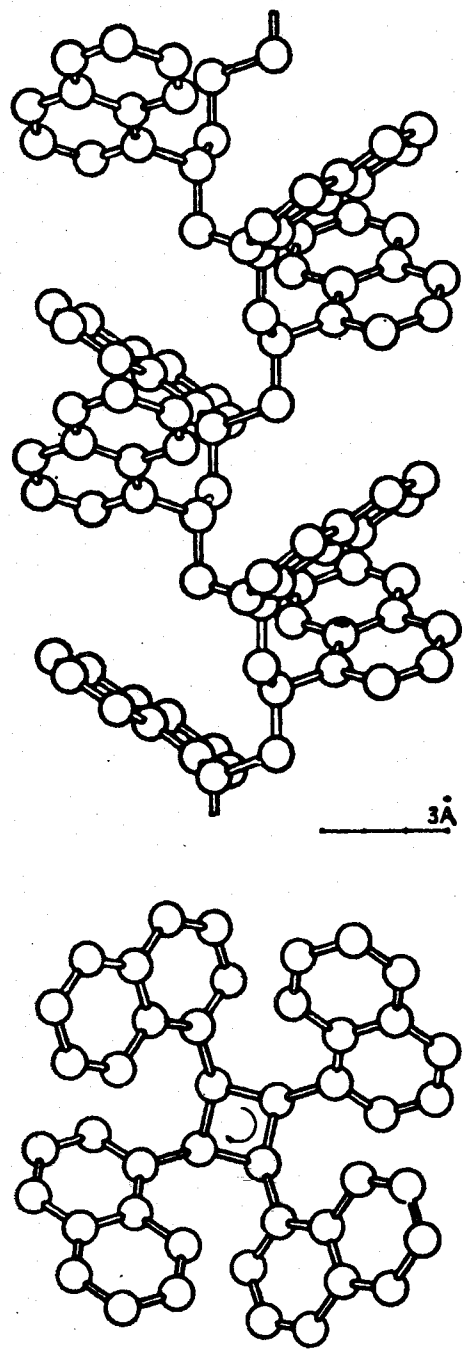


FIG. 1. Conformation in the crystal state of poly-α-vinylnaphthalene macromolecule (side and end views).

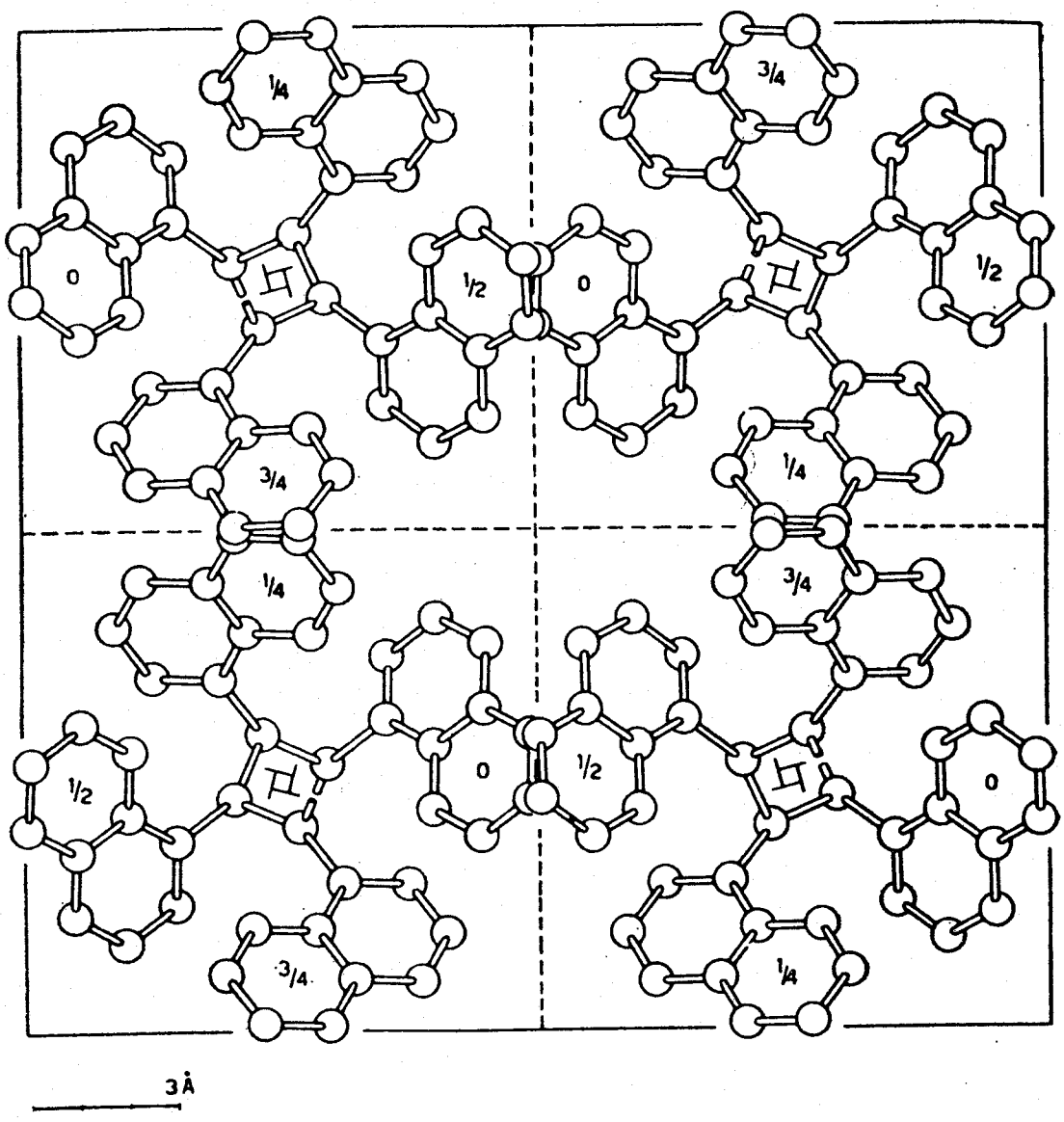


FIG. 2. Model of the structure of poly-α-vinylnaphthalene projected on (001).

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CRYSTAL STRUCTURE OF *CIS*-1,4 POLYBUTADIENE

by G. NATTA and P. CORRADINI

(26 June 1959)

[*Nuovo Cimento*, Suppl. **15**, (10) 111 (1960)]

ABSTRACT

Spectra of stretched polymer samples, performed at —30°C, have provided X-ray data which are fit for a complete determination of the crystal structure. *Cis*-1,4-polybutadiene crystallizes in a monoclinic unit cell with the following lattice constants: $a = 4{\cdot}60$ Å, $b = 9{\cdot}50$ Å, $c = 8{\cdot}60$ Å (chain axis), $\beta = 109°$. The systematic absences and considerations on the symmetry of the macromolecules and their mode of packing lead to the C_{2h}^6 space group for crystalline *cis*–1,4 polybutadiene. On the basis of this space group, a good agreement between calculated and observed structure factors is achieved.

Figure 1 shows the chain model characterized by the presence of a glide plane along the chain (chain symmetry *tic*); Fig. 2 shows the mode of packing in a way perpendicular and parallel to the chain axis.

A comparison was made among the chain structures of the different stereoisomers of polybutadiene; moreover, we emphasized the close structural analogy existing between *cis*-1,4 polybutadiene and *cis*-1,4 polyisoprene.

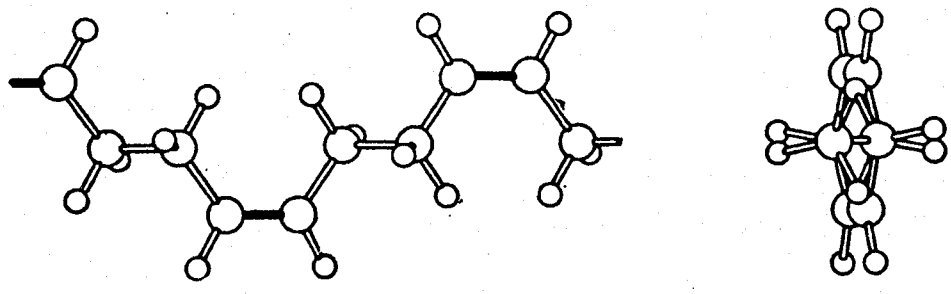


FIG. 1. Conformation in the crystal state of the chain of *cis*–1,4 polybutadiene.

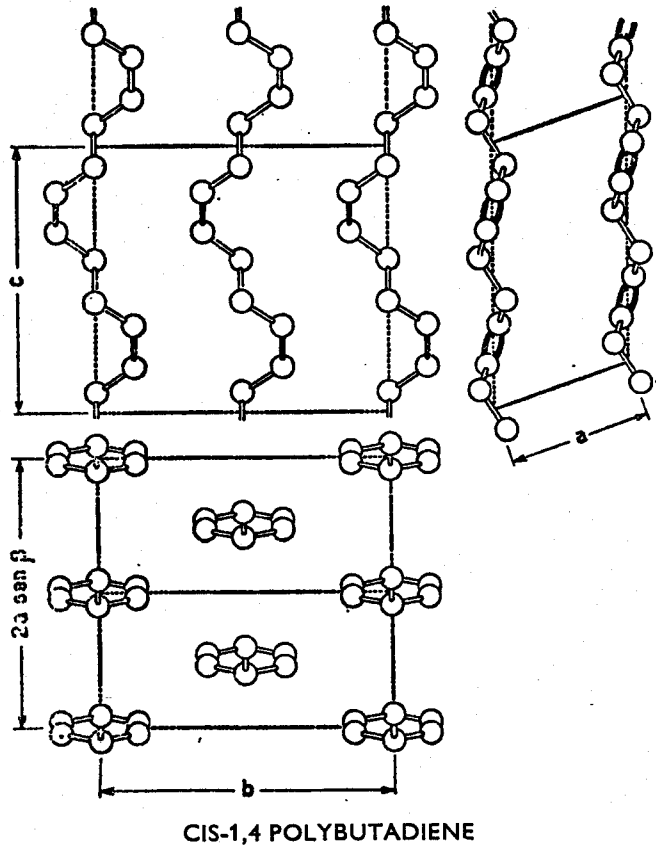


FIG. 2. Model of the structure of *cis*–1,4 polybutadiene.

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INFRARED SPECTRA OF STEREO-ORDERED POLYMERS OF VINYLAROMATIC MONOMERS. NOTE 1: ISOTACTIC POLYSTYRENE

by D. MORERO, E. MANTICA, F. CIAMPELLI and D. SIANESI

(26 June 1959)

[*Nuovo Cimento*, Suppl. **15**, (10) 122 (1960)]

ABSTRACT

In this paper the I.R. spectra of atactic polystyrene are compared with those of isotactic polystyrene, either amorphous or crystalline.

This comparison has allowed us to suggest that an almost complete identity exists between the I.R. spectra of atactic and amorphous isotactic polystyrenes; the observed differences are very slight; only the splitting of the band at 1070 cm^{-1} of atactic polystyrene into two at 1061 and 1078μ respectively, in amorphous isotactic polystyrene is remarkable.

One must also consider that such a splitting can be attributed to the presence of short chain portions which are regularly spiralized in the amorphous isotactic polystyrene, as a residue of crystallinity in the amorphous product.

Considerable differences are, on the contrary, observed between the amorphous-isotactic and the crystalline-isotactic polystyrene; the regular spiralization of the chains causes the appearance of some new bands, the most characteristic of which are at 784, 897, 920, 1052, 1083, 1260 cm^{-1}.

An examination with polarized light of a crystalline, isotactic polystyrene film, oriented by stretching, allowed us to obtain a good interpretation of the I.R. spectrum.

Whereas, the I.R. spectrum of atactic polystyrene can be interpreted as the sum of the bands originated by the monosubstituted phenyl group and by the CH_2 and CH groups, the spectrum of crystalline isotactic polystyrene agrees perfectly with what can be theoretically foreseen from the study of the vibrations of the identity period comprising three monomeric units arranged according to a helix having a C_3 symmetry.

On the other hand, it has been impossible to observe those I.R. absorption bands, attributable to the crystalline lattice; all the I.R. bands which are characteristic of crystallinity can be assigned to the interactions between adjacent monomeric units of the same chain and not to the interactions between adjacent chains.

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INFRARED SPECTRA OF POLYBUTADIENES. NOTE I: SYNDIOTACTIC-1,2 POLYBUTADIENE

by D. MORERO, E. MANTICA and L. PORRI

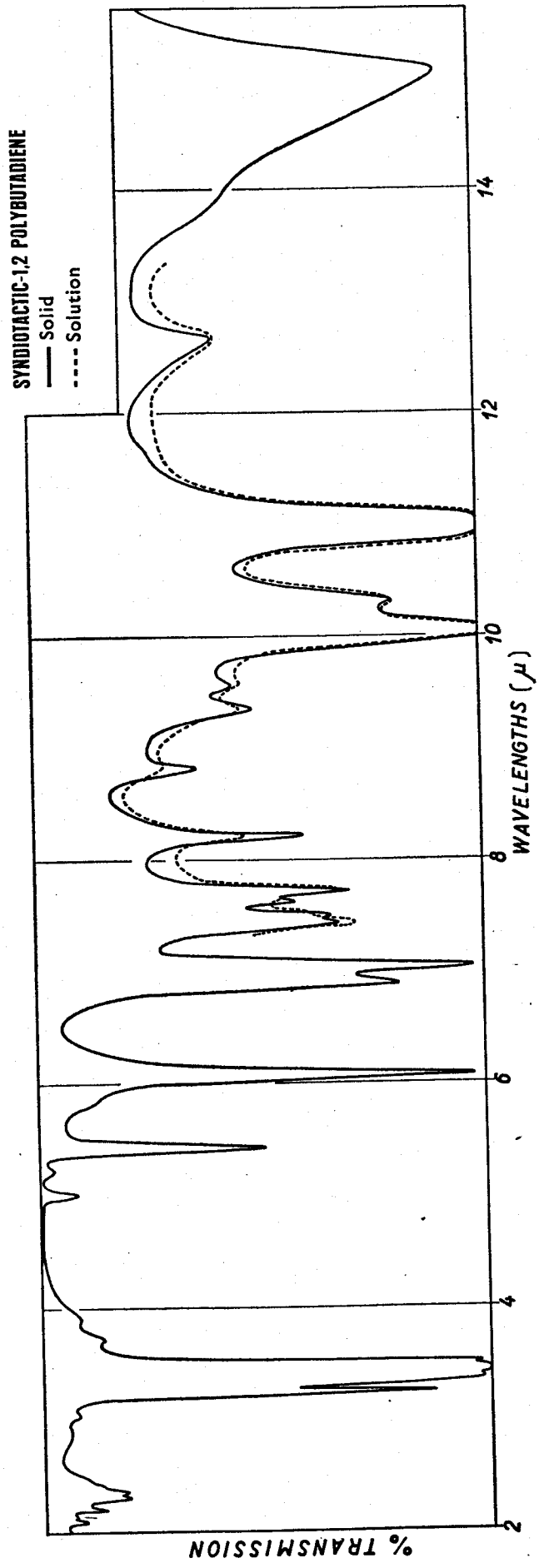
(26 June 1959)

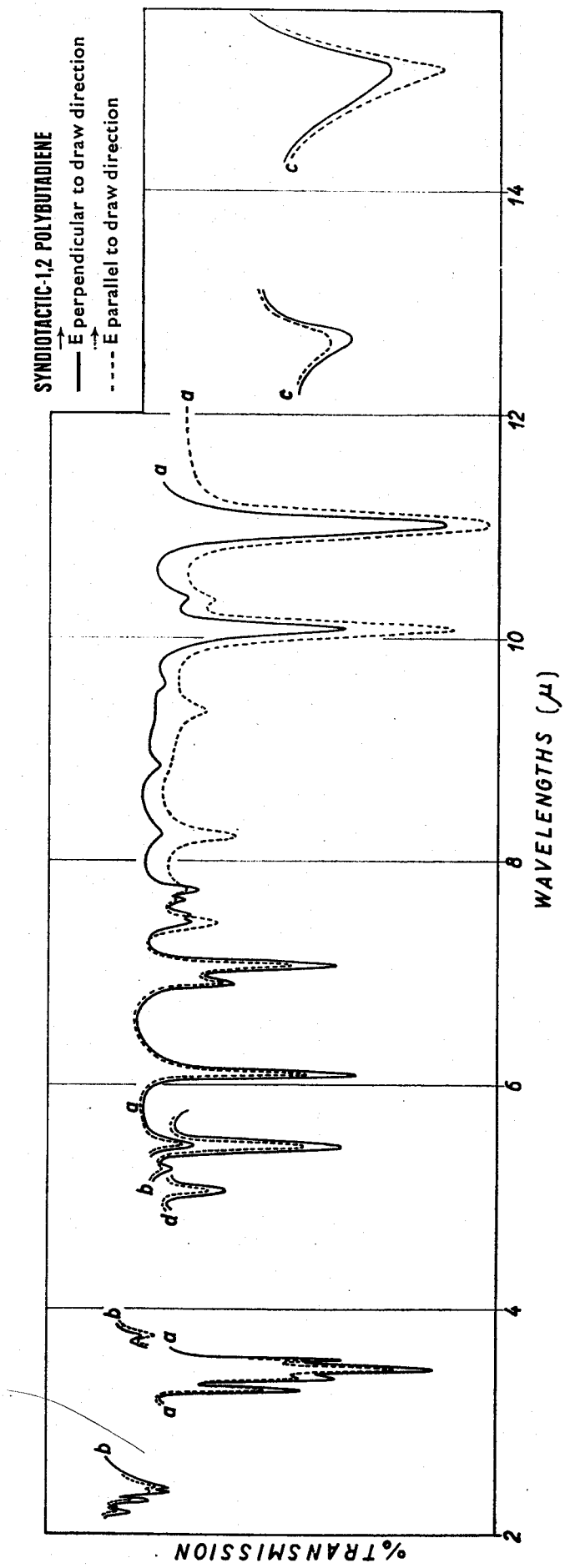
[*Nuovo Cimento*, Suppl. **15**, (10) 136 (1960)]

ABSTRACT

The infrared spectrum of syndiotactic-1,2 polybutadiene was studied on polymer prepared by polymerization of butadiene with the aid of a catalyst based on triethyl aluminum and vanadium triacetylacetonate, and subsequent cold extraction with benzene. The absorption spectrum in the range from 2 to 15μ has been obtained by a Perkin-Elmer Model 21 double beam spectrophotometer equipped with a NaCl prism on films obtained by evaporation from solutions or prepared by moulding between metal plates heated to 160°C. Also studied was the behaviour of cold stretched samples by polarized light, using AgCl transmission polarizers. The results obtained are shown in Figs. 1 and 2.

Also discussed were the assignments of the I.R. absorption bands considering a single macromolecule and the two monomeric units constituting the unit cell. A further simplification was introduced considering the chain of the carbon atoms as planar. By these approximations the symmetry elements were fixed and it was concluded that the symmetry elements define a factor group isomorphous with the point group C_{2v}. The number of normal modes under the different symmetry species (A_1, A_2, B_1 and B_2) was calculated, and the polarization and selection rules for the Raman and I.R. activities were considered for the fundamental frequencies and the harmonic and combination tones.


SYNDIOTACTIC-1,2 POLYBUTADIENE
Solid
Solution
14
12
10
8
6
4
2
WAVELENGTHS (μ)
% TRANSMISSION


SYNDIOTACTIC-1,2 POLYBUTADIENE
E perpendicular to draw direction
E parallel to draw direction
% TRANSMISSION
WAVELENGTHS (μ)
2
4
6
8
10
12
14
a
b
c
d
g

Assignments have been proposed for some bands present in the spectrum, taking into account the known correlations and the polarization properties of the bands expected theoretically and found in experiments.

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ORGANOMETALLIC COMPLEXES AS CATALYSTS IN IONIC POLYMERIZATION*

by G. NATTA and G. MAZZANTI

(30 June 1959)

[*Tetrahedron* **8**, 86 (1960)]

ABSTRACT

The synthesis and properties of some organometallic complexes containing titanium and aluminum, which have been isolated by us in the pure state by crystallization from solvents, are here described. Whereas some of these complexes contain bridge chlorine atoms between titanium and aluminum, others do not contain halides in their molecules.

The catalytic properties exhibited by these complexes for the polymerization of ethylene and of α-olefins, are described.

Finally the nature of the co-ordinated anionic polymerizations and the causes of the stereospecificity in the polymerization of the vinyl monomers are discussed.

During the previous Symposium on the Chemistry of Co-ordination Compounds in Rome[1] we had given a report on the importance assumed by certain catalytic systems containing transition metals and metal-organic bonds, acting by a mechanism which has been defined by us as anionic co-ordinated.[2]

As may be known, the catalysts discovered by Ziegler belonging to that class had enabled him to prepare low-pressure linear polyethylene.[3] Working with Ziegler type catalysts, our School succeeded in discovering sterically differentiated polymers of α-olefins[4] and of diolefins.[5] Later we discovered highly stereospecific catalysts which enabled us to obtain crude polymers having a high content of crystallizable macromolecules.[6]

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* This communication was presented in a summarized form at the International Conference on Coordination Chemistry held in London, April 1959.

Several authors have given an interpretation of the mechanism of ethylene polymerizations, as well as of the stereospecific polymerizations of propylene based on the hypotheses of the structure of the catalytic complexes. These hypotheses, however, were not supported by direct, experimental proofs of the structure of the catalytic complexes. Some of these authors were only partially acquainted with our previous work.

It is therefore useful to report here on the structure and catalytic activity of several complexes having a well defined composition, containing titanium and aluminum, and isolated in the pure state by crystallization from solutions.

In papers already published or in press in Italian journals we describe in more detail their preparation, chemical properties and structure.

I. CRYSTALLIZABLE COMPLEXES CONTAINING TITANIUM AND ALUMINIUM

(a) *Complexes having the general formula* $(C_5H_5)_2TiCl_2AlR_1R_2$ *in which* R_1 *and* R_2 *are chlorine atoms or ethyl groups*

We have prepared three different complexes belonging to this class.[7] In Table 1 their overall formulae and physical properties are indicated.

TABLE 1. PHYSICAL PROPERTIES OF COMPLEXES OF THE GENERAL FORMULA $(C_5H_5)_2TiCl_2AlR_1R_2$ (WHERE R_1 AND R_2 ARE CHLORINE ATOMS OR ETHYL GROUPS)

Complex	*Melting temperature (°C)*	*Magnetic moment B.M.*
$(C_5H_5)_2TiCl_2Al(C_2H_5)_2$	126–130	1·70
$(C_5H_5)_2TiCl_2AlC_2H_5Cl$	88–92	1·57
$(C_5H_5)_2TiCl_2AlCl_2$	155–150	1·72

All complexes are highly soluble in aromatic solvents and can be crystallized from n-heptane. The three complexes referred to above were prepared by us in two different ways:

(1) By reacting *bis*(cyclopentadienyl) titanium dichloride with an excess of aluminum alkyl compound,[7] according to the following:

$$(C_5H_5)_2TiCl_2+Al(C_2H_5)_3 \rightarrow (C_5H_5)_2TiCl_2Al(C_2H_5)_2+\tfrac{1}{2}C_2H_4+\tfrac{1}{2}C_2H_6$$
$$(C_5H_5)_2TiCl_2+Al(C_2H_5)_2Cl \rightarrow (C_5H_5)_2TiCl_2AlC_2H_5Cl+\tfrac{1}{2}C_2H_4+\tfrac{1}{2}C_2H_6$$
$$(C_5H_5)_2TiCl_2+AlC_2H_5Cl_2 \rightarrow (C_5H_5)_2TiCl_2AlCl_2+\tfrac{1}{2}C_2H_4+\tfrac{1}{2}C_2H_6$$

(2) By reacting *bis*(cyclopentadienyl) titanium monochloride respectively with diethyl-aluminum-monochloride, ethyl-aluminum-dichloride or aluminum-trichloride,[8] as follows:

$$(C_5H_5)_2TiCl+ClAl(C_2H_5)_2 \rightarrow (C_5H_5)_2TiCl_2Al(C_2H_5)_2$$
$$(C_5H_5)_2TiCl+ClAl(C_2H_5)Cl \rightarrow (C_5H_5)_2TiCl_2Al(C_2H_5)Cl$$
$$(C_5H_5)TiCl+AlCl_3 \rightarrow (C_5H_5)_2TiCl_2AlCl_2$$

The study of the chemical properties of these complexes and the X-ray examination of their lattice structure carried out on single crystals, enabled us to conclude that the two cyclopentadienyl nuclei are bound to the titanium atom, while the latter is bound to aluminum through two bridge chlorine atoms.

From all the above-mentioned complexes it is possible, by treatment with anhydrous hydrochloric acid, to recover *bis*(cyclopentadienyl) titanium dichloride[7] in high yield.

The presence of chlorine bridges, similar to those existing in other electron-deficient molecules, e.g. Al_2Cl_6 molecules, is confirmed by the reaction with trimethylamine.

If an excess of this compound is reacted, in heptane, with the complex $(C_5H_5)TiCl_2Al(C_2H_5)_2$, a precipitate is obtained which is formed by *bis*(cyclopentadienyl) titanium monochloride; after removal of the solvent by evaporation, the complex of trimethylamine with Al-diethyl-monochloride $(CH_3)_3N—Al(C_2H_5)_2Cl$ can be isolated by distillation (0·5 mm Hg: 79-80°C).[8]

The structure of the complex $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$ has been confirmed by the determination of its crystalline structure by X-ray examination.[9] As indicated in Fig. 1, the Ti–Al distance is about 3·54 Å, the Cp–Ti–Cp angles are 130° and the Ti–Cl–Al angles are about 90°. The unit cell constants are as follows:

$$a = 15{\cdot}77 \text{ Å}; \; b = 14{\cdot}24 \text{ A}; \; c = 7{\cdot}54 \text{ Å}$$

space group P_{nma}

X-ray investigations, for the other complexes of this class, confirm the existence of chlorine bridges in the molecule.

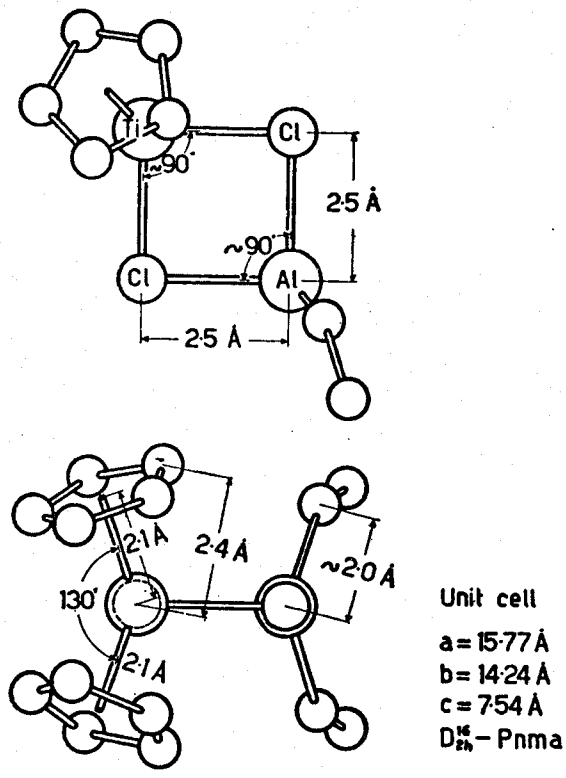


FIG. 1. Spatial model of the complex having formula: $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$

(b) *Complex* $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$

By reacting *bis*(cyclopentadienyl) titanium monochloride in benzene at 80° with aluminum triethyl in excess, a red solid product is obtained after removal of benzene, which can be purified by crystallization from n-heptane.[10]

The purified product (tabular crystals) is very soluble in aromatic hydrocarbons, melts (dec.) at 169–171° and is diamagnetic.

The results of chemical analysis and the determination of molecular weight are in agreement with the formula $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$.[10]

The two cyclopentadienyl nuclei are bound to titanium. In fact, by treating an ether solution of this complex with HCl and chlorine, *bis* (cyclopentadienyl) titanium dichloride is recovered in good yields (95–97 per cent). The X-ray examination on single crystals of this complex enabled us to establish that the molecule possesses a binary axis of symmetry and that the Ti–Ti distance is 3·07 Å, while the Ti–Al distance is 2·83 Å. The Ti–Ti–Al angle is 91°40′ and the angle between the two Ti–Ti–Al planes is 100°30′ (Fig. 2).

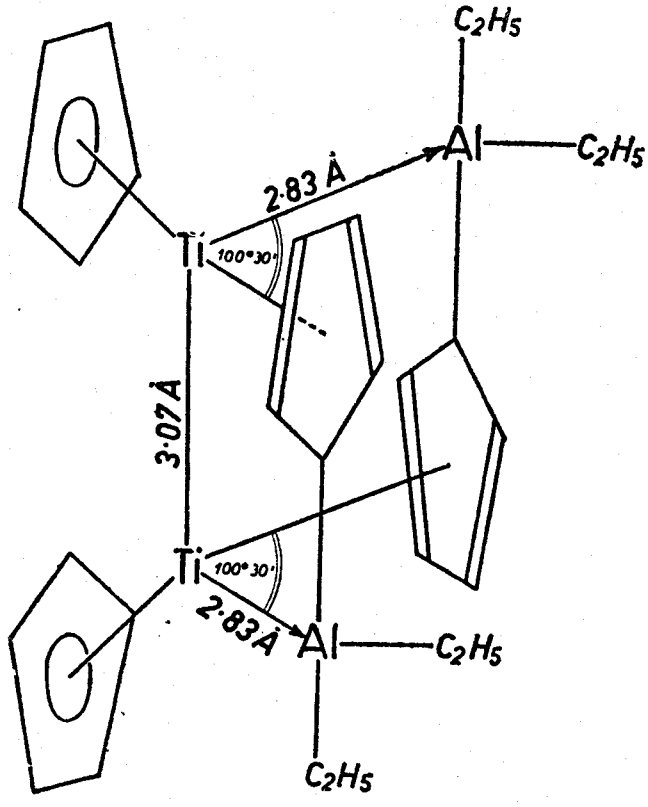


FIG. 2. Spatial model of the complex having formula: $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$

(c) *Complexes* $Al_2TiCl_8C_6H_5$ *and* $AlTiCl_5C_6H_5$

A solid crystalline, violet complex, containing titanium and aluminum was isolated by a Friedel–Crafts reductive reaction on $TiCl_4$. The conditions adopted were similar to those used by Fischer for the preparation of transition metal complexes, in which the metal is bound to aromatic nuclei by means of bonds of the π-type.

When the reaction was carried out between $TiCl_4$, $AlCl_3$, Al and benzene at 80° for several hours, a complex having an overall formula $Al_2TiCl_8C_6H_5$[11] was obtained. From Table 2, it can be seen that the composition of this product does not change when varying, within rather wide limits, the ratios between the moles of the various reactants used in its preparation. This complex melts at 110–115° (dec.) and is very soluble in benzene and toluene and only slightly soluble in aliphatic hydrocarbons. It undergoes a rapid change in presence of oxygen and moisture, giving hydrochloric acid and phenol.

It reacts exothermally with water in absence of oxygen yielding benzene. This behaviour agrees with the presence of phenyl groups bound to a metal by σ bonds.

By decomposition with dilute hydrochloric acid and titration with ferric sulphate it was established that titanium is present in the trivalent form.

When treating this complex, at room temperature or lower, with compounds containing lone electron pairs, such as e.g. tetrahydrofuran, dibutyl ether, pyridine or trimethylamine, elimination of one molecule of $AlCl_3$ takes place. This fact might prove the presence in the complex of one $AlCl_3$ molecule linked in a labile way, in agreement with a formula of the type: $[AlTiCl_5C_6H_5] \cdot AlCl_3$.

If the reaction with tetrahydrofuran is carried out at higher temperature (50–60°C) and for longer time, the above mentioned complex undergoes considerable decomposition and, besides the tetrahydrofuranate of aluminium trichloride ($AlCl_3 \cdot 2C_4H_8O$), it is possible to

TABLE 2. COMPOSITION OF THE PRODUCT OBTAINED BY REACTING $TiCl_4$, Al, $AlCl_3$ AND BENZENE, AT 80°C

Starting reagents					*Time (hr)*	*Product obtained*			
$TiCl_4$ (moles)	$AlCl_3$ (moles)	Al (moles)	C_6H_6 (moles)	*Molar ratio* $TiCl_4/AlCl_3/Al/C_6H_6$		(1) Yields %	Al %	Ti %	Cl %
0·09	0·09	0·27	1·4	1:1:3:15	13	60	11·77 —	10·25 —	60·65 60.60
0·06	0·06	0·12	1·2	1:1:2:20	6	20	11·67 11·64	10·30 10·50	60·80 —
0·09	0·117	0·180	1·8	1:1·3:2:20	20	92	11·60 11·47	10·38 —	60·90 —
0·03	0·06	0·09	0·51	1:2:3:17	18	80	—	—	61·40
0·05	0·03	0·40	1	1:0·6:8:20	15	25	11·90	10·30	61·10
Calculated for $Al_2TiCl_8C_6H_5$							11·67	10·35	61·30

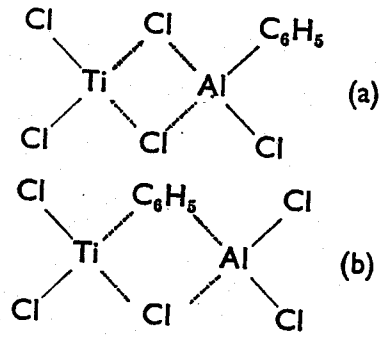
(1) = referred to $TiCl_4$

isolate a crystalline, green precipitate which proves to be a tetrahydrofuranate of titanium trichloride having the formula $TiCl_3 \cdot 3C_4H_8O$.[11] By treatment of a toluene solution of $[AlTiCl_5C_6H_5] \cdot AlCl_3$ at —60° with

tetrahydrofuran, a microcrystalline precipitate is obtained, dark-red in colour, insoluble in aromatic and aliphatic hydrocarbons.

When operating with a deficiency of the electron donor reactant in respect to the amount of $AlCl_3$ the precipitate corresponds to the formula $TiAlCl_5C_6H_5$.[11]

Analytical results and chemical behaviour of these complexes agree with both the structural formulae:



Formula (a) appears to be much more probable, at least in the normal state, than (b) as the bridges are symmetrical in respect to the axis passing through the titanium and aluminum atoms.

In formula (a) titanium is bound to aluminum by means of chlorine bridges, similar to those already found in the crystallizable complexes having general formula $(C_5H_5)_2TiCl_2AlR_1R_2$.

II. NATURE OF COMPLEXES CONTAINING TITANIUM AND ALUMINUM

Titanium generally shows a less tendency to form complexes in comparison with the heavier transition metals belonging to the same period. Therefore it may be of interest to discuss the nature of the complexes prepared by us. Most correspond to lower degrees of oxidation than the maximum; some of which are rather unusual for titanium. Certain titanium complexes, containing only one metal atom having a degree of oxidation 4, were already known, but the chief interest, from the viewpoint of catalysis, is shown by the complexes containing more than one metal atom in their molecule. A degree of oxidation 4 is found in the compound $(C_5H_5)_2TiCl_2$, which, by itself, does not behave as a catalyst acting with an anionic co-ordinated mechanism. Assuming that titanium having a degree of oxidation 4 receives six electrons from each cyclopentadienyl group and two electrons from each chlorine ion, the number of electrons given by the ligand groups

is 16 and the total number of electrons is 34. The number of electrons of krypton is therefore approached, without being reached. A similar electronic configuration should be presented by the complex $(C_5H_5)_2Ti(C_6H_5)_2$ as the bonds between phenyl groups and titanium are of the σ type, in contrast with the cyclopentadienyl groups which are bound to titanium by means of σ–π bonds.

When the degree of oxidation of titanium decreases, a tendency appears to form complexes containing more than one metal atom. $TiCl_3$ and $TiCl_2$ as distinct from $TiCl_4$ (which is a liquid, non-ionic compound), have high melting points. Their known crystalline modifications are all characterized by a co-ordination number 6. They exhibit an ionic nature, greater than $TiCl_4$, though the large force fields due to the presence of ions of a strong electro-positive metal, having a low valence and small diameter, do cause a close co-ordination of chlorine ions and their compact packing (mostly hexagonal compact). Owing to the large diameter of chlorine atoms, such a packing exhibits voids in which titanium atoms can find a place (in the different modifications of $TiCl_3$ and in $TiCl_2$).[12]

Only the titanium atoms on the edge of each layer formed by packing of one plane of Ti atoms between two planes of Cl atoms, are not completely co-ordinated and can bind themselves with other groups. This may explain an epitactic adsorption of aluminum alkyls or chloroalkyls, by which the electro-negative groups complete the coordination of peripheral titanium atoms, while the aluminum atoms (having a small diameter) can epitactically occupy the positions of the metal corresponding to a peripheral growth of the lattice of $TiCl_3$.[1]

Titanium complexes having a degree of co-ordination 6 are more stable in the solid state owing to the force fields of the crystal. Crystalline complexes stable even in solution, having a degree of coordination 8, are those corresponding to the general formula $(C_5H_5)_2TiCl_2AlR_1R_2$.

As already pointed out, the X-ray examination revealed the presence of bridge bonds between Ti and Al, a tetrahedral pattern for the four groups co-ordinated to Al and also a slightly distorted tetrahedral configuration of the two cyclopentadienyl groups together with the two chlorine atoms in relation to titanium. The 3-centre bridge bonds allow aluminum to assume an sp^3, and titanium a d^4sp^3 hybridization Trivalent titanium possesses only one (unpaired) electron on d-orbitals, and this is the reason for paramagnetic properties shown by complexes of this type.

The red complex $[CpTiCpAlR_2]_2$ appears to be of rather unusual structure. This is the very first case of a titanium complex corresponding to a degree of oxidation 1. The X-ray examination demonstrates the existence of two types of cyclopentadienyl groups: two of them, belonging to one type, are bonded by σ–π bonds to the Ti atoms, while the two others are linked to Al by means of σ–σ bonds (Fig. 2).

The position of the latter two cyclopentadienyl groups suggests that they may be bridge-linked both to titanium and to aluminum and furthermore are bonded by π bonds to titanium. The complex is diamagnetic owing to a probable Ti–Ti bond, confirmed by the small distance (3·1 Å) between the two Ti atoms. Furthermore, one can suppose that each Ti atom gives an electron pair to an Al atom, thus forming a bond of dative type.

A deeper X-ray study is being undertaken in our Institute; this study will better elucidate the structure of this complex, which also appears to be electron deficient.

III. CATALYTIC PROPERTIES OF CRYSTALLIZABLE COMPLEXES CONTAINING TITANIUM AND ALUMINUM

Table 3 shows that benzene solutions of the three complexes corresponding to the general formula $(C_5H_5)_2TiCl_2AlR_1R_2$ are able to promote, by themselves, ethylene polymerization yielding polymers of high molecular weight. However, the complex containing no alkyl groups exhibits an extremely low activity.

TABLE 3. CATALYTIC ACTIVITY OF COMPLEXES OF THE GENERAL FORMULA $(C_5H_5)_2TiCl_2AlR_1R_2$ (R_1 AND R_2 BEING —Cl OR —C_2H_5) IN THE POLYMERIZATION OF ETHYLENE AT 95°C AND 40 ATM

Catalyst		*Solvent*		*Time (hr)*	*Crystalline polyethylene (g)*	*Terminal groups found in the polymer*
Type	*moles*	*Type*	*cm³*			
$(C_5H_5)_2TiCl_2Al(C_2H_5)_2$	0·003	n-heptane	40	8	7	—C_2H_5
$(C_5H_5)_2TiCl_2AlC_2H_5Cl$	0·0035	n-heptane	40	8	8	—C_2H_5
$(C_5H_5)_2TiCl_2AlCl_2$	0·0046	toluene	50	21	3	—C_5H_5

In the case of complexes containing ethyl groups, it has been found, using ^{14}C labelled alkyls, that each polymeric chain contains one of the ethyl groups initially present in the complex. On the other hand, in

the case of the complex containing 4 chlorine atoms per molecule, we were able to establish, using ^{14}C labelled cyclopentadienyl groups, the presence of these groups linked to the polymeric chains.[13] Ethylene polymerization by means of these complexes might, therefore, take place according to a mechanism similar to the one observed with catalysts acting by means of an anionic co-ordinated mechanism, by insertion of the monomeric molecules on a metal-organic bond which can be of the Al–C type or even of the Ti–C type.

However as far as it is known we cannot exclude that the polymerization of ethylene, by means of the above complexes, takes place only after the complex has been transformed into an activated form in which one bridge chlorine atom has been substituted by an alkyl group or by a cyclopentadienyl group. In this way the relatively low activity shown by these complexes could be explained.

The possibility that the chain growth in anionic co-ordinated polymerization takes place through insertion of a polarized monomeric molecule on a bridge of an electron deficient molecule containing alkyl bridge bonds, had been already considered by Natta.*

Later, a mechanism of this type was proposed also by other

TABLE 4. CATALYTIC ACTIVITY OF COMPLEXES OF THE GENERAL FORMULA $(C_5H_5)_2TiCl_2AlR_1R_2$ (WHERE R_1 AND R_2 ARE —Cl OR —C_2H_5) IN THE POLYMERIZATION OF ISOBUTYL-VINYL-ETHER, IN TOLUENE SOLUTION, AT —78°C

Catalyst	*Monomer/catalyst molar ratio*	*Time (hr)*	*Conversion of the monomer (%)*	$[\eta]$	*Properties of the polymer*
$(C_5H_5)_2TiCl_2AlCl_2$	400	2	97	2·03	91% insoluble in acetone: highly crystalline by X-rays.
$(C_5H_5)TiCl_2AlC_2H_5Cl$	300	3	34	2·15	55% insoluble in acetone; highly crystalline by X-rays.
$(C_5H_5)_2TiCl_2Al(C_2H_5)_2$	35	10	0	—	—

$[\eta]$ = intrinsic viscosity in toluene at 30°C

* Opening Lecture of the Congress of Pure and Applied Chemistry, Paris, July (1957);[2] and Lecture given in Rome at the Symposium on the Chemistry of Co-ordination Compounds.[1]

authors.[14] The lower activity of the complex not containing alkyl groups could be explained by the much higher energy of activation required for a bridge-like arrangement of the cyclopentadienyl nucleus (linked by π-σ bonds to titanium, in the non-activated state) between titanium and aluminum.

The hypothesis that catalytic activity is connected with an activated form of this type could explain the lack of catalytic activity of other titanium *bis*(cyclopentadienyl) compounds which are not able to form bridges in the molecule, such as *bis*(cyclopentadienyl) titanium dichloride, *bis*(cyclopentadienyl) titanium diphenyl or dimethyl, which do not alone promote ethylene polymerization.

By decreasing the number of alkyl groups in the complexes having the general formula $(C_5H_5)_2TiCl_2AlR_1R_2$, a cationic activity arises in these compounds, which enables them to promote, e.g. stereospecific polymerization of vinyl ethers (Table 4)[15]. In this case, contrary to what happens in ethylene polymerization, neither alkyl nor cyclopentadienyl groups initially bound to the catalytic complex, can be found in the polymer.

The complex $(C_5H_5)_2TiCl_2AlClC_2H_5$ is an interesting example of a catalyst able to promote stereospecific polymerization through two different mechanisms, either cationic or anionic, depending on the ability of the monomers to polymerize by one or by the other mechanism.

The complex free of halogen atoms $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$ can promote the polymerization of ethylene.[10]

As shown in Table 5, the polyethylenes contain high molecular weight fractions that, by X-ray examination, prove to be highly crystalline and also low molecular weight fractions according to a wide dispersion in molecular weights.

The $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$–$\alpha TiCl_3$ catalytic system polymerizes ethylene, yielding polymers having very high molecular weight and crystallinity (Table 5).

The same catalytic system promotes propylene polymerization at rates comparable with those obtained with the typical catalysts $Al(C_2H_5)_3$–$\alpha TiCl_3$, yielding polymers remarkably richer in isotactic macromolecules (not extractable by boiling n-heptane) (Table 6). These isotactic fractions possess higher molecular weights.[10]

The higher stereospecificity and higher degree of polymerization can be ascribed to the fact that chain transfers between the growing polymeric chains and the alkyl groups present in solution in the catalytic

TABLE 5. CATALYTIC ACTIVITY OF THE COMPLEX $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$ IN THE POLYMERIZATION OF ETHYLENE, IN THE PRESENCE AND IN THE ABSENCE OF $TiCl_3$, USING TOLUENE AS SOLVENT OF THE MONOMER

Organometallic compounds		*$TiCl_3$ moles 10^3*	*Polymerization conditions*			*Polyethylene (g)*	*Fractionation of the polymer*					
							Ether extractable fraction (%)	*Boiling heptane extractable fraction*		*Residue*		
Type	*moles 10^3*		*Temperature (°C)*	*Pressure (atm)*	*Time (hr)*			*(%)*	*$[\eta]$*	*(%)*	*$[\eta]$*	*Crystallinity (%)*
$[(C_5H_5)_2TiAl(C_2H_5)_2]_2$	2·8	0	90	10	19	6·25	55	14·5	0·11	30·5	1·87	86
$[(C_5H_5)_2TiAl(C_2H_5)_2]_2$	2·2	0	90	40	8	11·3	13·3	13·9	0·12	72·8	2·75	85
$[(C_5H_5)_2TiAl(C_2H_5)_2]_2$	3·4	1·95	80	3	5	67·2	0·3	0·8	—	98·9	8·90	81
$Al(C_2H_5)_3$	6·5	2·08	80	3	5	82	0	1·4	—	98·6	8·45	84

$[\eta]$ = intrinsic viscosity in tetralin at 135°

TABLE 6. PROPYLENE POLYMERIZATION IN THE PRESENCE OF THE CATALYTIC SYSTEMS $TiCl_3$–$[(C_5H_5)_2TiAl(C_2H_5)_2]_2$ AND $TiCl_3$–$Al(C_2H_5)_3$. POLYMERIZATION CONDITIONS: TEMPERATURE 75°C; PROPYLENE CONSTANT PRESSURE 5 ATM; TIME 7 HOURS

Catalyst			*Solvent*		*Polypropylene (g)*	*Average rate of polymerization* $\frac{g\ C_3H_6}{g\ TiCl_3 \cdot h}$	*Isotactic polymers not extractable with boiling heptane*	
Organometallic compounds		*$TiCl_3$ moles 10^3*	*Type*	*cm^3*			*(%)*	*$[\eta]$*
Type	*moles 10^3*							
$[(C_5H_5)_2TiAl(C_2H_5)_2]_2$	4·15	3·7	toluene	250	20·9	5·7	94·5	3·96
$Al(C_2H_5)_3$	9·0	4·1	toluene	250	68·6	15·5	83·1	2·58
$[(C_5H_5)_2TiAl(C_2H_5)_2]_2$	2·45	2·6	n-heptane	300	45·6	16·2	93·0	6·99
$Al(C_2H_5)_3$	8·4	4·2	n-heptane	500	97	21·3	85·2	4·17

$[\eta]$ = intrinsic viscosity in tetralin at 135°C

system, occur to a more limited extent in comparison with polymerization by means of the $Al(C_2H_5)_3$–$TiCl_3$ catalytic system. In fact, this reduced alkyl-transfer should be accompanied by a lower probability of inversion in steric configuration of the monomeric units entering the growing chain.[16]

TABLE 7. CATALYTIC ACTIVITY OF THE COMPLEX $[AlTiCl_5C_6H_5]\cdot AlCl_3$ IN THE POLYMERIZATION OF ETHYLENE–POLYMERIZATION CONDITIONS: TEMPERATURE 80 °C, INITIAL PRESSURE 25 ATM, TIME: 14 HOURS

$[AlTiCl_5C_6H_5]\cdot AlCl_3$ moles	*Solvent*		*Polyethylene (g)*	*Fractionation of the polymer*					
	Type	*cm^3*		*Waxy polymers extractable with boiling acetone (%)*	*Boiling heptane extractable fraction*		*Residue*		
					(%)	*$[\eta]$*	*(%)*	*$[\eta]$*	*Crystallinity (%)*
0·007	benzene	100	12·6	28·0	6·4	0·14	65·0	1·28	85
0·003	heptane	100	15·5	26·1	23·4	0·15	49·4	0·90	86

$[\eta]$ = intrinsic viscosity in tetralin at 135°C

The complex having the formula $(AlTiCl_5C_6H_5)\cdot AlCl_3$, dissolved in benzene or suspended in heptane, promotes ethylene polymerization yielding waxy, low molecular weight polymers together with solid

polymers containing high molecular weight fractions, crystalline under X-ray examination[11] (Table 7).

In the I.R. spectra of the polyethylenes thus obtained, an absorption band at 14·33 μ, attributable to phenyl groups bound to the polymeric chains, is easily detectable. Although the formation of linear polyethylenes, in which at least a part of the chains contains, as terminal groups, the phenyl group initially bound in the complex, may be ascribed to a polymerization mechanism of anionic type, the complex $(AlTiCl_5C_6H_5)\cdot AlCl_3$ exhibits also an acidic character. It can promote fast polymerization of propylene, yielding oily polymers, similar to the products of the polymerization of this monomer by means of $AlCl_3$ or $TiCl_4$. In these low molecular weight polypropylenes no phenyl group can be detected by I.R. analysis.

The solid, microcrystalline complex $AlTiCl_5C_6H_5$ promotes ethylene polymerization at a rate much higher than that observed with the complex $(AlTiCl_5C_6H_5)\cdot AlCl_3$, yielding polymers which are free of oily, low molecular weight fractions (Table 8).

In the I.R. spectra of fractions having lower molecular weight (extractable by heptane), it was possible to detect the presence of phenyl groups bound to the polymeric chains.

This complex promotes the polymerization of propylene[11] (Table 8) but with an activity much lower than that of the most typical stereospecific catalysts[6] yielding linear polymers containing fractions made up of atactic macromolecules, stereoblock[17] fractions and fractions consisting of isotactic macromolecules.[4]

In the I.R. spectra of fractions having lower molecular weights (extractable by ether or by n-heptane) the presence of bands at 13, 16 and 14·33 μ was detected, attributable to benzylidene groups.

The initiation growth of the first polypropylene chains in the presence of complex $TiAlCl_5C_6H_5$ could therefore occur by addition of a monomeric molecule according to a reaction of the following type:

$$\overset{(+)(-)}{(TiAlCl_5)}C_6H_5 + CH_2{=}CH{-}CH_3 \rightarrow \overset{(+)(-)}{(TiAlCl_5)}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}C_6H_5$$

Transfer reactions with the monomer[18] may successively originate other polymeric chains, according to an anionic mechanism, as proposed by us for other catalysts acting in the stereospecific polymerization of propylene.[19]

IV. NATURE OF ANIONIC, CO-ORDINATED POLYMERIZATION

In previous papers we have already escpressed our view on the nature of anionic co-ordinated catalysis.

We shall limit ourselves to point out here the contribution made by the study of the catalytic properties of the new organometallic complexes of definite composition.

All catalytically active complexes contain two metal atoms in their molecule. When comparing these results with those obtained using the most typical catalysts of the Ziegler type, for which complexes of defined composition have not been isolated so far in a pure crystallizable form, it can be assumed that, also for these catalysts, the active components are formed by electron deficient organometallic complexes, containing at least two metal atoms in their molecules.

Whereas ethylene polymerization can also take place in the presence of catalysts soluble in the polymerization medium, anionic co-ordinated polymerization of alpha-olefins takes place only with catalysts acting in the presence of a heterogeneous solid phase. In order that this polymerization should be stereospecific, a crystalline structure or a molecular aggregate having an ordered structure must be present in the catalysts.

In catalysts containing titanium and aluminum, the same types of bridge bonds between the two metals are present, being the Ti atom, either part of a soluble complex or present on the surface of a crystalline lattice.

In the latter case the initially incomplete co-ordination of titanium in certain peripheral regions of the lattice facilitates chemisorption of organometallic compounds of strongly electropositive metals, having a small ionic radius (Al, Be, Mg).

Some authors[20] have stated that in polymerizations occurring in the presence of typical Ti–Al catalytic systems, the polymeric chains grow on titanium. According to these authors[20] we could not have foreseen this possibility and our statement referring to the growth of the polymeric chains on aluminum should be considered as incorrect. The possibility of existence of catalytic systems containing only titanium compounds had been previously demonstrated by us in preparing catalysts for the polymerization of ethylene and propylene by reacting *bis*(cyclopentadienyl) titanium diphenyl with $TiCl_4$. It can be assumed that, by means of this reaction, complexes containing at least two Ti atoms are formed.[21] In such cases the polymeric chain grows on a

TABLE 8. CATALYTIC ACTIVITY OF THE COMPLEX $AlTiCl_5C_6H_5$ IN THE POLYMERIZATION OF ETHYLENE AND OF PROPYLENE

$AlTiCl_5C_6H_5$ moles	Monomer	Polymerization conditions			Polymer (g)	Fractionation of the polymer						
						Ether extractable fraction (%)	Boiling heptane extractable fraction			Residue		
		Temperature (°C)	Pressure (atm)	Time (hr)			(%)	[η]	Crystallinity (%)	(%)	[η]	Crystallinity (%)
0·007	ethylene	85	20	3	114	0·25	1·1	0·11	80	98·65	9·0	87
0·004	propylene	110	25	16	24	80·3	10·85	0·89	45	10·15a	3·90	72

[a] In the case of polypropylene the residue after heptane extraction consists of isotactic macromolecules.

titanium atom (probably on the more electropositive one), or on a bridge between two Ti atoms. These catalysts have poor activity. A low activity is also shown by the catalysts obtained from methyl-titanium trichloride.[22] In order to have catalysts showing a high activity, the presence of another metal in the complex seems to be necessary.

The hypothesis that, also in the case of catalysts prepared from titanium halides and Al-trialkyls, the polymeric chain grows on a titanium-alkyl bond, disagrees with the following experimental results:

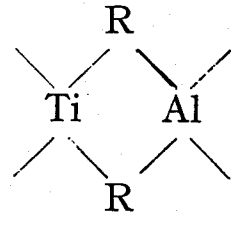
(1) The presence of phenyl groups, bound to the polymeric chains, has been ascertained in the case of ethylene polymerization by catalysts prepared from Al-triphenyl and $(C_5H_5)TiCl_2$. Terminal phenyl groups are not present in polyethylenes prepared with catalysts obtained from $(C_5H_5)_2Ti(C_6H_5)_2$ and Al-triethyl.[23]

(2) Investigations made by adsorbing $Al(C_2H_5)_3$ containing ^{14}C labelled alkyls on $TiCl_3$ and then polymerizing in the presence of non-labelled $Al(C_2H_5)_3$, proved that practically all the alkyl groups bound to aluminum, previously adsorbed on α-$TiCl_3$, are found as terminal groups in polymeric chains. On the other hand it cannot be considered that all these alkyl groups were initially engaged in titanium alkylation.[24] Furthermore, at the polymerization end the major part of all the polymeric chains produced remain chemically bound to aluminum[25] as indicated by the chemical analysis of the polymerization products. This is probably due to a dissociation of each catalytic complex into two parts, one containing the titanium atom, the other containing alkyl groups (including polymeric chains) bound to aluminum. This dissociation is followed by an association involving other aluminum alkyls from the solution.

As previously noted, when dealing with the activity of complexes having general formula $(C_5H_5)_2TiCl_2AlR_1R_2$, we cannot exclude that in the case of Ti–Al catalytic systems the polymerization occurs by insertion of the monomeric molecules into a bridge in which alkyl groups link Ti to Al by means of 3-centre bonds.

In such a case it is difficult to distinguish whether the chain grows on Ti or on Al.

It may be assumed that the partial ionic dissociation of a complex takes place as indicated in Fig. 3.



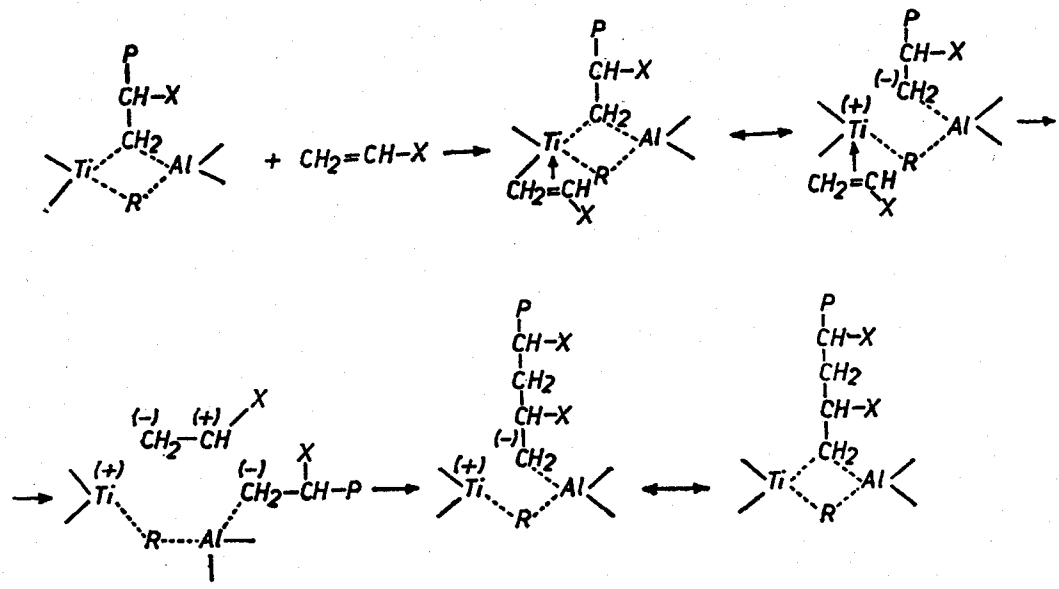


FIG. 3.

A first step of association of the monomer with the transition metal, caused by the high electronic density of the double bond and by the electron deficiency of the transition metal, is admissible. Kinetic data with α-$TiCl_3$—$Al(C_2H_5)_3$ catalytic systems agree with this hypothesis. In this way an explanation is available for the fact that the rate of certain transfer processes and the rate of growing process are both of the same order in respect to the monomer concentration,[26] as they were two parallel reactions following the same intermediate state. This step should be followed by a polarization of the double bond of the entering monomeric unit, as indicated in Fig. 3.

The chain growth must be ascribed to the neutralization of the charge on the CHR group, belonging to the new monomeric unit, with the terminal CH_2 group of the polymeric chain, whilst it can be foreseen that the CH_2 group of the new monomeric unit links itself to the more electropositive metal, which is aluminum.

V. STEREOSPECIFICITY IN IONIC CO-ORDINATED POLYMERIZATIONS

Many authors have interpreted our statement that stereospecific polymerization of α-olefins takes place only with catalysts acting in heterogeneous phase, as to be extended also to the polymerization of other monomers.

It must be borne in mind that our School was the first to obtain isotactic and syndiotactic polymers from diolefins and that these sterically

regular polymers were prepared by means of soluble catalysts.[27] Furthermore, we have extended the stereospecific polymerizations of vinyl ethers to some soluble catalysts[15] different from those proposed by Schildknecht.[28]

When the monomer contains two groups rich in electrons (two double bonds in diolefins or one double bond and one oxygen with a lone electron pair in the case of vinyl ethers) an association of the monomeric molecules with the electron deficient catalysts should be possible before the addition to the growing polymeric chains, even if the catalyst does not contain a heterogeneous phase, able to adsorb the monomer. In such cases a stereospecific polymerization can take place through soluble catalytic complexes.

In fact, soluble catalysts are the reaction product between chromium-acetylacetonate and Al-trialkyls used by us for the synthesis of isotactic and syndiotactic polymers of diolefins.[27]

Also soluble are the compounds having a weak cationic activity and able to form etherates [$(AlClR_2)_2$; $(AlCl_2R)_2$; $TiCl_2(OR)_2$] used by us for the cationic stereospecific polymerization of alkyl-vinyl-ethers.[15] Therefore, excepting the polymerizations of α-olefins, stereospecific polymerizations are not necessarily connected with the presence of insoluble catalysts acting in the heterogeneous phase from the beginning of the polymerization.

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147

THE DETERMINATION OF THE MOLECULAR WEIGHT OF POLYPROPYLENE

by G. MORAGLIO

(3 July 1959)

[*Chimica e Industria* **41**, 897 (1959)]

ABSTRACT

The formulae, so far determined, for the purpose of calculating the molecular weight from intrinsic viscosity data, both for atactic and isotactic polypropylene, are examined.

The relationship between molecular weight and intrinsic viscosity is then determined, by viscosity measurements, for fractions of atactic polypropylene in tetralin at 135°C, by experimental methods widely used in most laboratories. The corresponding equation is:

$$[\eta] = 1{\cdot}93 \times 10^{-4}\ \overline{M}_v^{\ 0.74}$$

($[\eta]$ in 100 $cm^3\ g^{-1}$).

A comparison between the results for the two types of polymers has allowed us to conclude that the formulae used in viscometric determinations at high temperature for atactic polypropylene may be extended to the isotactic polypropylene, and, consequently, to any type of linear polypropylenes, having an intermediate degree of steric order.

148

EVALUATION OF THE VISCOSITY AVERAGE MOLECULAR WEIGHT OF ETHYLENE-PROPYLENE COPOLYMERS

by G. MORAGLIO

(3 July 1959)

[*Chimica e Industria* **41**, 984 (1959)]

ABSTRACT

On the basis of the known relationship between intrinsic viscosity and molecular weight for the homopolymers of ethylene and of propylene, we have calculated for the same temperature and solvent conditions the constants of the equation:

$$[\eta] = K'M^a$$

for the various compositions of the ethylene–propylene copolymers.

TABLE 1. K′ CONSTANTS FOR VARIOUS PERCENTAGES IN MOLES OF ETHYLENE (% B)
($a = 0.74$)

% *B*	$K' \times 10^4$	% *B*	$K' \times 10^4$
5	2·020	55	3·020
10	2·115	60	3·140
15	2·205	65	3·260
20	2·295	70	3·385
25	2·390	75	3·515
30	2·485	80	3·645
35	2·585	85	3·790
40	2·690	90	3·940
45	2·795	95	4·240
50	2·910	—	—

For this purpose we applied the Fox–Flory theory, which has been extended by Stockmayer and co-workers to include copolymers.

The reported table shows the final results obtained.

The constants thus found allow an approximate evaluation, which however is sufficient for technical purposes, of the viscosity average molecular weight $\overline{M}_v$ for this type of copolymer.

149

TETRAHYDROFURANATES OF TITANIUM TRICHLORIDE

by G. F. PREGAGLIA, G. MAZZANTI and D. MORERO

(6 July 1959)

[*Annali Chimica* **49**, 1784 (1959)]

ABSTRACT

By heating violet $TiCl_3$ with tetrahydrofuran, a crystalline, blue, needle-shaped complex is separated. The reaction is enhanced if small amounts of zinc or metallic aluminum are added to the titanium salt. The analytical datum suggests the formula $TiCl_3 \cdot 3C_4H_8O$ (I), while it excludes the possibility of the tetrahydrofuran ring opening followed by the formation of Ti–O–C bonds.

The blue crystals of the tetrahydrofuranate (I) become green, when they are heated in a closed tube at 80°C. A liquid phase, which was identified as tetrahydrofuran was also separated. The green complex had the formula $TiCl_3 \cdot 2C_4H_8O$ (II) and by the further addition of tetrahydrofuran at 50°C, a tetrahydrofuranate (III) was formed.

The I.R. spectrum of this last complex differs from that of the etherate (I); in particular a splitting of the band is observed at 858 cm^{-1} with two minor ones at 855 and 836 cm^{-1}. This behaviour could be explained with a non-equivalent disposition of the coordinated tetrahydrofuran nuclei in the complex (III).

150

STEREOSPECIFIC POLYMERIZATION OF VINYLAROMATIC MONOMERS. NOTE III: VINYL DERIVATIVES OF POLYNUCLEAR AROMATIC HYDROCARBONS

by D. Sianesi, A. Macchi and F. Danusso

(20 July 1959)

[*Chimica e Industria* **41**, 964 (1959)]

ABSTRACT

The anionic coordinated polymerization, with AlR_3 and titanium chloride catalysts, may be applied to various vinyl monomers with polynuclear aromatic substituents. In spite of the steric hindrance of these substituents, a remarkable reactivity is often observed.

The monomers examined were: 1-vinylnaphthalene, 2-vinylnaphthalene, 1-vinyl-4-chloronaphthalene, 1, 2, 3, 4-tetrahydro-6-vinylnaphthalene, 4-vinyldiphenyl, *p*-cyclohexylstyrene, 9-vinylanthracene, 9-vinyl-phenanthrene.

Highly crystallizable isotactic polymers have been obtained from 1-vinylnaphthalene. Polymers obtained from other monomers were not crystallizable, even though the polymerization conditions were typical of a stereospecific reaction.

The reactivity of the examined monomers and the crystallizability of the polymers which can be obtained depend on the nature of the substituent according to relationships already observed for the alkyl- or halo-substituted styrenes (see papers 114 and 122).

151

A NEW METHOD OF SEPARATION AND DETERMINATION OF ALUMINUM AND TITANIUM

by L. GIUFFRÈ and F. M. CAPIZZI

(22 July 1959)

[*Annali Chimica* **49**, 1834 (1959)]

ABSTRACT

A rapid potentiometric method for the separation and determination of the aluminum and titanium cations, as aluminum/EDTA and titanium/hydrogen peroxide/EDTA complexes is described here. This method utilizes the ability of cationic exchange resins to hold quantitatively, under established conditions, only the aluminum cation, which after elution and addition of a known excess of a standardized solution of EDTA is titrated potentiometrically, by indirect means, with standardized solutions of ferric salts.

Moreover, the indirect, potentiometric determination with a standard solution of ferric salt is described, with reference to the sum of the two cations of titanium and aluminum, which are complexed as aluminum/EDTA and titanium/hydrogen peroxide/EDTA.

152

PROGRESS IN STEREOSPECIFIC POLYMERIZATION*

by GIULIO NATTA

(5 Aug. 1959)

[*Makromol. Chemie* **35**, 93 (1960)]

SUMMARY

Results of new research work in the field of polymers with an ordered steric structure, obtained by stereospecific polymerization, are reported. Some of the results concern the relationship between steric structure and crystallinity; these show that a regular steric structure is a necessary, but not a sufficient condition for the crystallizability of the polymers.

In the isotactic polymers of $CH_2=CHR$ type monomers, the shape and size of the R group not only determine the different conformations of isotactic helices (with a number of monomeric units per pitch varying from 3 to 4) but in some particular cases are responsible for the lack of crystallinity.

It is possible, through chemical processes which modify the shape and size of the R substituent, to obtain crystalline polymers from isotactic, amorphous, not crystallizable polymers.

The crystalline structure of syndiotactic polypropylene is described for the first time and is compared with the structure of other syndiotactic polymers.

Furthermore the structure of crystalline polymers of "di-isotactic type", obtained by polymerizing $RCH=CHR_1$ type monomers is discussed, and a nomenclature for the different possible stereoisomers is suggested.

Cases of polymorphism, isomorphism and di-isomorphism in the macromolecular field are examined and a new type of isomorphism among different monomeric units is discussed. Crystalline copolymers of isomorphous monomeric units have a melting point which is intermediate between the melting points of the corresponding pure homopolymers.

The effects which influence the steric purity of polymers having an ordered structure are discussed and the influence of steric purity on the physical properties and mainly on the mechanical properties of the polymers (especially in the case of polybutadiene obtained at the Polytechnic of Milan with a content of *cis*-1,4 units higher than 99 per cent) is pointed out.

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* Lecture held at the International Symposium on Macromolecules, I.U.P.A.C. Wiesbaden, 1959.

INTRODUCTION

The stereospecific polymerization processes, which had found their first and most important applications in the field of α-olefin and diolefin polymers, have been the object during the last years of further research with *Ziegler* type catalysts and other different catalytic systems, and have also been extended to other series of monomers. The results which some years ago had already made a stir in macromolecular science, have been added to and improved. For instance, we have succeeded in obtaining polydiolefins of high steric purity and discovered completely new types of crystalline polymers which are remarkably interesting both scientifically and practically.

In this communication I shall refer to some of the research works carried out at the Milan Polytechnic especially that concerning the new types of crystalline polymers and the relations between steric structure and crystallinity of polymers. We have discovered series of new polymers having a regular steric structure such as syndiotactic poly-α-olefins and a completely new group of crystallizable macromolecules resulting from the polymerization of monomers with an internal double bond.

The discovery of these new polymers, for which we proposed the denomination "di-isotactic polymers", does not only call for new problems of terminology, but also gives an impulse to new researches that will lead to a better understanding of the stereospecific polymerization mechanisms.

For lack of time, I shall not refer here to other works accomplished in my Institute in the field of stereospecific catalysts. On the relationship between molecular structure and catalytic activity of some organometallic complexes of titanium, isolated in their pure state by crystallization, I have recently reported at the London Congress on the Chemistry of the Coordination Compounds[1] and at the Congress of the International Union of Pure and Applied Chemistry in Munich.[2]

ISOTACTICITY AND CRYSTALLINITY

First of all, I wish to point out the relationship existing between chain structure and crystallinity in the sterically regular polymers.

On the basis of a systematic work on stereospecific polymerization and on the structure of the obtained polymers, we could demonstrate that the regularity in the chain configuration is for many classes of

polymers the necessary condition, but not the sufficient one, for obtaining crystalline polymers.

The different shape and bulkiness of the R substituents in the isotactic polymers of CH_2=CHR monomers is the reason for the different conformations assumed by the isotactic helices in the crystals.[3]

TABLE 1. X-RAY DATA ON SOME TYPICAL ISOTACTIC POLYMERS WITH DIFFERENT CHAIN CONFORMATIONS

Polymer	*Helix type**	*Chain axis* Å	*Unit cell*	*Space group*
Polypropylene	3_1	6.50	Monoclinic $a = 6.65$Å, $b = 20.96$Å, $\beta = 99°20'$	$C2/c$
Poly-*a*-butene**	3_1	6.50	Rhombohedral $a = 17.70$Å	$R3c$ or $R\bar{3}c$
Polystyrene	3_1	6.63	Rhombohedral $a = 21.90$Å	$R3c$ or $R\bar{3}c$
Poly-5-methylhexene-1	3_1	6.50		
Poly-5-methylheptene-1	3_1	6.40		
Poly-3-phenylpropene-1	3_1	~6.40		
Poly-4-phenylbutene–1	3_1	6.55		
Poly-*o*-methylstyrene	4_1	8.10	Tetragonal $a = 19.01$Å	$I4_1cd$
Poly-α-vinyl naphthalene	4_1	8.10	Tetragonal $a = 21.20$Å	$I4_1cd$
Polyvinyl cyclohexane	4_1	6.50	Tetragonal $a = 21.76$Å	$I4_1a$
Poly-3-methylbutene-1	4_1	6.84		
Poly-4-methylpentene-1	7_2	13.85	Tetragonal $a = 18.60$Å	$P\bar{4}$
Poly-4-methylhexene-1	7_2	14.00	Tetragonal $a = 19.64$Å	
Poly-*m*-methylstyrene	11_3	21.74	Tetragonal $a = 19.81$Å	

* It is to be understood that, besides the right-handed X_n helix, there is also the corresponding left-handed helix.
** Modification 1.

Some X-ray data concerning isotactic polymers with different chain conformations are reported in Table 1. All these data, except the values concerning the elementary unit cell of poly-4-methylpentene-1,[4] are the result of the examinations performed in our Institute.[5]

Figure 1 shows the models with threefold symmetry of polypropylene and of polystyrene chains [$(AB)_3$ according to Bunn[6, 7]) with a period of 6·50 and 6·65 Å respectively]; Fig. 2 shows the models with fourfold symmetry of poly-*o*-methylstyrene chain [$(AB')_4$ with a period of 8·10 Å)[7]] and of polyvinyl cyclohexane [$(A'B')_4$ with a period of 6·50 Å]; Fig. 3 shows the models of chains, with a more complex symmetry, of poly-4-methylpentene-1 [$(A'B')_{7/2}$ with a period of 13·85 Å] and of poly-*m*-methylstyrene [$(A'B')_{11/3}$ with a period of 21·74 Å].

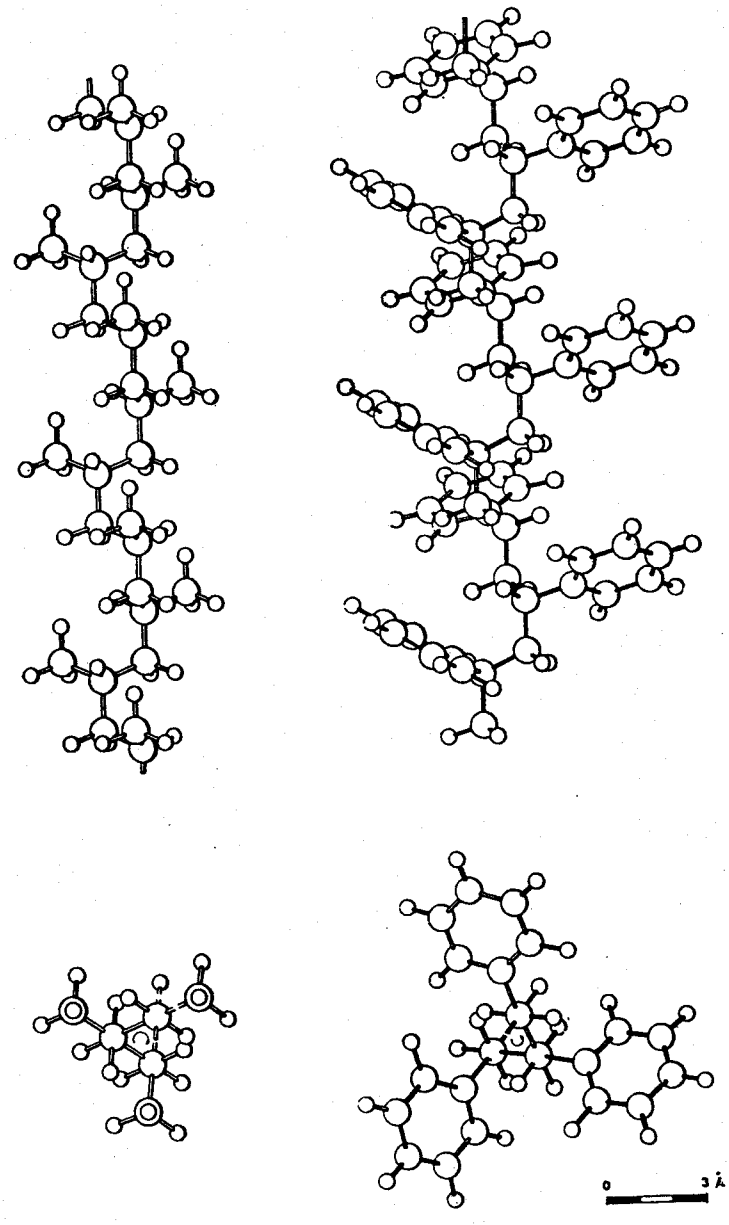


FIG. 1. Polymer chain with threefold symmetry
(3_1 polypropylene, 3_1 polystyrene; also hydrogen atoms are drawn)

The shape and bulkiness of the R side groups in some particular cases may also cause lack of crystallinity.

We particularly studied a series of polymers of substituted aromatic monomers; the polymers were obtained using stereospecific catalysts (containing Ti halides and organometallic compounds).[8] The result of these experiments is that by polymerizing such monomers on a stereospecific catalyst it is possible to obtain also completely amorphous products. Some of these products can crystallize after particular thermal treatments carried out in the presence of small quantities of solvents or swelling agents; in other cases the products are not crystallizable by any means. While for instance isotactic polymers of

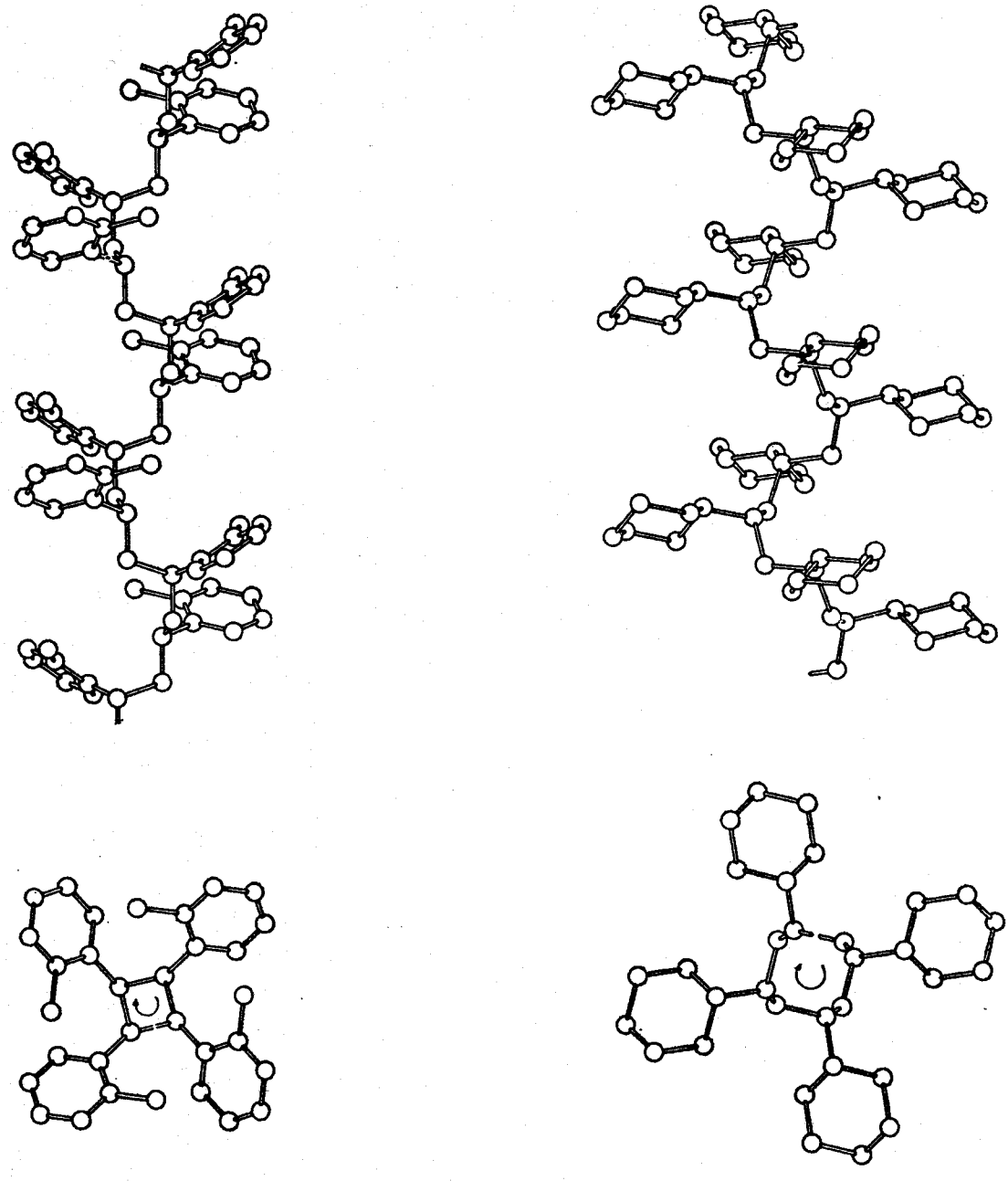


FIG. 2. Polymer chains with fourfold symmetry
(4_1 poly-*o*-methylstyrene, 4_1 polyvinyl cyclohexane)

o- and of *m*-methylstyrene are crystalline, polymers of *p*-methylstyrene are amorphous. With regard to monofluorostyrenes, polymers of the *o*- and *p*-isomers are crystalline, whereas polymers of the *m*-isomers are not. Thus polymers of *m*- and *p*-chlorostyrene are amorphous. The isotactic polymer of 1-vinyl naphthalene is crystalline; that of its isomer, 2-vinyl naphthalene, is amorphous.[8]

However, we could demonstrate that some polymers are isotactic even if they are not crystallizable. This fact had already been foreseen by us on the basis of certain analogies in the course of polymerizations,

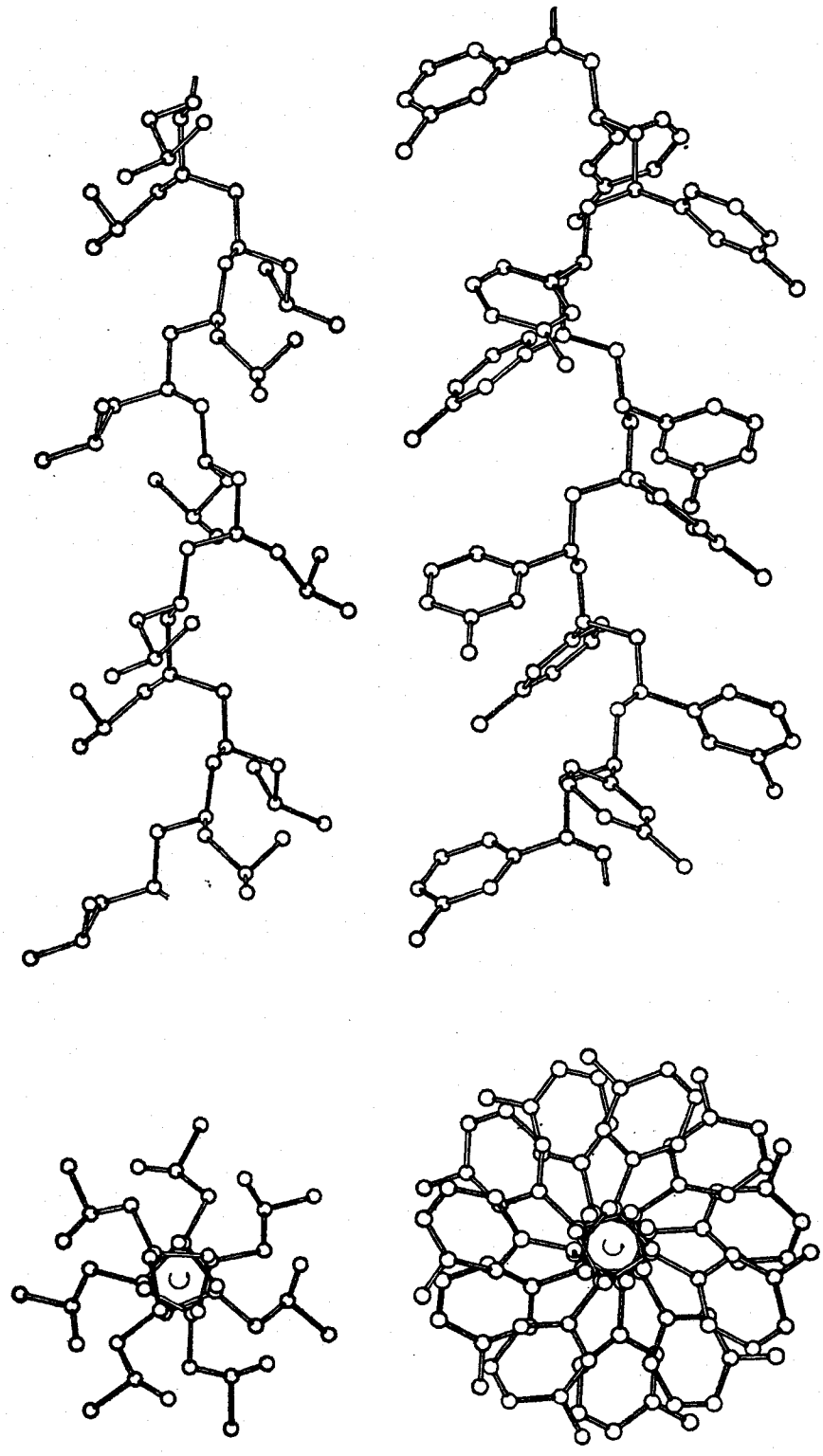


FIG. 3. Polymer chains with 7_2 symmetry (poly-4-methylpentene-1) and with 11_3 symmetry (poly-*m*-methylstyrene)

in the distribution of molecular weights and in the chemical nature of the polymers.

Now we have demonstrated it for certain, with two different methods which I briefly summarize below:

(a) One of the methods consists in subjecting amorphous polymers

(obtained with stereospecific catalysts) to chemical treatments that modify the steric bulkiness of side groups, without modifying the main chain structure. For instance among halogenostyrene polymers, chlorostyrene polymers are amorphous, even if they are polymerized under the same conditions in which styrene and *p*-fluorostyrene give crystalline polymers. The complete catalytic hydrogenation of the benzene ring accompanied by dehalogenation, as accomplished with Raney-Ni at 200°C, turned the amorphous polymers of *p*-chloro-, of *m*-chloro-, of *p*-bromo-, and of *m*-fluorostyrene into crystalline polymers.[9]

Fig. 4a shows for comparison the spectra of amorphous poly-*p*-chlorostyrene, of hydrogenated poly-*p*-chlorostyrene, of isotactic polyvinyl cyclohexane; the third showing the same crystalline structure as the second, as also shown from the I.R. spectra (see Fig. 4b).

Owing to the fact that we think that the ring hydrogenation cannot change the conformation of an atactic chain into an isotactic one, we must conclude that the main chain of the studied polychlorostyrenes was already isotactic, even if the polymer was not crystalline.

(b) Another way to explain the lack of crystallinity in some isotactic polymers is the copolymerization of the monomer that gives amorphous polymers with another monomer, having a slightly different chemical nature, shape and size, which under the same conditions of polymerization gives crystalline isotactic polymers. For instance *p*-methylstyrene, which by itself gives amorphous homopolymers when copolymerized with styrene gives crystalline polymers having unit cell of the same type as that of isotactic polystyrene and values of the lattice constants in the direction normal to the chain axis, slightly different from those of isotactic polystyrene and increasing with the increase of the percentage of *p*-methylstyrene.

The identity period along the chain axis, corresponding to three monomeric units (6·65 Å), remains unaltered.

By extrapolating to the pure *p*-methylstyrene homopolymer, the X-ray data observed for styrene copolymers containing from 0 to 50 per cent of *p*-methylstyrene, we calculated the following lattice constants:

$$a = b > 25\ \text{Å}, \qquad c = 6.65\ \text{Å}, \qquad d < 1.00\ \text{g/cm}^3$$

while the constants of the isotactic polystyrene are:

$$a = b = 21.9\ \text{Å}, \qquad c = 6.65\ \text{Å}, \qquad d < 1.12\ \text{g/cm}^3$$

The density of the amorphous poly-*p*-methylstyrene is 1·04; this value is higher than that foreseen[7] for a crystalline poly-*p*-

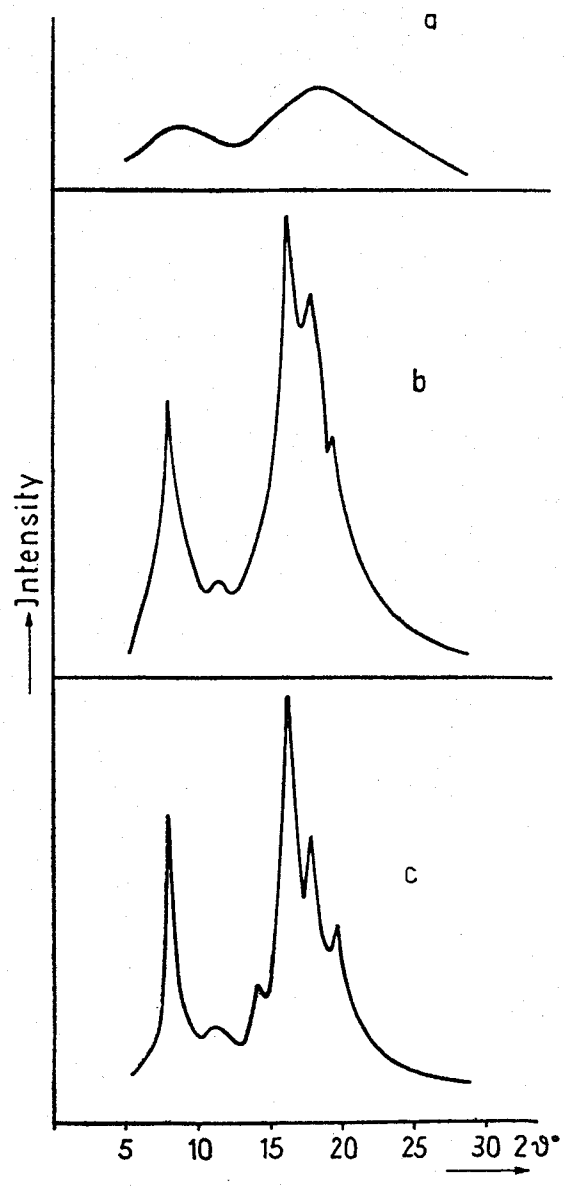


FIG. 4a. X-ray powder spectra (Cu$K\alpha$) registered with a *Geiger* counter of: (a) Isotactic amorphous poly-*p*-chlorostyrene, (b) hydrogenated and dehalogenated poly-*p*-chlorostyrene, (c) Isotactic polyvinyl cyclohexane.

methylstyrene isomorphous with the isotactic crystalline polystyrene.

Styrene–*p*-methylstyrene copolymers containing more than 50 per cent of *p*-methylstyrene generally are amorphous, but if they are hydrogenated they crystallize.

It is clear that hydrogenation increases the size of the cyclic group in such a way that the ratio length/width is smaller for the methylcyclohexyl than for the methylphenyl group, thus allowing a better packing of the chains (isotactic helices) in the crystals. It is therefore demonstrated that not all the vinyl polymers with isotactic structure are crystalline.

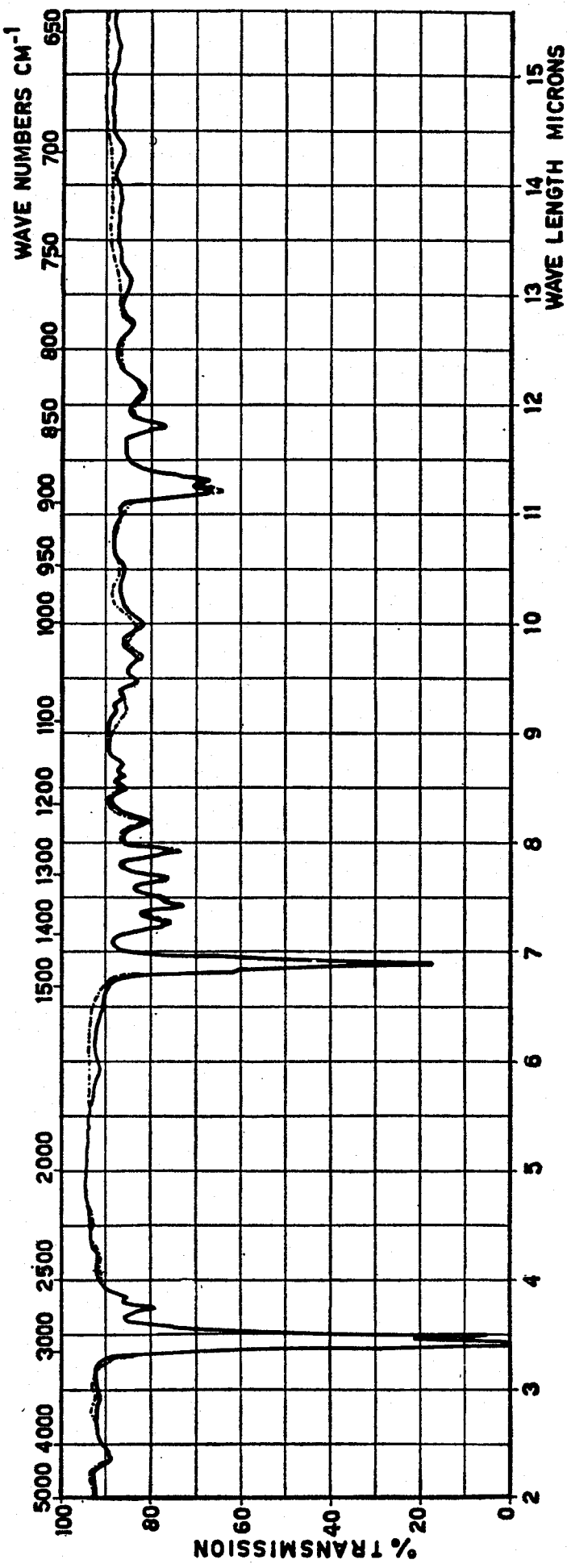


FIG. 4b. I.R. spectra of isotactic polyvinyl cyclohexane (———) and of hydrogenated and dehalogenated isotactic non crystalline poly-*p*-chlorostyrene (—.—.)

Independently of the kinetic factors which exert an influence upon crystallization rates, crystallinity is generally achieved only when the best possible packing of the chains (which in isotactic polymers must assume a helicoidal conformation, in which all the monomeric units are equivalent) leads to the formation of crystals whose density is not significantly lower than that of the amorphous polymer.

POLYMORPHISM IN STEREOREGULAR POLYMERS

Many cases of polymorphism were observed in the field of polymers with a sterically regular structure. They may depend on many reasons:

1. Phenomena of real polymorphism, due to the existence of different modifications having different crystal structures; each structure is stable in particular conditions: i.e. temperature, pressure, stress. For instance, *trans*-1,4-polybutadiene, at about 60°C, turns into a different crystalline modification (Fig. 5) with a shorter identity period along the chain axis (4·68 Å), while the identity period of the modification

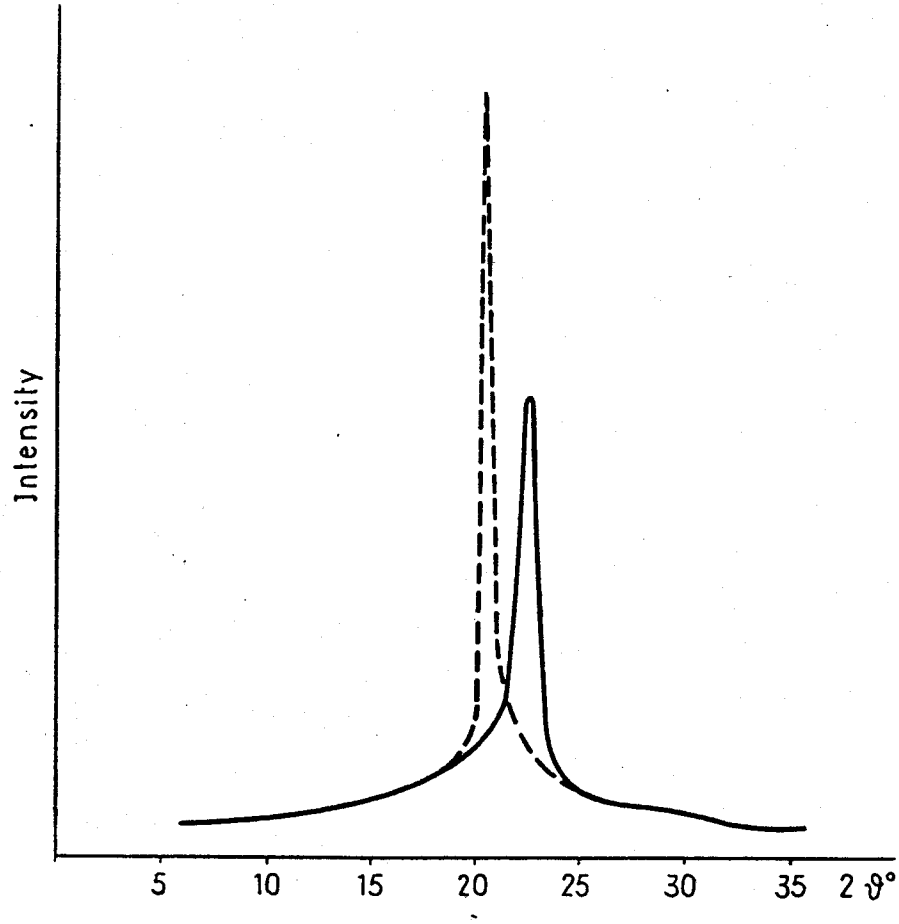


FIG. 5. Comparison between the X-ray powder spectra (Cu$K\alpha$) of the two modifications of *trans*-1,4-polybutadiene (the spectrum of the modification stable at room temperature is full drawn)

stable at a low temperature is 4·92 Å. This transformation, in the oriented fibres, is accompanied by a contraction of crystals (which remain oriented) in the direction of the chain axis, parallel with the fibre axis with production of mechanical work if the fibre is kept under stress.

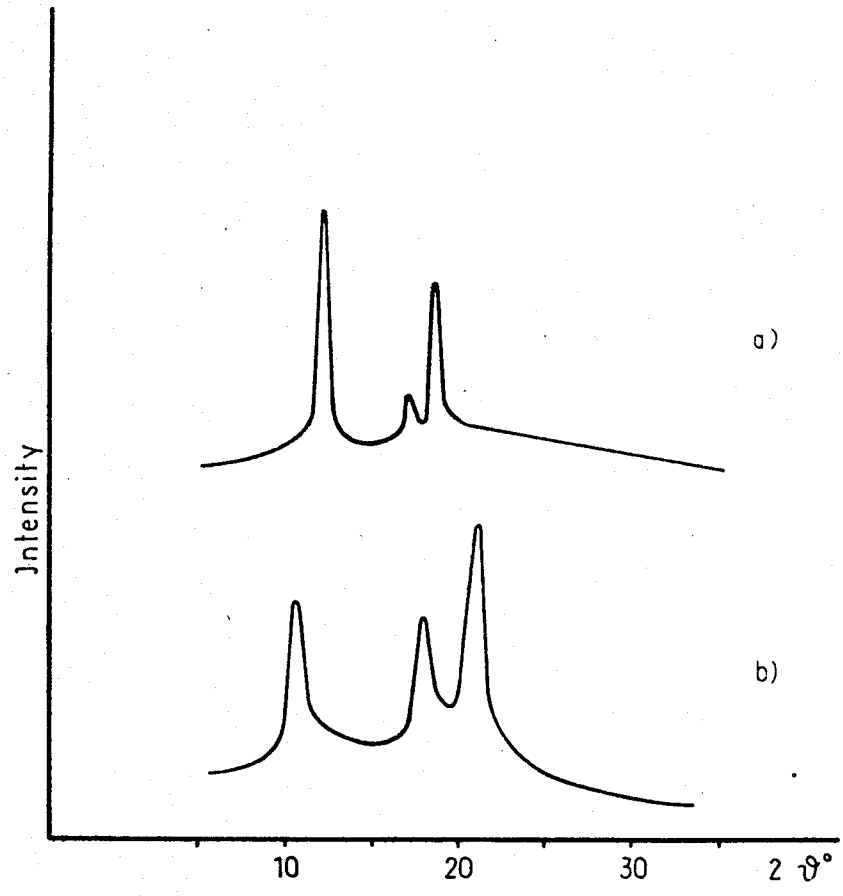


FIG. 6. X-ray powder spectra (Cu$K\alpha$) of the two modifications of poly-α-butene: (a) modification 2, (b) modification 1.

Therefore it is possible to consider a thermodynamic cycle (reversible in theory if viscous flow were avoided), turning heat into mechanical work, through the heating of the stretched fibre to a higher temperature and the cooling to a lower temperature.

2. Polymorphism due to the existence of unstable crystalline modifications. For instance the poly-α-butene chain can have different conformations according to the conditions under which the polymer crystallizes[10]; if it is crystallized from the melt, it generally shows a non threefold helix which tends to transform itself into the more stable modification of a threefold helix. In Figs. 6 and 7 a comparison is made between the X-ray and I.R. spectra of these modifications.

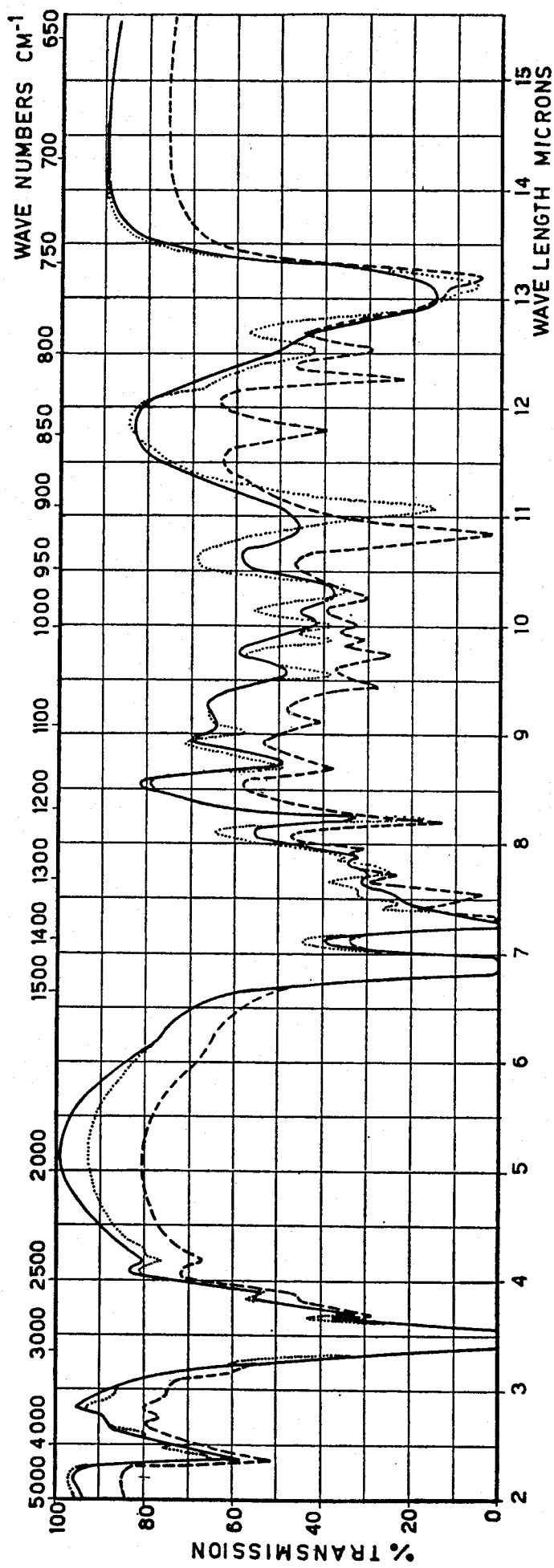


FIG. 7. I.R. spectra of isotactic poly-α-butene
——: crystalline state, modification 1;
- - - - -: crystalline state, modification 2;
: molten state

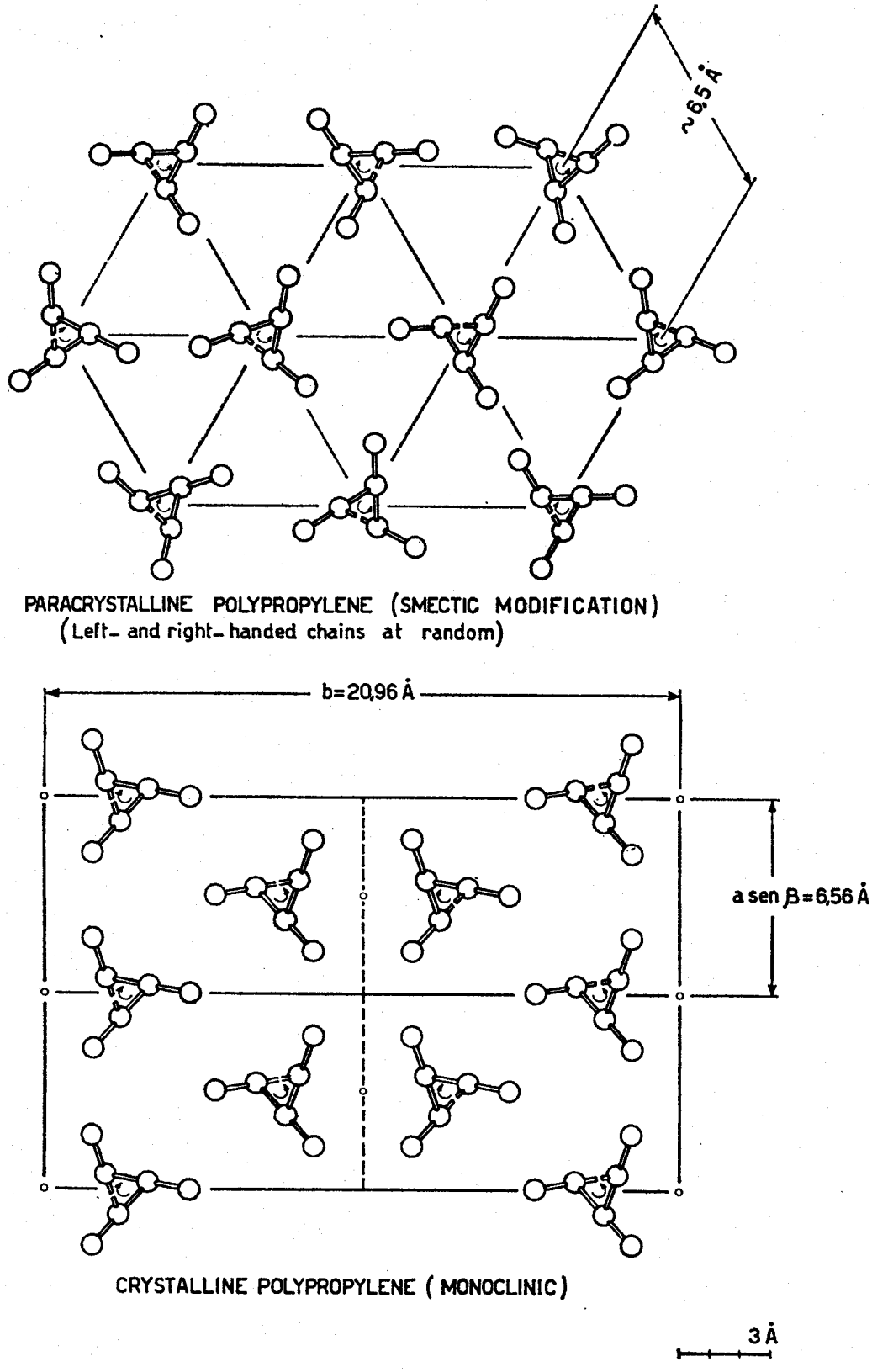


FIG. 8. Projection on (001) plane of the structure of isotactic polypropylene in its paracrystalline and crystalline modifications

3. Particular polymorphism phenomena may exist when the chains can pack in a different way even if they maintain the same helix symmetry (and therefore the same identity period along the chain axis).

In the case of the isotactic polypropylene, right- and left-handed chains may exist; we must think that usually they are present in equal proportions. As shown in Fig. 8, in the crystalline modification having a monoclinic unit cell ($d = 0.94$), right- and left-handed helices are regularly disposed facing one another two by two. By a rapid cooling of the melted polymer we obtained a paracrystalline smectic modification, in which probably right- and left-handed helices are placed at random[11].

The density value of the latter modification (0·88) is lower than that of the monoclinic modification. Polymeric chains of this smectic form may be oriented by cold stretching ($t < 70°C$) without transformation in the stable modification.

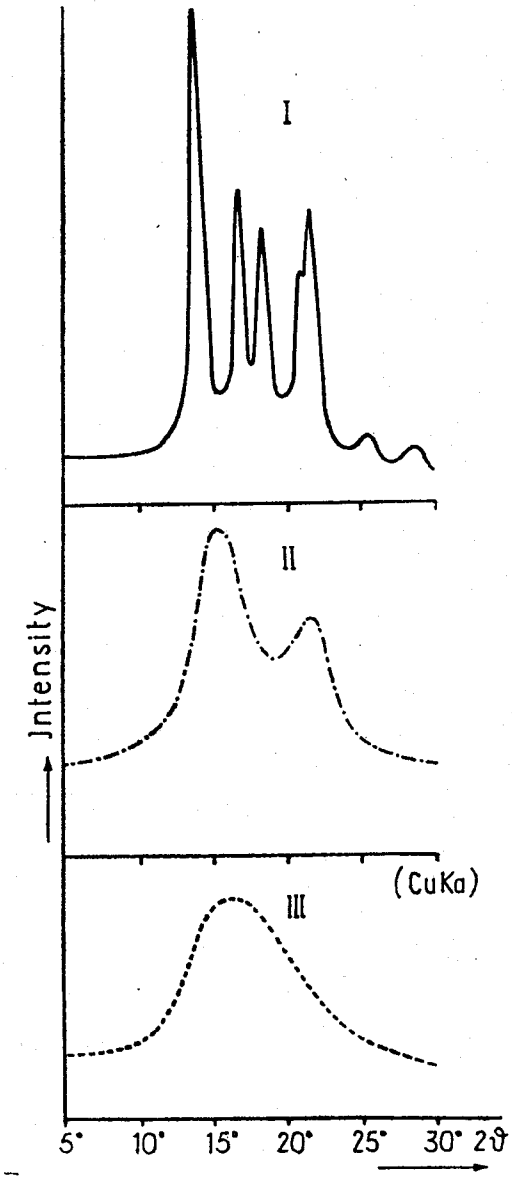


FIG. 9. X-ray powder spectra (Cu$K\alpha$) registered with a Geiger counter of isotactic polypropylene: (I) monoclinic, (II) smectic (pseudo-hexagonal), (III) amorphous

The X-ray spectra (Fig. 9) show that the two modifications have a different structure, whereas the infrared spectra between 7 and 14 microns are practically identical. This is due to the fact that the conformation of each chain in both modifications is identical (and the two I.R. spectra (Fig. 10) are identical because they are practically the spectra of the isolated threefold helix and nearly independent of the packing of the helices).

4. Polymorphism phenomena of unstable modifications existing only in particular conditions (i.e. in copolymers) will be described in the subsequent chapter on isomorphism and isodimorphism of monomeric units in the polymeric field.

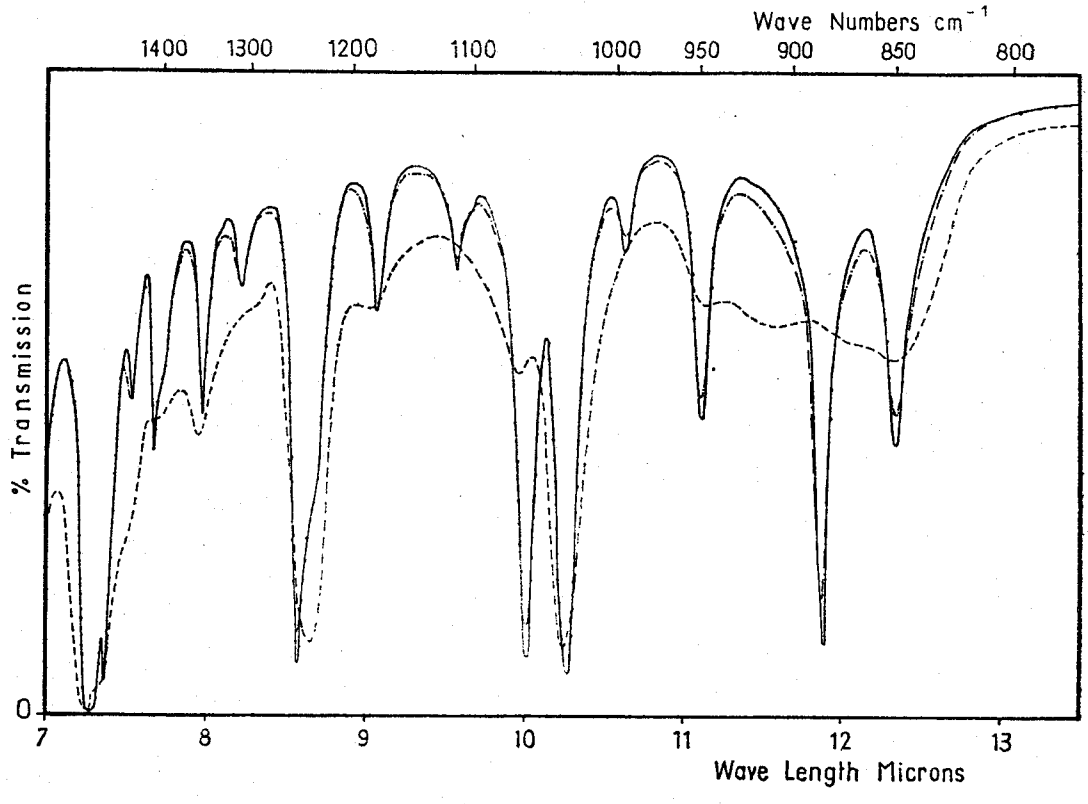


FIG. 10. I.R. spectra of isotactic polypropylene.
———: monoclinic;
———: smectic (pseudo-hexagonal);
---------: molten state

5. Besides the typical cases of polymorphism previously described, we observed for some isotactic polymers the formation of enantiomorphous crystals entirely formed either of right-handed or of left-handed helices. For instance enantiomorphous chains of poly-*tert.*-butylacrylate, as shown in Fig. 11, and of poly-5-methyl-hexene, contrary to what happens for other isotactic polymers (i.e. for polypropylene), give crys-

tals where only isomorphous helices can be present. Only if a right-handed helix can transform itself into a left-handed one through physical processes (i.e. through melting and subsequent cooling) we can speak of true polymorphism.

SYNDIOTACTIC POLY-α-OLEFINS

In 1955 we described[12] the first syndiotactic highly crystalline polymer. It is one of the two polybutadienes with 1,2-enchainment that we obtained by means of stereospecific polymerization of butadiene with organometallic catalysts formed by reacting certain oxygenated or nitrogen compounds of transition metals with metalalkyls.[13] According to the type of catalyst and in particular to the ratio between metalalkyls and transition metal compound and to the operating conditions, we obtained atactic, syndiotactic and isotactic polymers with 1,2-enchainment.[14] Also polyvinyl chloride and polyacrylonitrile show a very limited degree of order of the syndiotactic type.

Polymers to which a syndiotactic structure was ascribed, were subsequently obtained from other vinyl oxygenated monomers (methacrylates, etc).[15] However from literature it does not appear that syndiotactic polymers of α-olefins have been obtained until now.

Many years ago we tried to produce syndiotactic poly-α-olefins in different ways, but, although for certain polymers obtained in particular conditions we had long ago seen indications of the existence of a crystalline modification different from the stable isotactic one, only recently did we obtain crystalline polymers of α-olefins having a syndiotactic structure, completely free from the presence of a crystalline modification with isotactic structure.

Among our first attempts, I recall the hydrogenation of diolefinic polymers with 1,2-enchainment, having a syndiotactic structure.[16] Hydrogenation, in the conditions in which the isomerization of the main chain of other stereo-ordered (isotactic) polymers is not observed ($T < 200°C$), should give a polymer structure corresponding to that of syndiotactic poly-α-butene.

However, even with a practically complete hydrogenation (>95 per cent) of 1,2-syndiotactic polybutadiene, only an amorphous product was obtained. This was therefore, not a product having a crystalline structure similar to that of the non saturated polymer, as may now be foreseen if we admit isomorphism of the vinyl group with the ethyl group in the respective macromolecules.

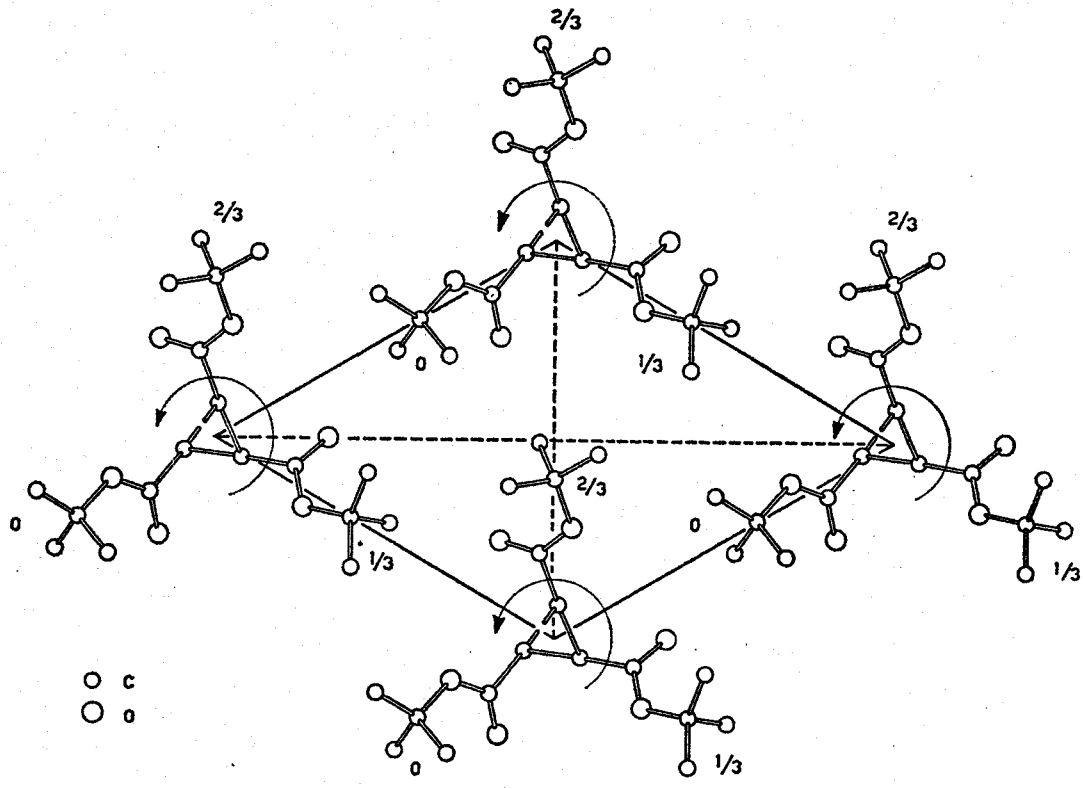


FIG. 11. Mode of packing of isotactic poly-*tert*-butyl acrylate

This is probably due to the larger bulkiness of the $-CH_2-CH_3$ group with respect to the $-CH=CH_2$ vinyl group which for its size already compels the main chain to assume a deformed conformation in comparison with the planar one, and to the fact that such a structure would not satisfy the principle of the staggered bonds.

Recently we succeeded in preparing crystalline syndiotactic polypropylene[17] by direct synthesis from propylene and in obtaining it free from isotactic crystallinity. In the crystalline state it shows a conformation of the main chain very different from that of the known syndiotactic polymers (i.e. syndiotactic polybutadiene and polyvinyl chloride), which have planar or nearly planar chain structures. The crystalline structure of syndiotactic polypropylene is interesting[18] because its main chain has a particular helix conformation (Fig. 12). The identity period along the chain axis is 7·3 Å corresponding to 4 monomeric units. This notwithstanding, all the monomeric units are structurally equivalent. The main chain, besides the twofold screw axis parallel to the chain axis, shows two twofold symmetry axes normal to the chain axis itself.

For syndiotactic polypropylene, such a chain conformation gives a good packing; this fact explains why the melting point of the syndio-

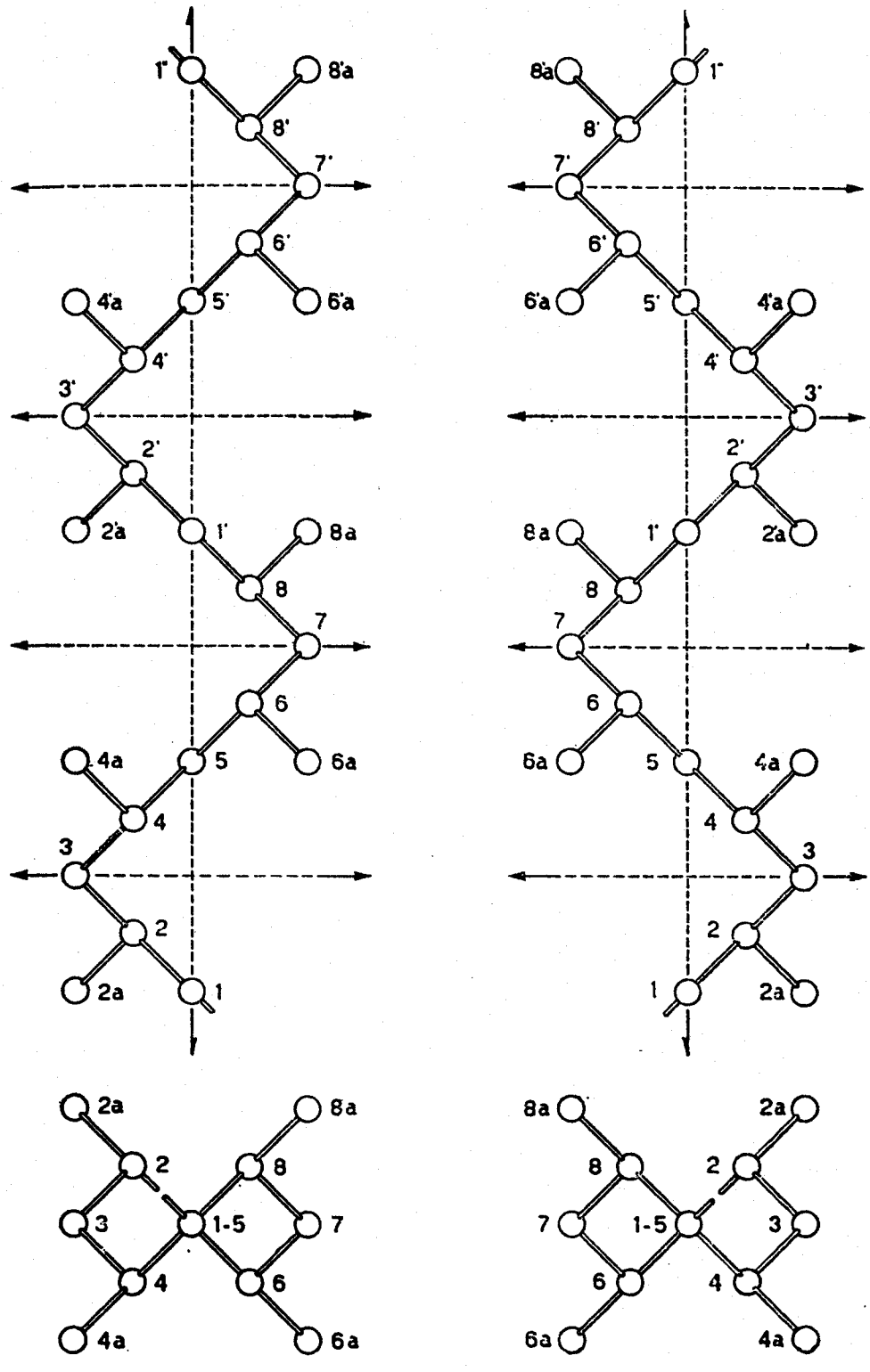


FIG. 12. Syndiotactic polypropylene. Side and end views of enantiomorphous chains

tactic polymer is relatively high, in analogy with what happens for isotactic polypropylene. In Fig. 12 two enantiomorphous helices of syndiotactic polypropylene are drawn. The mode of packing of these chains is shown in Fig. 13. With regard to other poly-α-olefins, we can foresee

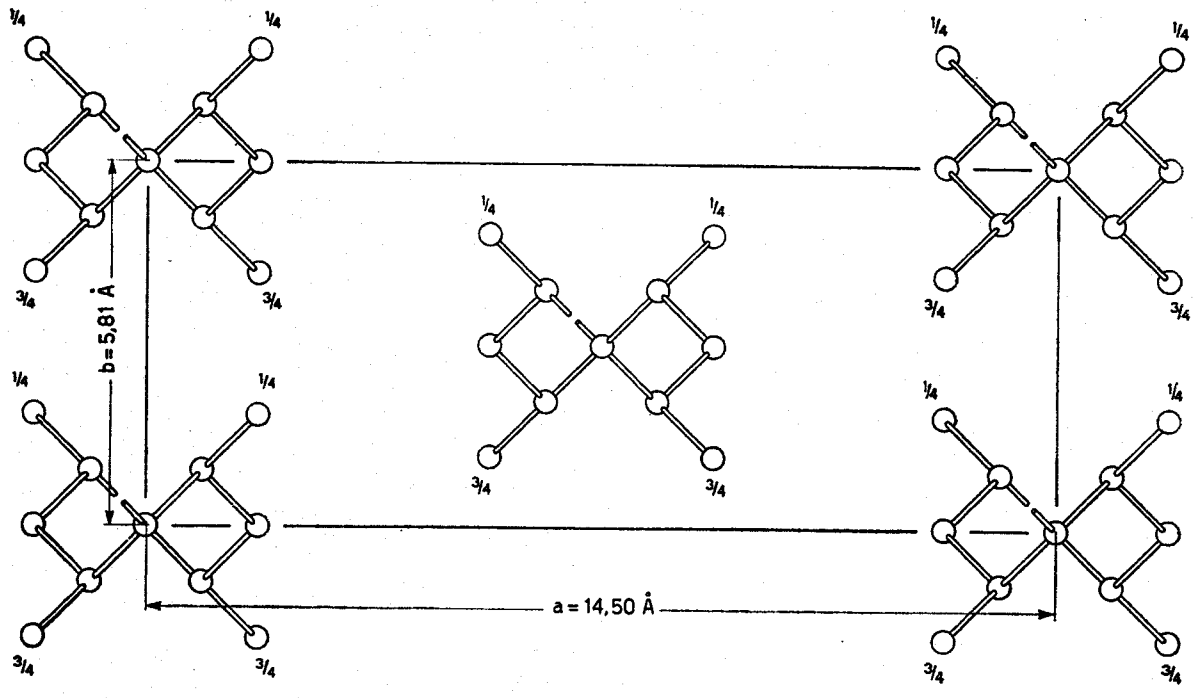


FIG. 13. Mode of packing of syndiotactic polypropylene

that, in analogy with what happens with isotactic polymers, not all the syndiotactic polymers should crystallize.

The preparation of crystalline syndiotactic poly-α-olefins enlarges the field, which is already complex, of configuration isomers of poly-α-olefins. As for the isotactic polymers, the physical properties and in particular the thermal and mechanical ones of syndiotactic polymers depend on their steric purity. Different products, which noticeably differ from one another in their physical properties and therefore also in their possible technical applications, may be obtained and distinguished according to their steric structure and purity.

The possible co-existence in the same chain of isotactic and syndiotactic crystallizable parts further complicates the problem of the relationship between properties and steric structure of poly-α-olefins.

ISOTACTIC AND SYNDIOTACTIC POLYMERS OF NON HYDROCARBON VINYL MONOMERS

The discovery of isotactic and syndiotactic vinyl polymers roused in many research laboratories a big impulse towards the discovery of stereoregular polymers deriving from other types of monomers.

The research previously carried out by Schildknecht on polyvinyl ethers[19], by Price on the polymers of 1–2 epoxides,[20] by Garrett

and Miller on acrylates[21] and by Fox and Garrett on methacrylates[15] led to the recognition of new crystalline polymers. We prepared a series of crystalline polymers from vinyl monomers containing oxygen, nitrogen, silicon, halogens, etc.; all of them have an isotactic structure and some of them were obtained with a high steric purity.[22]

TABLE 2. X-RAY DATA ON SOME CRYSTALLINE ISOTACTIC NON HYDROCARBON POLYMERS

Polymer	*Chain axis* Å	*Helix type**
Poly(allylsilane)	6·45	3_1
Poly(allyltrimethylsilane)	6·50	3_1
Poly-5-(trimethylsilyl)pentene-1	6·55	3_1
Polyvinyl methylether	6·30	3_1
Polyvinyl isobutylether	6·50	3_1
Polyvinyl neopentylether	6·40	3_1
Polyisopropylacrylate	6·50	3_1
Poly-*tert*-butylacrylate	6·45	3_1
Poly-*o*-fluorostyrene	6·63	3_1
Poly-*p*-fluorostyrene	8·30	4_1
Poly-*o*-methyl-*p*-fluorostyrene	8·05	4_1
Polymethylisobutoxyethylene	13·77	7_2

* It is to be understood that, besides the right-handed X_n, there is also the left-handed helix X_{x-n}.

In Table 2 we show the identity periods and the helix types, as obtained from measurements, performed on some of these polymers.[23] Vinylether monomers furnish crystalline polymers with catalysts of different types (preferably with those reacting through a cationic mechanism) if they are polymerized at a very low temperature. Generally stereospecificity using soluble ionic catalysts, is limited to low temperatures ranging from —100° to —35°C. Just polymerizing branched alkyl acrylates using heterogeneous catalysts we obtained crystalline polymers having a high melting temperature and a high crystallinity, even working at room temperature or slightly above[24].

The anionic coordinated catalysis processes that polymerize α-olefins in general do not permit the polymerization of monomers with a "lone electron pair" such as O, N, etc., owing to the fact that these behave as poisons when they associate with the catalytic complex in a stable way. A series of coordination catalysts having a cationic or

an intermediate (between anionic or cationic) behaviour act stereospecifically on vinylethers or on other monomers, which do not polymerize with most of the known Ziegler catalysts.

DI-ISOTACTIC POLYMERS

In 1958[25] I had already described the first di-isotactic hydrocarbon polymers obtained polymerizing deutero-propenes, and more precisely polymers of *cis* and *trans* propene-1-d_1, with the typical stereospecific catalysts of α-olefins (α-$TiCl_3$–AlR_3). Working with these catalysts, in the same conditions in which a good stereospecificity for α-olefins can be observed, an isomerization of the two geometrical isomers does not occur during the polymerization (at least not in such a proportion as to confuse the results).

The two polymers obtained with the *cis* and *trans* isomers, are both crystalline, but their I.R. spectra differ from each other and from the I.R. spectrum of the crystalline polymer obtained by polymerizing a mixture of *cis* and *trans* 1-deutero-propene-1. Even though such polymers observed by X-rays show the same crystalline lattice and therefore cannot be distinguished by this method, the differences observed in the I.R. spectra allow us to establish that some stereospecific catalysts (such as α-$TiCl_3/Al(C_2H_5)_3$), during the polymerization determine the disposition not only of the tertiary carbon atom of the $HCCH_3$ group, but also of the HCD group.

In fact, the differences existing in the I.R. spectra, of the two types of crystalline polymers respectively obtained from the *trans* and *cis* isomers, can be only ascribed to a different, but regular steric order of deuterium atom in respect to the methyl group. As may be seen from Fig. 14, with X-ray examination showing the structures to be identical and the two polymers isotactic with respect to the $CHCH_3$ groups, two different and regular conformations (enantiomorphous) are possible for the CHD group.

In Fig. 15 the two types of chains are schematically drawn in the same way previously used to describe the polymers which are simply isotactic, supposing that the main chain is zig-zag stretched on a plane. In one case all the deuterium atoms D are situated on the same side of the methyl groups, in the other case on the opposite side. In both cases there is an isotactic structure for the CHD groups. The chain is therefore formed of successions of CHD groups, which are isotactic among themselves, and of $CHCH_3$ groups, which are also isotactic among

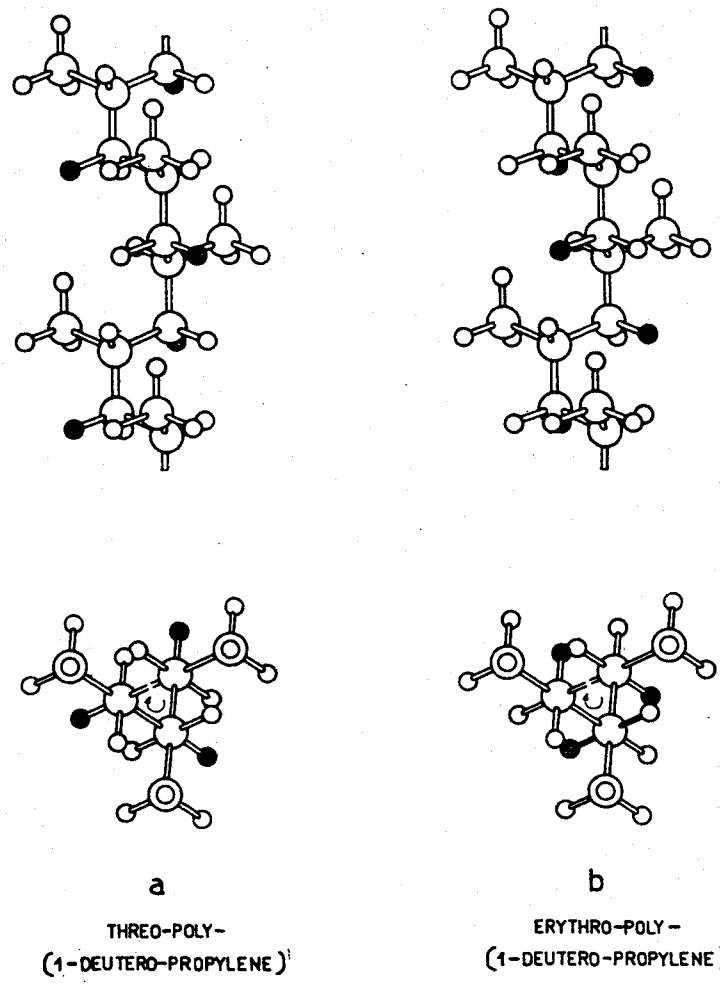


FIG. 14. Side and end views of the chain of di-isotactic polypropylene $1d_1$.

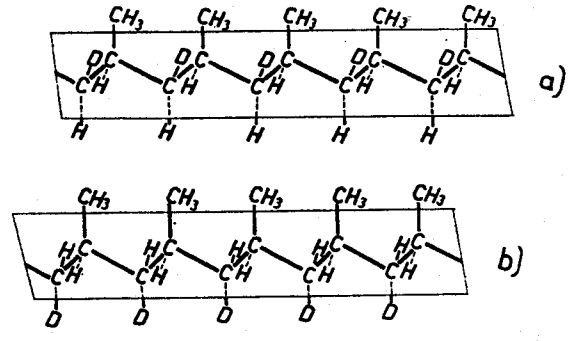


FIG. 15. Schematic drawing of di-isotactic polypropylene $1d_1$;
(a) *threo*-poly-1-deutero-propylene
(b) *erythro*-poly-1-deutero-propylene

themselves; therefore we call "di-isotactic" the polymers showing a double isotacticity in the main chain.

For the two different types of structure, we used the prefixes "threo" and "erythro" to distinguish polymers in which a substituent

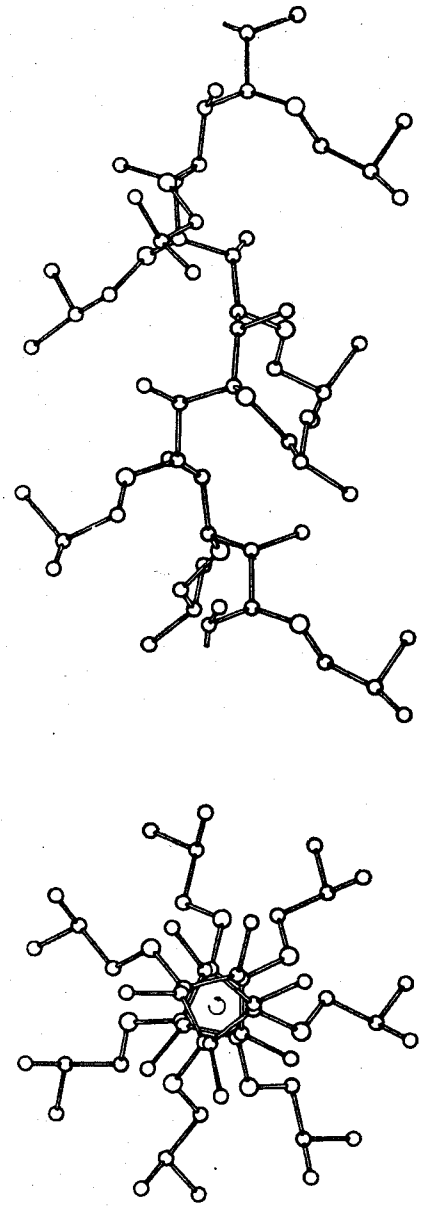


FIG. 16. Side and end views of the chain of crystalline *threo*-di-isotactic polymethylisobutoxyethylene (helix type 7_2).

respectively is, in the drawing shown in Fig. 15, on the same side (a) or on the opposite side (b) of the other substituent.

Other di-isotactic polymers have been obtained in our Institute polymerizing monomers of the CHR=CHR′ type, where R and R′ are different chemical groups[26]. For these polymers we could demonstrate that from the trans isomer it is possible to obtain the *threo*-di-isotactic polymer. Fig. 16 shows the chain conformation with 7_2 symmetry of threo-di-isotactic 1-methyl-2-isobutoxyethylene, obtained by direct synthesis using stereospecific catalysts which act on the internal double bond. This compound is not only the first di-isotactic polymer possessing a remarkable chemical difference among the substituents

in both tertiary carbon atoms, but it is also the first example of crystalline isotactic polymer of a monomer containing an internal double bond. Actually all the isotactic polymers previously known, whose main chain is exclusively formed of carbon atoms, were polymers of vinyl monomers.

ISOMORPHISM PHENOMENA IN THE FIELD OF LINEAR MACROMOLECULES

Whereas the isomorphism phenomena in the field of the mineral and organic (low molecular weight) substances have been deeply studied, the same phenomena in the macromolecular field have not, because the number of the known crystalline polymers available for a systematic study was still limited.

The discovery of new important series of crystalline polymers obtainable by stereospecific polymerization, allowed us to observe different types of isomorphism in the macromolecular field. These isomorphism phenomena cause continuous variations, in relation to their composition, of some parameters of the crystalline lattice, in analogy with what happens in solid solutions of low molecular weight substances (Fig. 17).

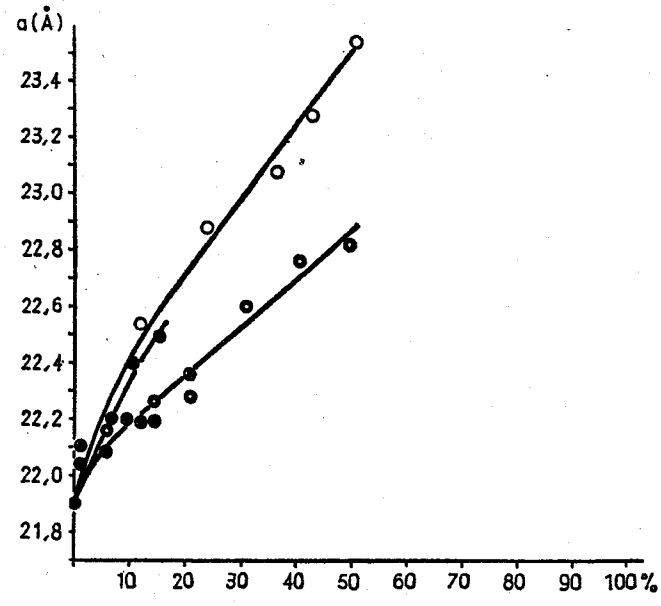


FIG. 17. Variation of the *a* constant of isotactic polystyrene as a function of the percentage of copolymerized units of differently substituted styrenes. Crystalline copolymers of styrene with:
○ *p*-methylstyrene, ● *p*-chlorostyrene, ◘ *p*-fluorostyrene, ⊙ *o*-methylstyrene

It is possible to foresee different types of isomorphous substitutions in the lattices of crystalline linear macromolecules. Here we point out some typical cases:

1. *Isomorphism of Macromolecules*

This isomorphism has been observed when macromolecular chains have only little different chemical nature or structure, almost the same identity period along the chain and do not differ — or differ very little — in the cross dimensions, so that pack themselves in the same crystalline lattice forming solid solutions.

For instance we have observed isomorphism in the following cases:

(a) An isomorphous substitution among the helix chains having the same orientation but a different arrangement (up or down) of the side groups takes place, for instance, in some α-olefin polymers (but not in all of them). When this substitution can take place, it does not modify the side dimensions of the lattice.[3]

(b) On the contrary the random substitution of right-handed helix chains with left-handed ones causes, when it takes place, paracrystalline unstable structures (smectic form of polypropylene) which are looser even if they show the same identity period of the stable form.[11]

(c) A solid solution of polymers formed by isotopic atoms naturally does not modify the lattice constants. The I.R. spectra of solid solutions of polypropylene and of poly-deuteropropylene present a continuous linear variation of the intensity of certain bands in relation to the composition of the polymer.

On the contrary a propylene deutero-propylene copolymer has the same X-ray spectrum and the same lattice constants, but shows remarkable variations of some I.R. crystallinity bands according to the composition; these bands disappear when the percentage of one monomer ranges from 33 to 67 per cent.[25]

(d) Solid solutions of macromolecules can be foreseen among polymers of different monomers, characterized by the same type of lattice structure, by the same identity period of the main chain and only by small differences in the form and size of the side groups. Solid solutions of this type should be easily prepared when the melting temperature or the solubility of the two polymers are not very different, so that their simultaneous separation in the solid form from their liquid mixtures is possible.

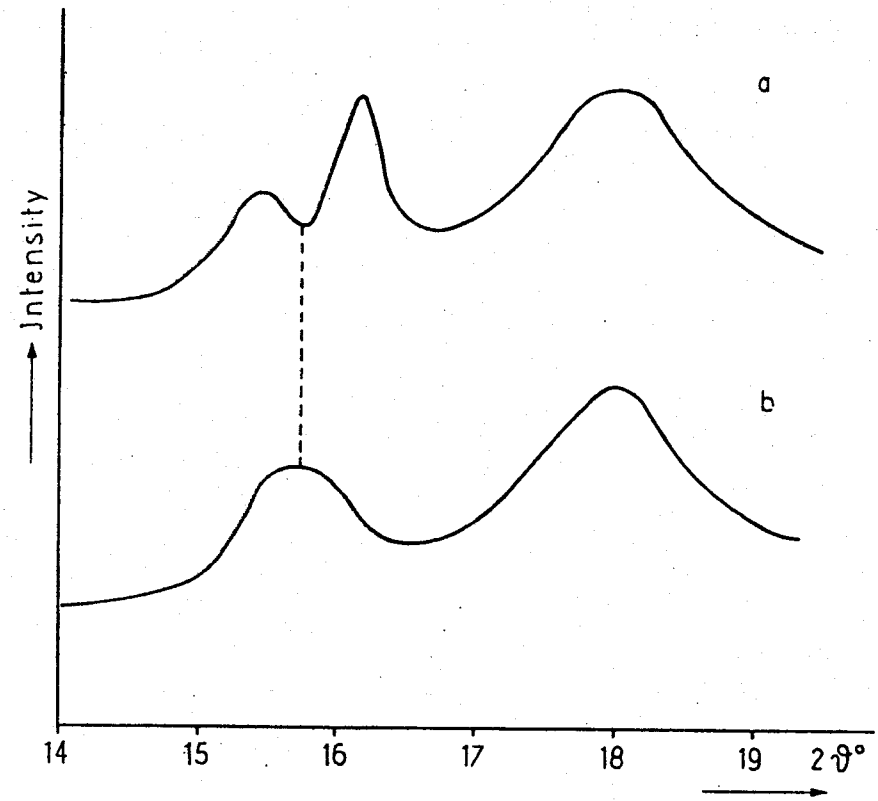


FIG. 18. X-ray powder spectra (Cu$K\alpha$) registered with a Geiger counter of: (a) mechanic mixture, 50 per cent isotactic polystyrene, 50 per cent styrene–*p*-methylstyrene copolymer (molar fraction 30 per cent of *p*-methylstyrene), (b) the same mixture after fusion and annealing at 180°C.

(e) Chain isomorphism allowing true solid solutions, has been observed by us when co-crystallizing chains of homopolymers and crystalline copolymers (i.e. styrene–*p*-methylstyrene) which show the same identity period.[27] The solid solutions exhibit lattice constants which are intermediate between those of the copolymer employed and of polystyrene depending on the relative proportions (Fig. 18).

2. *Isomorphism Phenomena among Monomeric Units*[27]

(a) This very peculiar and new case of isomorphism sometimes occurs, when copolymerizing monomers which have chemical nature, shape and dimensions slightly different from each another and at the same time are able to give homopolymers having an analogous crystalline structure, the same identity period and slightly different lattice constants.

In those cases we observed also that the copolymers are crystalline and have physical properties varying in a continuous way as a function of the composition of the copolymer; for instance the lattice constants are intermediate between those of the pure homopolymers.

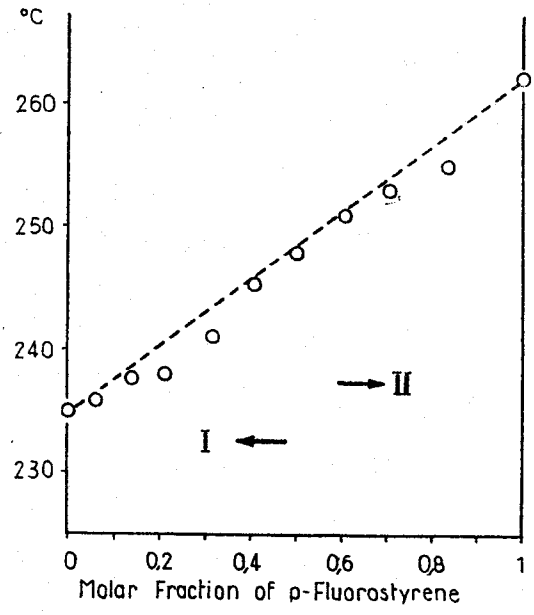


FIG. 19. Melting temperature of crystalline styrene and *p*-fluorostyrene copolymers:
(I) Crystallites with threefold helix
(II) Crystallites with fourfold helix

Whereas the introduction by copolymerization of non isomorphous monomeric units generally lowers the melting point, according to the well-known Flory formula, until amorphous polymers were obtained, it has now been observed that the random introduction of isomorphous units causes a continuous variation of the melting point, which generally assumes intermediate values among those of the pure homopolymers (Fig. 19). The regular variations of many physical properties follow the analogies existing with the isomorphism phenomena previously known for molecules of isomorphous ions, even if in the copolymers described here the monomeric units are linked by chemical bonds and they cannot be separated by physical means, as happens in the normal solid solution of isomorphous products. The phenomenon which we shall call *"isomorphism among monomeric units"* has been observed by us in different systems, at least in some composition ranges. With regard to vinyl polymers, we believe that the isomorphous monomeric units that are present in the same chain, must also show the same steric configuration. With regard to *o*-fluorostyrene and styrene copolymers, which exhibit the same crystalline structure and practically the same lattice constants, there is isomorphism for all the compositions. The X-ray spectra always show a high crystallinity while the I.R. ones show a quick lowering of crystallinity as the content of the component contained in a less concentration

increases. The disappearence of some I.R. crystallinity bands takes place for contents ranging between 30 and 70 per cent of one of the two components. The comparison between the crystallinity variations observed by the I.R. and the X-ray examinations, allowed us to improve our knowledge on the relationship existing between the structure and the crystallinity of systems formed by polymers and by different copolymers.

Whereas, in the I.R. spectra, the crystallinity bands are due to interaction of the atoms belonging to the same chain, which assumes a regular conformation in the crystals, the X-ray spectra show the regularity of packing of the chains, which may exist even if the single chain contains small irregularities due to the presence of different isomorphous monomeric units.

(b) *Isodimorphism.* Crystalline modifications have been observed even in certain cases in which homopolymers show different crystalline structures. In the case of isotactic styrene and *p*-fluorostyrene polymers, for instance, the stable modifications of the homopolymers show different symmetries. Nevertheless these copolymers are crystalline: the ones richer in styrene exhibit the structure of the isotactic polystyrene stable form (threefold helix), those richer in *p*-fluorostyrene show the structure of the *p*-fluorostyrene stable form (fourfold helix). Therefore there is a particular type of isomorphism that, in analogy with what is observed for the solid solutions of crystalline products of low molecular weight, can be called "isodimorphism". We can admit the possibility of existence of the same crystalline modification in the copolymer for both monomeric units even if sometimes it is unstable (or even more if it does not exist) for one of the two pure homopolymers.

It is interesting to note that the introduction of a monomeric unit of bigger size (i.e. *p*-fluorostyrene, *p*-methylstyrene, etc., in the polystyrene chain) always causes a remarkable deformation of the lattice constants; this fact does not always occur in the opposite case, that is when a smaller monomeric unit is introduced (i.e. introduction of styrene in the poly-*p*-fluorostyrene chain).

The formation of mixed crystals, for the styrene-*o*-fluorostyrene system, is possible because of the same identity period and the small differences in the dimensions of fluorine and hydrogen atoms.

The lattice constant in the direction of the chain axis remains, therefore, unvaried, while a slight variation of the lattice constants in the directions normal to the chain can be observed.

(c) *Isomorphism in systems with crystallinity in a limited composition*

range. In some cases, if monomers giving only amorphous homopolymers are copolymerized with monomers giving crystalline homopolymers, crystalline copolymers can be obtained. This can be observed when the monomeric units of the component, whose homopolymer is amorphous, are present in the copolymer in small quantity, even if this quantity is sufficient to modify remarkably the copolymer lattice constants in comparison with those of the crystalline homopolymer. This is what happens with the isotactic copolymers between styrene and *p*-chloro- or *p*-methylstyrene. These crystalline copolymers and the homopolymers that, on the contrary, are amorphous, are obtained by means of the same polymerization mechanism at rates which are only slightly different from those of styrene (Fig. 20) (see Paper 160).

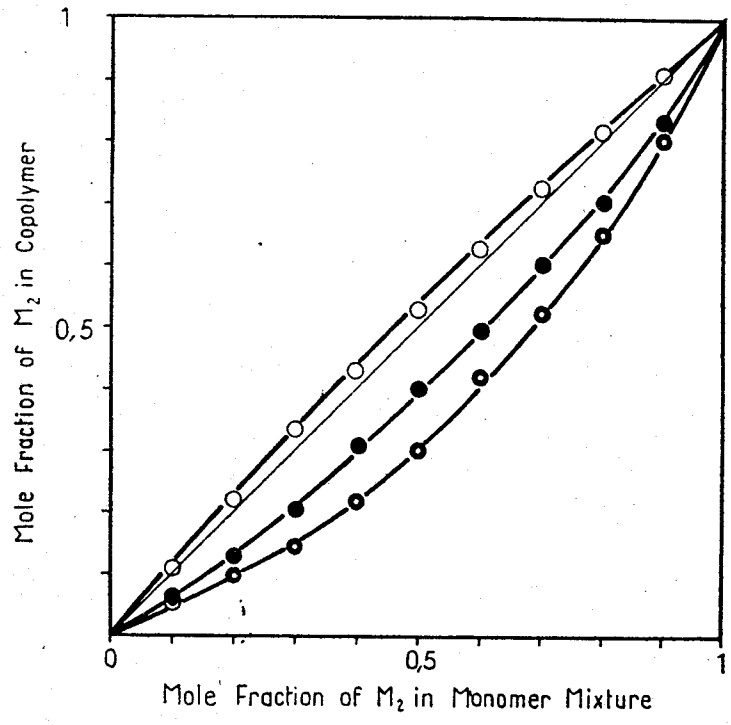


FIG. 20. Composition curves of stereospecific copolymerization of styrene with differently substituted styrenes (titanium chloride-aluminium triethyl catalytic system, T = 40°C)
M_2: ○ = *p*-methylstyrene ● = *p*-fluorostyrene ○ *p*-chlorostyrene

As we have already suggested, it is extremely interesting in the study of copolymerization, to compare the crystallinity data obtained by the I.R. and X-ray spectra.

With regard to the I.R. spectra (Fig. 21) many crystallinity bands are originated by regular interactions among atoms belonging to the same chain which, generally, has a regular conformation only in crystals.

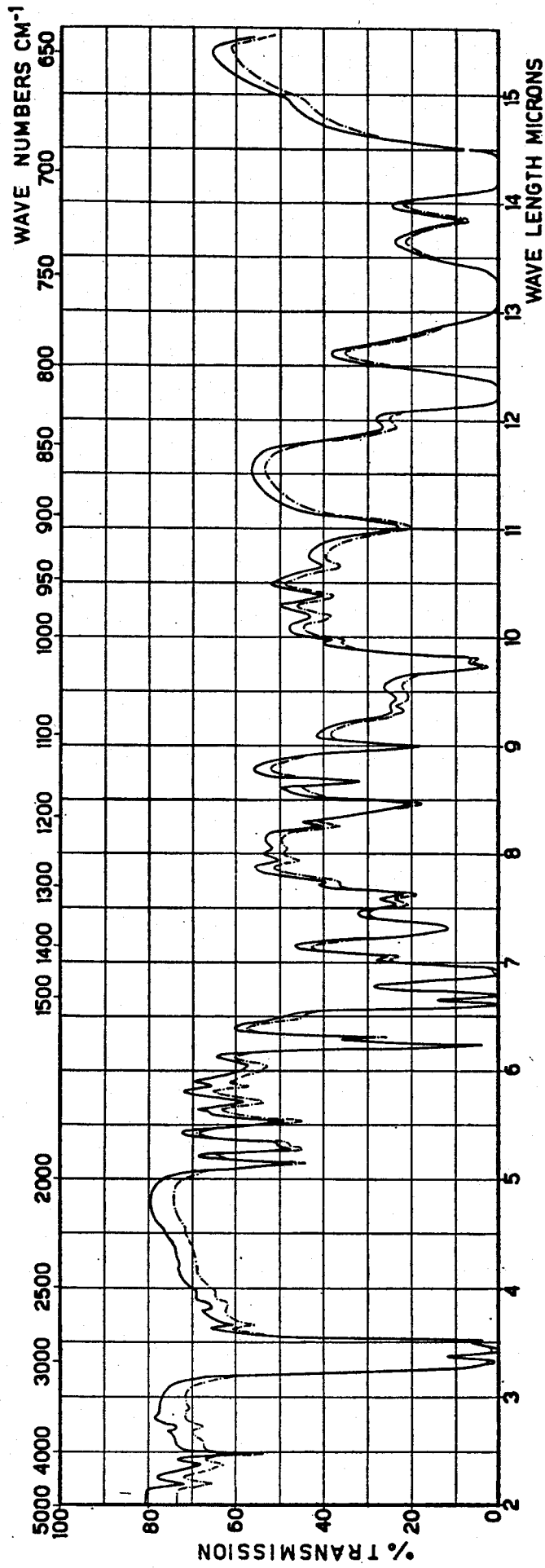


FIG. 21. I.R. spectra of a styrene-*p*-methylstyrene copolymer with a content of 35 per cent in moles of *p*-methylstyrene
———: before annealing, -·-·-·-: after annealing

The I.R. crystallinity, however, does not depend on the packing regularity in the three-dimensional lattice, owing to the fact that interactions among atoms belonging to different chains exercise a scanty influence on the crystallinity bands, at least in the wave length field we have considered. On the contrary, in the case of X-ray spectra (Fig. 22) definite reflections are possible only if a regular chain packing occurs in a three-dimensional crystalline lattice. Crystals formed by a solid solution of chains of different homopolymers must also have the I.R. crystallinity bands of each chain. On the other hand, crystalline copolymers of different isomorphous units give the typical X-ray spectra of the crystalline polymers, when there is a good side packing of the chains (Fig. 22), while the I.R. crystallinity bands, at least in the field

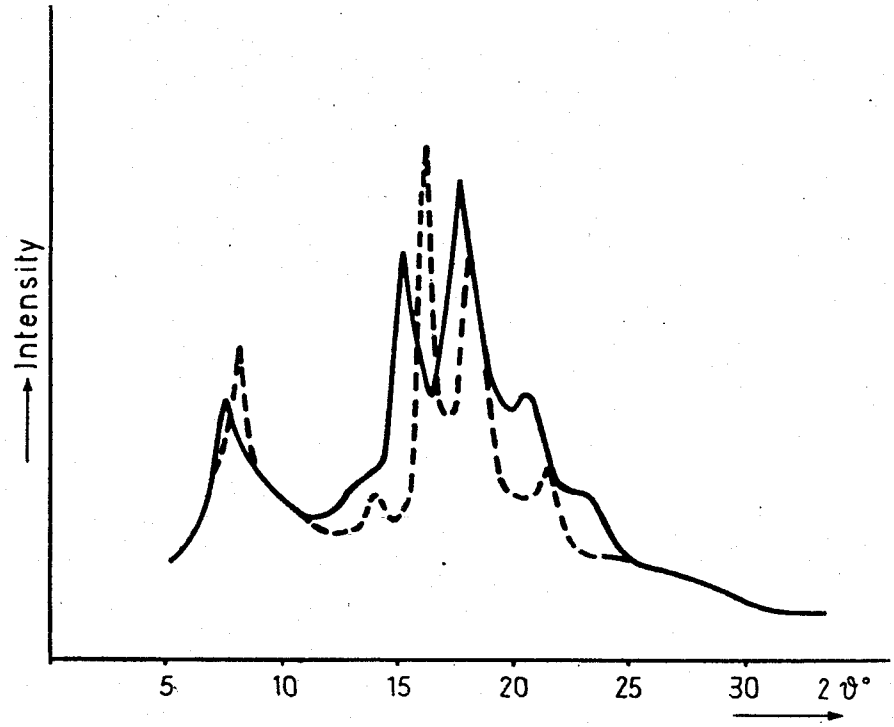


FIG. 22. Comparison between the X-ray powder spectra (Cu$K\alpha$) registered with a Geiger counter, of isotactic polystyrene (broken line) and of a styrene-*p*-methylstyrene copolymer. (43 per cent molar fraction of *p*-methylstyrene)

we examined (Fig. 21), disappear because of the disorder caused by the random distribution of the monomeric units in the single chains.

Thus a new and wide field of research aiming at the quantitative determination of factors regulating the isomorphism and isodimorphism phenomena in the macromolecular field has been opened. The above mentioned phenomena appear more complex than the well known ones for low molecular weight substances.

STEREOREGULAR POLYMERS HAVING A HIGH STERIC PURITY

In the polymers, in which monomeric units can show stereoisomerism phenomena, crystallinity and many physical properties, in particular the mechanical ones, are strongly influenced by the steric purity of the polymeric chains. It is therefore important to determine the factors influencing the steric purity of the stereoregular polymers, during the polymerization with stereospecific catalysts. I shall not describe here the known fractionation methods, which have been recently improved for a rapid and accurate characterization of stereoregular polymers. I only recall that for a more accurate characterization of the isotactic stereoblock polymers, for which, as regarding solubility, a competitive effect can be observed between molecular weight and steric purity on the solubility, we proposed a chromatographic fractionation process and found it suitable. This method uses, as adsorbing mass, a crystalline polymer of the same type, but with a higher melting point, and insoluble in the solvents used.

With regard to the fractionation of isotactic stereoblock polypropylene, we used as adsorbing mass an isotactic polypropylene insoluble in boiling n-octane. This adsorbing mass fixes preferably the macromolecules containing longer isotactic sections because of an epitactic adsorption phenomenon on the crystal surfaces.[28] By means of this method, starting from a polymer fraction obtained by simple extractions with solvents, we could separate macromolecules having a higher molecular weight, but a lower steric purity, from macromolecules having a higher crystallinity, but a lower molecular weight.[28]

From the examination of the "stereoblock" polymers[29] of α-olefins and diolefins, their lower crystallinity degrees and their lower melting temperatures cannot be always interpreted because of a statistical distribution of the steric irregularities (for instance, inversion of configuration) in a chain that is formed of monomeric units having the same steric configuration.

The structure which some years ago we attributed to stereoblock macromolecules, has been proved by subsequent results, at least for some polymers. These stereoblock macromolecules are in fact formed of a succession of chain sections differing in their configurations. This is attested by the interpretation we gave of the mechanism of the processes responsible for the inversions of the steric configuration of the monomeric units in the macromolecules of polypropylene obtained in the presence of heterogeneous catalysts, which contain active cen-

tres with different activity and besides with the possibility of enantiomorphous configurations.

In fact, we observed that the steric purity, in particular of raw polymers, is lowered when the concentration of the monomer is rather low.

This may be interpreted, if we admit that the growing molecule may pass by means of disassociation and subsequent association from one active centre to the other[30]. The rate of this process is connected, as some chain transfer processes, with the concentration of organometallic compounds in solution.

Furthermore we observed by the I.R. spectra that also the polypropylene chain sections that cannot be crystallized may be of two different types:

(1) Some of them are characterized by a greater number of couples of adjacent monomeric units having the same steric configuration. (2) Some others, present in the polymers having syndiotactic structure, are characterized by a greater number of couples having opposite steric configurations[31].

In polymerizing diolefins or monomers containing a lone electron pair, stereospecific polymerizations are possible even without the presence of a solid crystalline component in the catalytic system, and sometimes even with completely soluble catalysts, especially when the reaction is carried out at low temperature. This happens, for instance, in the polymerization of butadiene to 1,2 isotactic and syndiotactic polymers, in the polymerization of vinyl ethers and of acrylates to isotactic polymers[22]. In these cases the reasons for a lower stereospecificity may be of different nature. One of the most important, but not the only one, may lie in the chemical impurity of the catalytic complex.

For instance, there are catalytic systems prepared with the same reagents that, according to the ratios of the components and the operating conditions, furnish isotactic or syndiotactic polybutadienes or macromolecules of the two types and at the same time atactic macromolecules.[13, 14]

As regards polybutadiene with a high value of *cis* 1,4 content, the mode of distribution of the steric impurities is more important than the steric purity itself.

Some catalytic systems [obtained, for instance, from TiI_4 and $Al(C_2H_5)_3$[32]], give random copolymers of monomeric units with different configurations; because of that, in this case, also polymers having a high value of *cis*-1,4 units (about 93 per cent) show a low melting temperature, in the range of —8 to —10°C.

As regards the *cis*-1,4 unit content in polybutadienes, the data reported here were determined according to a method recently developed in our Institute.[33]

There are other catalytic systems prepared from other Ti halides[34] which give mixtures of macromolecules: among them, some are almost completely *trans*-1,4 whereas others are almost completely *cis*-1,4. Even if the raw polymers have a low percentage of *cis*-1,4 units, it is possible, by solvent fractionation, to separate macromolecules which are very rich in *cis*-1,4 units (92–95 per cent); these macromolecules melt at about 0°C and crystallize rapidly under stretching even at temperatures above room temperature or in a highly vulcanized state.[35]

In this case we can think that the steric impurities are not statistically distributed along the chains and this allows the existence in the macromolecules of sections containing *cis*-1,4 units sufficiently long to have a melting point very close to that of the sterically pure polymer.[36]

From these results we could point out the importance of the distribution of steric impurities and we undertook a systematic study of the polymerization of butadiene in order to develop highly selective and stereospecific catalysts. The result was that, at the Donegani Institute in Novara[37] and at the Polytechnic of Milan, raw polymers were synthesized which are very rich in *cis*-1,4 units. The melting point of raw polybutadienes with a percentage of *cis*-1,4 units higher than 99 per

TABLE 3. MELTING TEMPERATURES OF LINEAR CIS 1,4-POLYBUTADIENES HAVING DIFFERENT STERIC PURITY (ΔH_u = 2000 CAL/MONOMERIC UNIT)

%cis *1,4 monomeric units*	*calculated melting point (°C)*
100	+1
98·5	0
95	—3
90	—7
85	—11
80	—15
75	—19

Note: The calculated data take into account only the irregularities due to the presence along the polymer chain of *trans*-1,4-butadiene units or of butadiene units with 1,2-arrangement.

cent is about + 1°C, and the melting enthalpy about 2000 cal/mole.[36]

Both for *trans*-1,4 and *cis*-1,4 polybutadienes we are able now to obtain using stereospecific catalysis, raw polymers which are sterically purer (>99 per cent) than natural rubber (steric purity about 97 per cent) and purer than synthetic polyisoprenes, as far as it is reported in the literature.

The increase in steric purity is related not only to a change in certain properties, but, beyond certain limits, we observe the appearance of new and very interesting properties which are typical of sterically very pure polymers.

In the case of *cis*-1,4 polybutadienes only the presence of long sections of sterically pure chains permits the obtainment of vulcanized products which, in the absence of reinforcing agents, exhibit an elastic behaviour similar to natural rubber[25]. This behaviour is characterized by a remarkable increase in the elastic modulus, even over a wide range of temperatures above room temperature, as the deformation increases. This variation is due to the crystallization of the chains which line up parallel under stress. In certain temperature ranges the dynamic properties of *cis*-1,4 polybutadienes are higher than those of *cis*-1,4 polyisoprenes.

When considering all the results obtained during five years of research in the field of stereospecific polymerization one can fecl satisfied. Macromolecular chemistry is progressing with a rhythm not inferior to the one observed in other branches of science. In the field of synthetic rubbers and textiles, some new products cannot be any longer considered only as substitutes for natural products (whose use is justified only from economical reasons): in fact these new products represent a qualitative progress because they have suitable properties for new and very valuable applications.

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STEREOSPECIFIC POLYMERIZATION OF VINYLAROMATIC MONOMERS. NOTE IV: REACTIVITY OF THE MONOMERS IN THE OVERALL PROCESS

by G. NATTA, F. DANUSSO, D. SIANESI and A. MACCHI

(11 Sept. 1959)

[*Chimica e Industria* **41**, 968 (1959)]

ABSTRACT

The reactivities of a large series of vinylaromatic monomers in the overall process of stereospecific polymerization, carried out at 60°C, with a catalyst prepared from $TiCl_4$ and $Al(C_2H_5)_3$, are determined.

Results are discussed on the basis of either steric or polar effects caused by the substituent of the vinyl group. Reactivities are particularly affected by steric factors. In many cases, in which such an influence may be neglected, reactivity regularly increases with the increase of the electron density on the monomeric double bond.

Other interesting correlations between reactivity and nature of substituent are pointed out.

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CHAIN STRUCTURE OF ISOTACTIC POLYVINYL CYCLOHEXANE

by G. NATTA, P. CORRADINI and I. W. BASSI

(15 Sept. 1959)

[*Makromol. Chemie* **33**, 247 (1959)]

Many types of helical chains present in the crystals of different isotactic polymers have been described in the last years. They all correspond to successions of more or less distorted *trans* and *gauche* bonds.[1]

The chains of the polymers, which have an identity period along the fiber axis comprised between 6·4 and 6·7 Å, generally correspond to successions of undistorted *trans* ($\sigma_1 = 180°$) and *gauche* ($\sigma_2 = 60°$) bonds, repetition being achieved along a three-fold helix[2] [$(AB)_3$ or $(AC)_3$ according to the terminology of C. W. Bunn[3]].

Surprisingly, we have recently found that the chain of isotactic polyvinyl cyclohexane, which has an identity period along the fiber axis of 6·5 Å does not follow a three-fold helix, but a four-fold one.

Crystalline polyvinyl cyclohexane has been obtained in this Institute by polymerization of vinyl cyclohexane with the same catalysts which polymerized α-olefins, styrene and some substituted styrenes to isotactic polymers.

The isotactic structure of polyvinyl cyclohexane is also confirmed by the fact that through hydrogenation of isotactic polystyrene, and hydrogenation and dehalogenation of isotactic amorphous polychlorostyrenes we obtained products exhibiting the same X-ray diffraction lines as crystalline polyvinyl cyclohexane.[4]

All X-ray reflections given by a fiber of this polymer may be indexed on the basis of a tetragonal unit cell, with $a = 21{\cdot}9$ Å. The space group is $I\ 4_1/a$, as can be deduced from the systematic extinction of reflections hkl with $h+k+l = 2n+1$ and $hk0$ with $h = 2n+1$ and $k = 2n+1$.

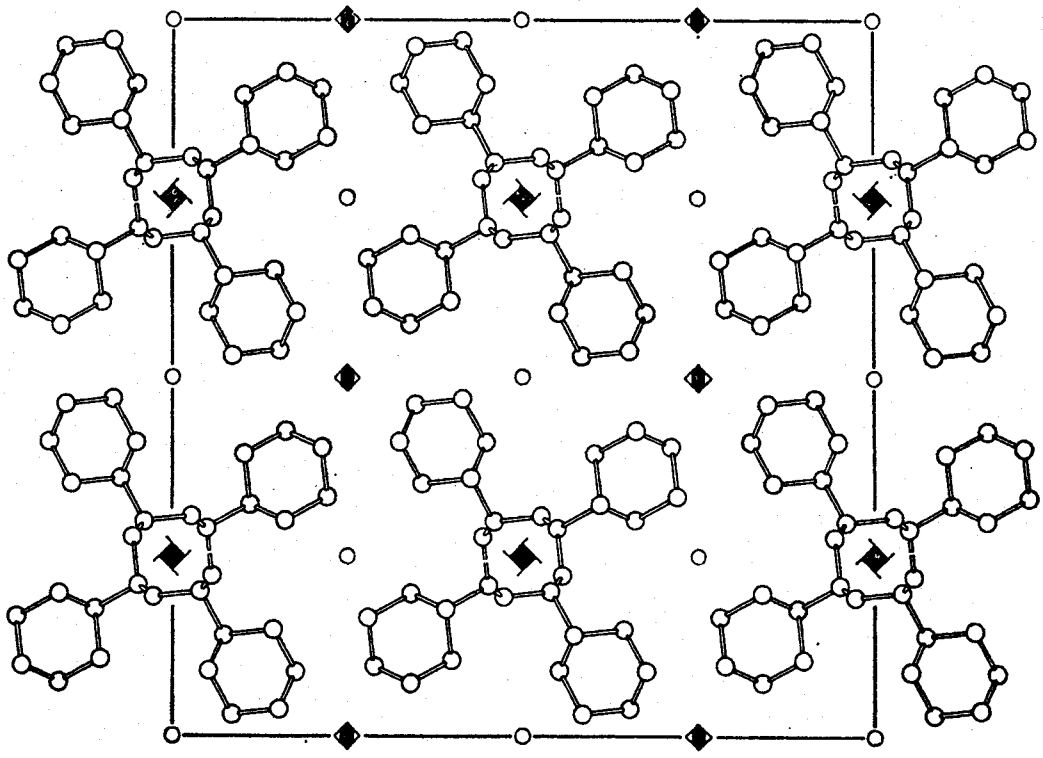


FIG. 1. Mode of packing of isotactic polyvinyl cyclohexane
(For the symbols drawn in Fig. 1. see Ref. 5)

The calculated density, with 16 monomeric units per unit cell, is 0·95 g/cm^3, in accordance with the experimental datum. Thus, successive monomeric units along the four-fold helices are equivalent from a crystallographic point of view, because they are repeated through the operation of the 4_1 and 4_3 axes, present in the space group.[5]

Each right-handed helicoidal chain is surrounded by four anticlined left-handed helicoidal chains and vice versa (Fig. 1). The mode of packing is slightly different from that shown by isotactic poly-*o*-methylstyrene, in which each four-fold helical chain is surrounded by four enantiomorphous but isoclined chains.[6] It is interesting to note that also poly-3-methylbutene possesses a four-fold chain structure, with an identity period along the fiber axis (6·85 Å) analogous to but slightly longer than that of polyvinyl cyclohexane (6·50 Å). In both cases, the rather large distortion of internal rotation angles from the minimum energy values of a polymethylenic chain must be attributed to the bulkiness of the side groups. We are now carrying out a complete evaluation of the structure of polyvinyl cyclohexane.

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FRACTIONATION OF PREDOMINANTLY ISOTACTIC POLYPROPYLENE

by M. PEGORARO

(15 Sept. 1959)

[*Rend. Ist. Lomb. Sci. e Lettere* **93**A, 624 (1959)]

ABSTRACT

Polypropylenes, which are free from amorphous polymers and which are obtained with $Al(C_2H_5)_3$–α-$TiCl_3$ catalysts in n-heptane, were fractionated by following the Desreux method on the basis of the melting point of the polymeric fractions, and by using only one solvent, toluene, at increasing temperatures from 100 to 135°C. It has been observed that the density, the crystallinity and the molecular weights of the fractions under consideration, essentially increase proportionally with the increase of the elution temperature; whereas the structural irregularities, determined by Flory's theory, decrease. The molecular weights of the examined polypropylenes seem to be polydispersed.

The method of fractional separation of polypropylene, dispersed in a column on an inert support, appears to be advantageous with respect to the traditional method, which uses a series of solvents having an increasing boiling point. Due to this great simplicity, one can obtain a higher number of fractions, thus allowing a more complete investigation of the properties and of the constitution of the polymer.

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CHAIN STRUCTURE OF POLY-*m*-METHYLSTYRENE

by P. CORRADINI and P. GANIS

(15 Sept. 1959)

[*J. Polymer Sci.* **43**, 311 (1960)]

ABSTRACT

The helicoidal conformation of isotactic poly-*m*-methylstyrene is defined by 3·67 monomeric units per pitch.

The conformation of the macromolecule of isotactic poly-*m*-methylstyrene is defined by a helix with a repeat of $21 \cdot 74 \pm 0 \cdot 25$ Å containing 11 monomeric units in 3 pitches (3·67 monomeric units per pitch) (Fig. 1). The conformation of the macromolecule has been determined by comparing the distribution of the intensity on all layers, theoretically diffracted by an isolated chain, with the intensity distribution observed on the fibre spectra (Fig. 2).

With regard to poly-*m*-methylstyrene, Y. Chatani (*J. Polymer Sci.* **47**, 491 (1960)) subsequently reported a value of 3·62 monomeric units per pitch. Considering the good agreement with our previous data, we believe that Y. Chatani did not examine a different polymorphous modification.

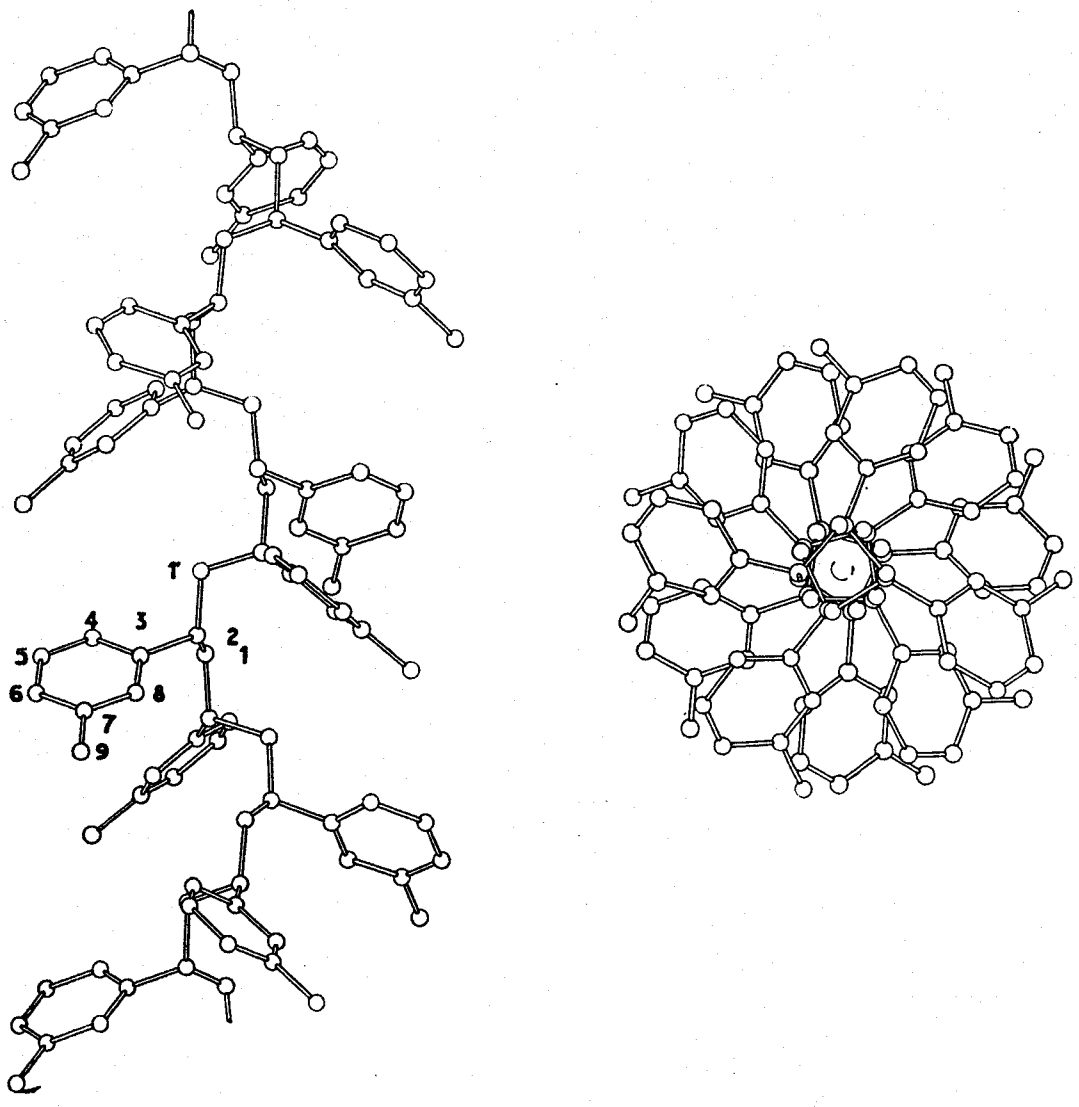


FIG. 1. Side and end views of the chain of poly-*m*-methylstyrene.

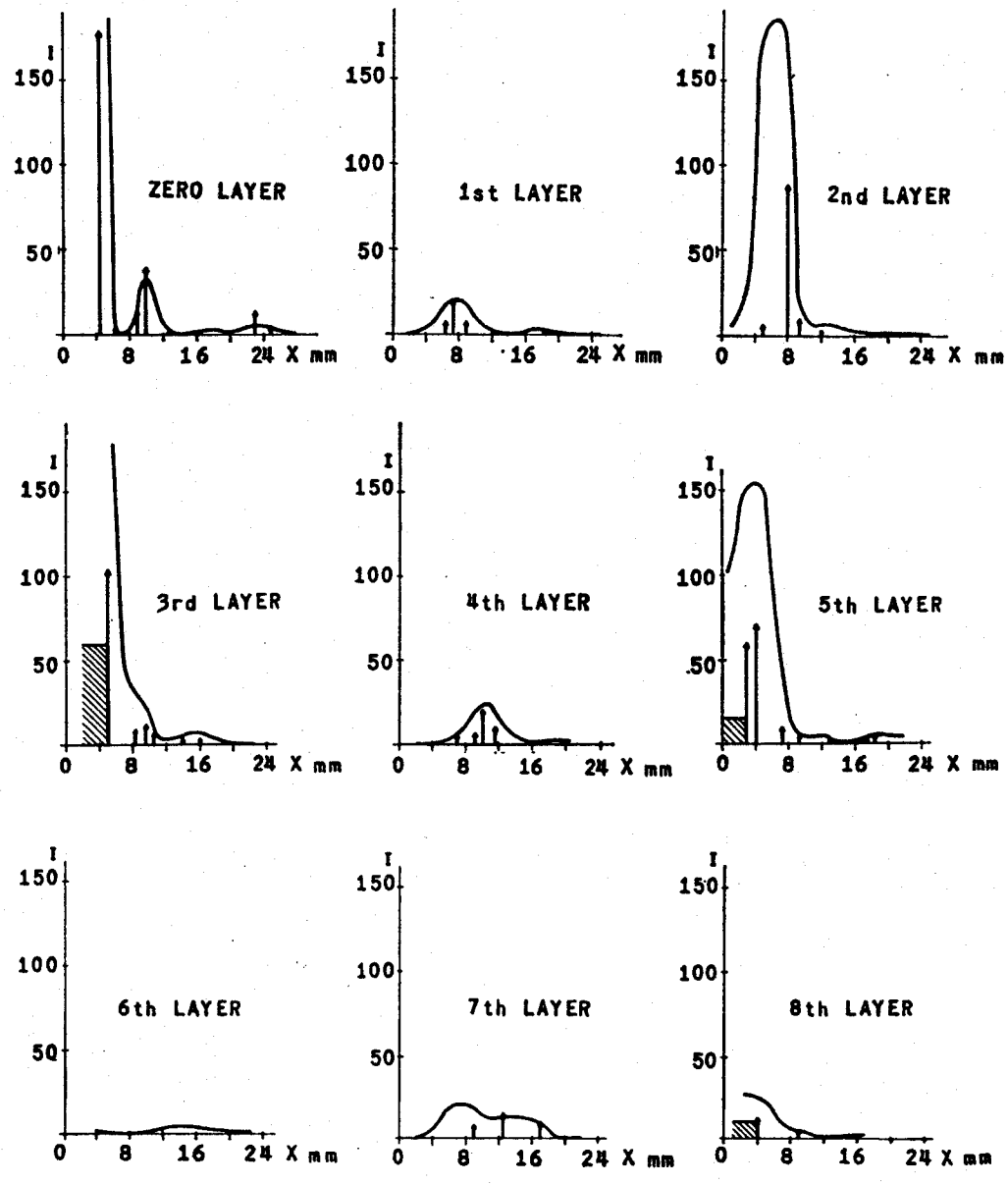


FIG. 2. Comparison of the intensities calculated by means of eq. (3) and the observed intensities (arrows).

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ON CRYSTALLINE POLYFLUOROSTYRENES

by D. SIANESI and P. CORRADINI

(8 Oct. 1959)

[*J. Polymer Sci.* **41**, 531 (1959)]

In a recent letter to the Editor, Wooten and Coover[1] announced that they obtained crystalline polyfluorostyrenes with the aid of a stereospecific catalyst from $Al(C_2H_5)_3$ and $TiCl_4$.

These authors were probably not familiar with the papers published by Natta and us on this topic since 1957, wherein we described the preparation, with the same catalytic systems, and the properties of crystalline polyfluorostyrenes.[2,3] In particular we reported that the polymers obtained from *ortho* and *para* isomers (melting temperatures 270 and 265°C, respectively) were easily crystallized. Both have isotactic structures, with different identity periods along the chain axis: poly(*ortho*-fluorostyrene) 6·63 Å, poly(*para*-fluorostyrene) 8·30 Å. The structure of crystalline poly(*ortho*-fluorostyrene) has been determined in detail.[4] Crystallizable copolymers from a mixture of fluorostyrene isomers have also been described.[5]

In our paper[3] we have described the polymers obtained under such polymerization conditions from *meta*-fluorostyrene as amorphous. We noted that they are not crystallizable by thermal treatments in spite of the fact that they possess an isotactic structure, as we demonstrated through hydrogenation and dehalogenation of amorphous poly-*meta*-fluorostyrene to crystalline isotactic poly(vinylcyclohexane).[6]

On the contrary, Wooten and Coover[1] stated that poly-*meta*-fluorostyrene is crystallizable as the *para* isomer, and they reported the melting temperature (220–250°C) and some crystallographic data for this polymer. It is surprising, however, to note that their tabulated values of the lattice distances quantitatively correspond to those known for the crystal lattice of linear polyethylene.

	d, Å	*Identity period*, Å
Supposed poly-*meta*-fluorostyrene[1]	3·73–4·13	2·56
Polyethylene[7]	3·74–4·13	2·54

This result may be explained by what we have often observed,[8] i.e. that in stereospecific polymerization with catalyst from $TiCl_4$ and $Al(C_2H_5)_3$, small quantities of crystalline polyethylene are generally detectable in the catalyst and therefore also detectable in the polymerization products obtained with such catalysts.

The polyethylene may be present in noticeable quantities if the polymer obtained is a small quantity with respect to the quantity of catalyst employed. On the other hand, an identity period of 2·56 Å has never been observed for isotactic or syndiotactic polymers; this identity period is too short to be considered possible for stereo-ordered vinyl polymers. On this basis, however, one could not explain the high crystalline melting temperature attributed by Wooten and Coover to the poly-*meta*-fluorostyrene.

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STEREOSPECIFIC POLYMERIZATIONS OF CONJUGATED DIOLEFINS. NOTE V: PREPARATION AND PROPERTIES OF ISOTACTIC 1,2-POLYBUTADIENE

by G. NATTA, L. PORRI, G. ZANINI and A. PALVARINI

(12 Oct. 1959)

[*Chimica e Industria* **41**, 1163 (1959)]

ABSTRACT

The polymerization catalysts obtained from aluminum trialkyls and chromium compounds possess particular properties which differentiate them from the catalysts obtained from compounds of other transition metals, such as Ti or V. Catalysts prepared from Ti or V have given, under our experimental conditions, only syndiotactic 1,2-polybutadiene; on the contrary those prepared from Cr have allowed us to obtain, by varying the conditions of the reaction between the aluminum trialkyl and the chromium compound (in particular the Al/Cr ratio and the reaction time), products having as crystalline fraction either syndiotactic 1,2 or isotactic 1,2 polybutadiene or both types of polymers.

We have studied in detail the polymerization by catalysts prepared from $Al(C_2H_5)_3$ and chromium triacetylacetonate, chromium hexacarbonyl and its derivatives (in which one or more CO groups are substituted by pyridine type bases), chromium hexa-isonitrile, respectively;

The products of polymerization obtained with such systems usually consist of a mixture of amorphous polymers (soluble in ether) and crystalline ones (insoluble in ether).

TABLE 1. POLYMERIZATION OF BUTADIENE WITH THE SYSTEM $Al(C_2H_5)_3$–$Cr(CNC_6H_5)_6$; SOLVENT (BENZENE) 80 cm^3; MONOMER 30 g; POLYMERIZATION TEMPERATURE 15°C; POLYMERIZATION TIME: 16 HR

Run no.	$Cr(CNC_6H_5)_6$ *moles* 10^{-3}	*Al/Cr molar ratio*	*Ageing of the catalyst, min.*[a]	*Polymer obtained, g*	*Fractionation*			
					acetone extract %[b]	*ether extract* %[c]	*residue*[d] %	*residue*[d] *RX*
1	1·49	2	2—3	0·3				syndio (e)
2	2·48	3	2—3	14·1	27	50	23	syndio (>50%) and iso)[f]
3	1·49	5	2—3	14·5	73	13	14	syndio (>50%) and iso
4	1·49	5	120	10·2	53·5	23	23·5	iso (traces of syndio)
5	1·49	5	240	9·7	43	24·5	32·5	iso
6	1·49	5	480	9·9	31	22·5	46·5	iso
7	0·745	7·5	2—3	6·4	43·1	41·5	15·4	syndio (>50%) and iso
8	0·745	7·5	120	5·15	36·5	38·5	25	iso
9	0·745	7·5	240	5·3	34·2	38·8	27	iso
10	0·745	7·5	480	5·1	30	33	34	iso
11	0·745	10	2—3	6·8	44	44	12	iso and syndio in equivalent amount
12	0·745	10	120	6·3	36·1	43	20·9	iso; traces of syndio
13	0·745	10	240	6·3	33·7	38·1	28·2	iso
14	0·745	10	480	6·3	32	37·5	30·5	iso
15	0·745	10	1·440	5·9	31·5	34·5	34	iso
16	0·745	10	2·880	6·1	29·4	29·1	41·5	iso
17	0·745	15	2—3	7·2	49	37·5	13·5	iso (>50%) and syndio
18	0·745	15	120	6·6	40	36	24	iso
19	0·745	15	240	6·8	34·4	31·6	34	iso

(*a*) Preparation and ageing of the catalyst at room temperature.
(*b*) Oily. I.R. analysis: *trans*-1,4 20–25 per cent; *cis*-1,4 0–5 per cent; 1,2 70–80 per cent.
(*c*) Amorphous by X-rays. I.R. analysis: *trans*-1,4 5–8 per cent; *cis*-1,4 20–25 per cent; 1,2 70–78 per cent; $[\eta]$ in toluene at 30°C: 2·5–3 100 cm^3/g.
(*d*) 30–45 per cent of the ether residue is extractable in boiling benzene. I.R. analysis: (*a*) for the prevailingly syndiotactic residues: 1,2 93–95 per cent; *cis*-1,4 4–5 per cent; *trans*-1,4 0–2 per cent; (*b*) for the prevailingly isotactic residues: 1,2 97–100 per cent; *cis*-1,4 0–3 per cent; *trans*-1,4 traces.
(*e*) syndio=syndiotactic.
(*f*) iso=isotactic.

The results obtained using the system $Al(Et)_3$–$Cr(CNC_6H_5)_6$ are reported in Table 1. From the data one can see that unaged catalysts provide, when used at a low Al/Cr ratio, products having, for the crystalline fraction, chiefly syndiotactic polybutadiene. By increasing the Al/Cr ratio, the percentage of isotactic polymer, present in the crystalline fraction, is increased; at Al/Cr ratios of about 15 the crystalline fraction is made up of almost exclusively isotactic polymer. The aged catalyst, in comparison with those unaged prepared at the same Al/Cr ratio, gives products that contain a higher percentage of isotactic polymer.

An almost analogous behaviour, as far as the change in stereospecificity with respect to the ratio Al/Cr and the aging of the catalyst is concerned, can be observed for those catalytic systems prepared from chromium triacetylacetonate, $Cr(CO)_6$, $Cr(CO)_3$ (pyridine)$_3$, $Cr(CO)_4$ (pyridine)$_2$. The behaviour of all the catalysts examined seems to indicate that the reaction between the aluminum triethyl and chromium compounds goes through successive stages, possibly each stage corresponding to catalytic complexes having a different stereospecificity in the polymerization of butadiene. Some of the physical characteristics of isotactic 1,2-polybutadiene are reported in Table 2, together with

TABLE 2. SOME PHYSICAL PROPERTIES OF CRYSTALLINE 1,2–POLYBUTADIENE

	Density	*Identity period* Å	*Melting temperature* °C
Syndiotactic	0·96	5·14	156
Isotactic	0·96	6·5	126(*)

(*) In a previous paper (paper 18), it was reported 120° C as melting temperature of isotactic polybutadiene; a purer product was subsequently obtained which melts at 126°C, like isotactic polybutene.

the properties of syndiotactic 1,2-polybutadiene. Isotactic polybutadiene gives an X-ray spectrum, which is characterized by four intense peaks corresponding to distances of 8·26; 5·00; 4·31; 3·54 Å. The amorphous part of the polymer gives a spectrum which possesses a wide halo in the interval $2\Theta = 5$ and $2\Theta = 30$ (Cu$K\alpha$) (see Fig. 1). An approximate evaluation of the crystallinity of the polymer, obtained by measuring the ratio between the diffracted intensity from the crystalline part and the total intensity diffracted from the crystal-

line and amorphous parts has given values ranging in the order of 45 per cent. This value does not increase appreciably by annealing the polymer.

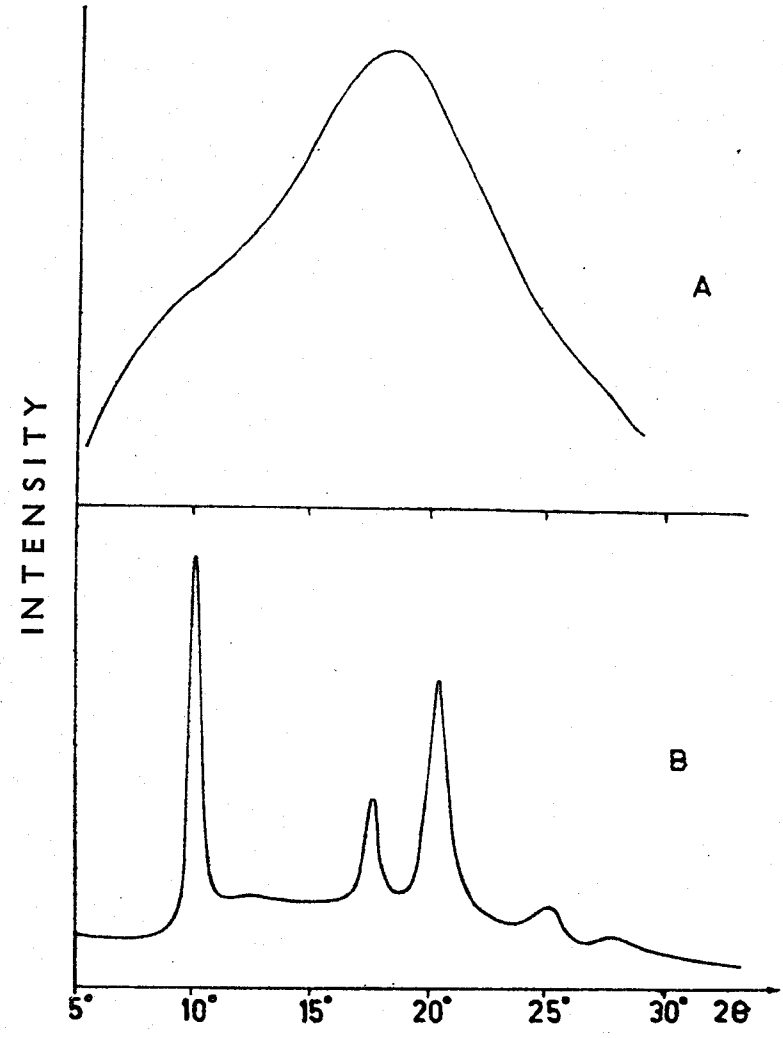


FIG. 1. X-ray spectra (Cu$K\alpha$) registered by Geiger counter of 1,2-polybutadiene, obtained with the aid of the catalytic system: $Al(C_2H_5)_3$-$Cr(CNC_6H_5)_6$ (Al/Cr = 10) (4-hr aging). (A) Ether extract; (B) Benzene extract, with an isotactic structure.

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PROPOSED NOMENCLATURE FOR DI-ISOTACTIC POLYMERS*

by G. NATTA, M. FARINA and M. PERALDO

(12 Oct. 1959)

[*J. Polymer Sci.* **43**, 142 (1960)]

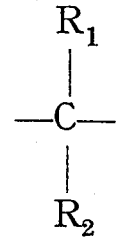
INTRODUCTION

With the discovery of certain sterically regular polymers obtained from unsaturated ethylenic monomers with an internal double bond, new problems of nomenclature have arisen because of the need of identifying and distinguishing all the possible tactic structures. This problem, analogous to that encountered with certain vinyl polymers in which a H atom of the CH_2 group of the poly-α-olefin main chain is substituted with a D atom,[1] arises now in the case of the stereoregular polymers of alkenyl ethers, which are derived from monomers of the CHR=CHOR'type; [2] in general it applies to all polymers which are derived from monomers of the CHR=CHR′ type, in which R and R′ are atoms or groups different from each other.

For the nomenclature of these polymers it is necessary to take into account the conventions which have been already introduced in the case of vinyl polymers, for which some time ago the names "isotactic" and "syndiotactic" were proposed and are now commonly accepted.[3,4] As can be seen from the proposals which were submitted to this Committee at the Nottingham Meeting,[5] an isotactic polymeric structure is characterized by the periodic repetition in the main chain of

* Presented to the Commission on Macromolecules of the International Union for Pure and Applied Chemistry at the Wiesbaden Meeting, Germany, October 12, 1959.

contiguous or not contiguous groups consisting of a carbon atom with two different substituents



where R_2 can be a H atom, the steric structure of said group being such that, by superimposition of the main chain carbon atoms of two subsequent groups, through translation (which may be followed by

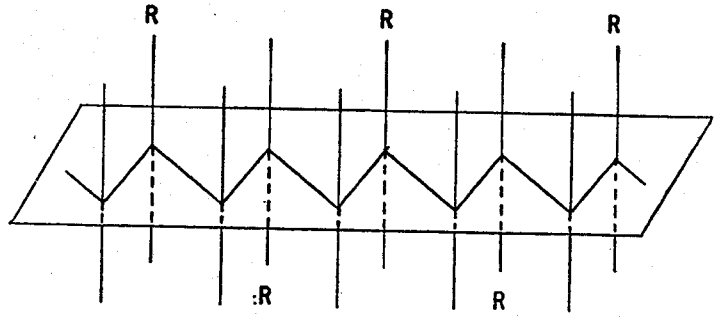


FIG. 1.

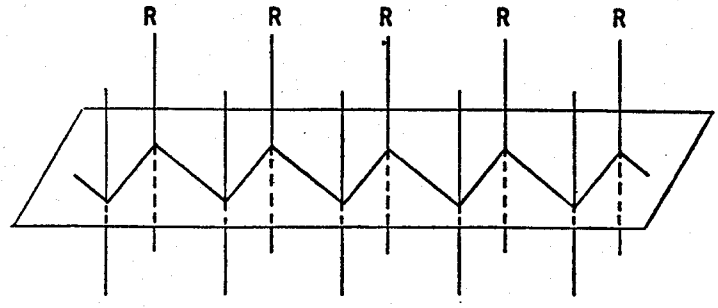


FIG. 2.

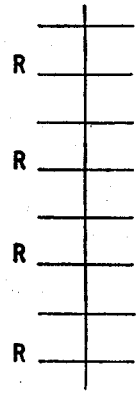


FIG. 3.

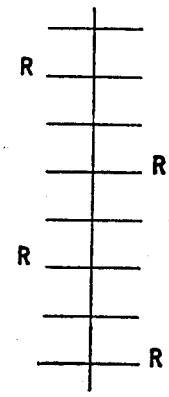


FIG. 4.

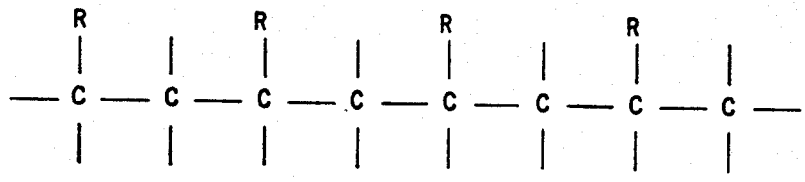


FIG. 5.

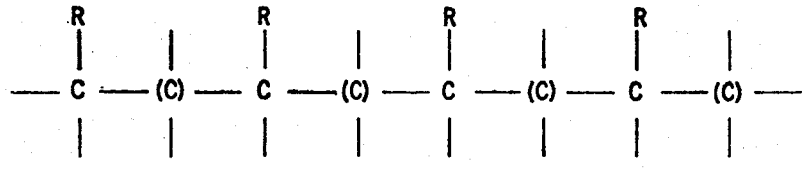


FIG. 6.

rotation) along the chain, their substituents are found to be superimposed.

In a syndiotactic structure, on the contrary, this superimposition is not possible for two adjacent groups, but it is observed only for alternate groups.

In the case of vinyl polymers and, in general, of all polymers having an even number of atoms for each structural unit in the main chain, if we suppose the main chain to be stretched in a zigzag fashion on a plane, all the substituents of the same type (R_1 or R_2) belonging to the above mentioned CR_1R_2 group are on the same side of the plane if the structure is isotactic, while they alternate with each other on both sides of the plane of the main chain if the structure is syndiotactic.

These two types of structure are drawn in Figs. 1 and 2, for the zigzag representation of the main chain; in Figs. 3 and 4 they are drawn according to the Fischer projection.

Obviously, in polymers the chain of which contains an odd number of atoms for each structural unit (e.g. in the case of isotactic polypropylene oxide[6]), the substituents are on the same side of the plane in which the main chain is stretched if the structure is syndiotactic, while they alternate on opposite sides if the structure is isotactic.

A representation sometimes used is obtained by projecting the plane in which the chain is stretched, on a plane normal to the paper, as indicated in Fig. 5. This last representation might be taken for a Fischer projection, to which it is typographically analogous; in the case of vinyl polymers the two representations are in fact equivalent. In this particular case the R groups in the isotactic structure are represented on the same side of the chain.

In order to avoid confusion between this latter representation and the Fischer projection, in the cases where the two representations are not equivalent, a typographic distinction can be made by printing them with different types. To make this difference even more marked, the chain atoms lying on the same straight line can be put between brackets, as shown in Fig. 6.

DI-ISOTACTIC POLYMERS

Linear polymers of 1,2-substituted ethylenic monomers having different substituents in the 1- and 2-positions can exist in various different simple tactic structures. The case of the tri-substituted ethylenic monomers CHA=CBD falls under the more general case of tetra-substituted monomers CAB=CDE, which, in regard to the possible tactic structures, corresponds to the case of monomer of the CHR=CHR′ type.

In this case, for the structures in which it is possible to recognize steric regularities of an isotactic type (isotacticity) for each of the sets of tertiary carbon atoms, we propose the name of "di-isotactic structures" (di-isotacticity, di-isotactic polymers, etc.).

To distinguish the two possible di-isotactic structures we propose the name "threo-di-isotactic" for the polymeric structure having, in the case of 1,2-disubstituted ethylenic monomers, all the R and R′ substituents on the same side of the plane in which the main chain is zigzag stretched (the R and R′ on opposite sides in the Fischer projection); we propose the name "erythro-di-isotactic" for the corresponding polymeric structure having all the R substituents on one side and all the R′ substituents on the opposite side of the plane in which the main chain is zigzag stretched (R and R′ on the same side in the Fischer projection).

Furthermore we propose the name "di-syndiotactic" for the structures in which it is possible to recognize steric regularities of a syndiotactic type for the two sets of tertiary carbon atoms. Those structures are drawn in Figs. 7–9 according to the zigzag representation, and in Figs. 10–12 according to the Fischer projection.

It is worth noting here that polymerization of pure stereoisomeric forms of CHR=CHR′ monomers can yield two types of di-isotactic polymers (erythro or threo), depending on the monomeric form employed (*cis* or *trans*), while, on the contrary, only one product with di-syndiotactic structure is obtained.

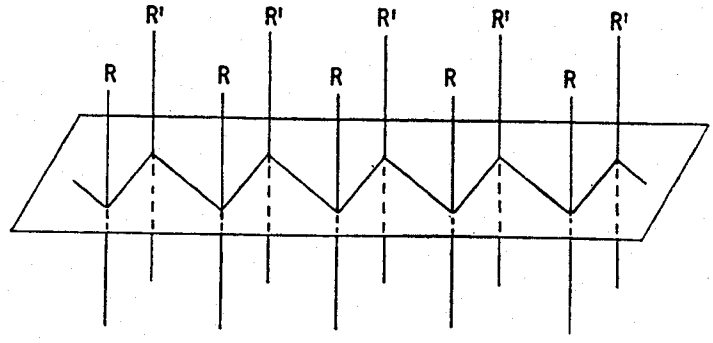


FIG. 7. Threo-di-isotactic.

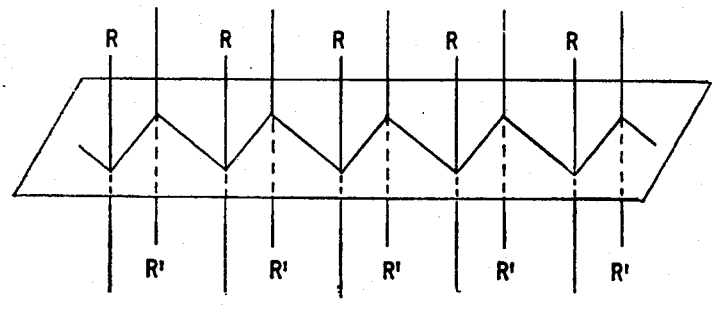


FIG. 8. Erythro-di-isotactic.

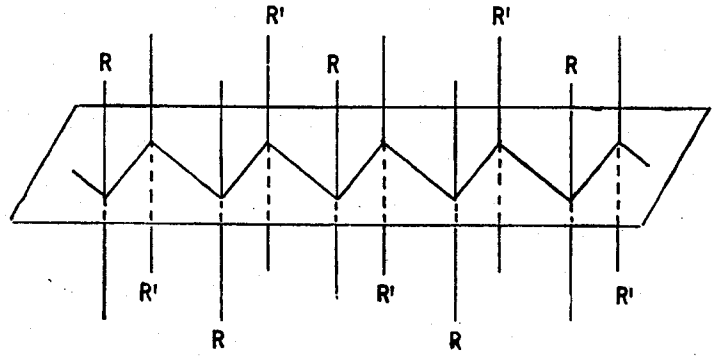


FIG. 9. Di-syndiotactic.

The terminology which we have used is in accordance with the current nomenclature for polymers having simple isotactic or syndiotactic structure.

As regards the particular use of the prefixes "erythro" and "threo", which are commonly used to define the relative steric configuration of two C atoms in a molecule, we feel that it is legitimate to extend to high polymers the definition reported by Newman[7]. According to this definition, "erythro" denotes the diastereomer that, when observed in the Newman representation in one of its eclipsed forms, presents superimposed at least two sets of substituents which are equal or similar; "threo" denotes the opposite isomer.

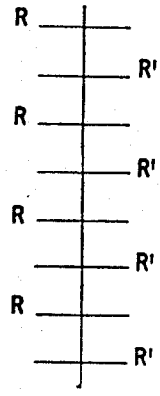


FIG. 10.
Threo-di-isotactic.

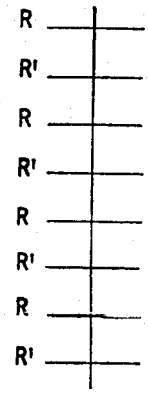


FIG. 11.
Erythro-di-isotactic.

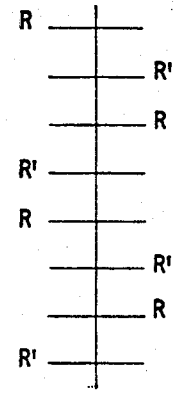


FIG. 12.
Di-syndiotactic.

If one applies those terms in the field of polyolefins, one sees that the known relations between structure of the olefinic monomer (*cis* or *trans*) type of opening of the double bond (*cis* or *trans*) and the resulting structure (erythro or threo) are valid.

Generalizing the use of the prefixes erythro and threo in the definition of the relative steric positions of the two sets of substituents R and R′ bound to different atoms of the chain, we can define as erythro-di-isotactic a polymer that, in the Fischer projection, has all the R and R′ substituents (which may or may not be contiguous) on the same side of the chain; we can then define as threo-di-isotactic a polymer which in the Fischer projection has all the R substituents on one side and all the R′ substituents on the opposite side of the chain. Finally we can define as di-syndiotactic a polymer that, in the Fischer projection, has both R and R′ substituents alternately on opposite sides of the chain.*

As we have already observed for the isotactic structures in the zigzag representation, in a threo-di-isotactic polymer the R and R′ substituents are on the same side of the plane (or in opposite sides in a erythro-di-isotactic polymer) only for a particular type of structural unit, i.e. —CHR—CHR′—.

The possibility of partially ordered structures also exists; in some cases their nomenclature can be easily derived. For instance, the polymer obtained by copolymerization with stereospecific catalysts of a mixture (in 1:1 molar ratio) of *cis*- and *trans*-1-deutero-1-pro-

* The definitions of the erythro and threo structures of $1d_1$ polypropylene, reported in Ref. 8, are inverted with regard to the original work.[1] However, the figures in Ref. 8 are correct, as can be seen from our Figs. 5 and 17.

pene has an isotactic structure with respect to the CH—CH_3 group and an atactic structure with respect to the CHD group; thus its name is (1-atactic, 2-isotactic) poly(1-deutero-2-methylethylene).

POLYMERS OF OLEFINS HAVING TWO IDENTICAL SUBSTITUENTS

A particular case of tactic polymers is observed when the two substituents R and R′ of the ethylenic monomer are equal; the structural unit is thus reduced to the — CHR — group and we have only one atom in the chain for each structural unit. In agreement with our general definition, an isotactic polyalkylidene can be depicted in the zigzag representation as in Fig. 13, which would be equivalent in the Fischer projection to the representation in Fig. 14; a syndiotactic polyalkylidene, can be depicted in the zigzag representation as in Fig. 15 and in the Fischer projection as in Fig. 16.

In such cases it may be sometimes convenient to use a system of nomenclature for the polymer deriving from the monomer employed.

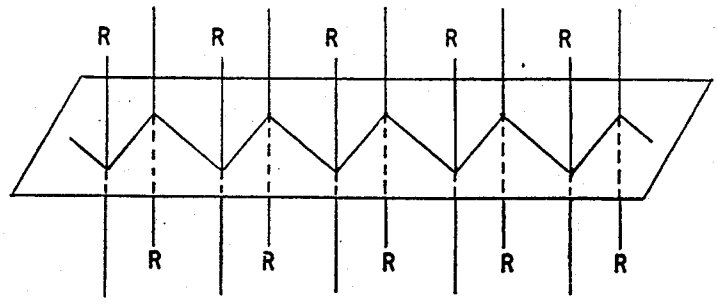


FIG. 13.

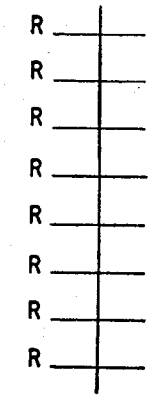


FIG. 14.

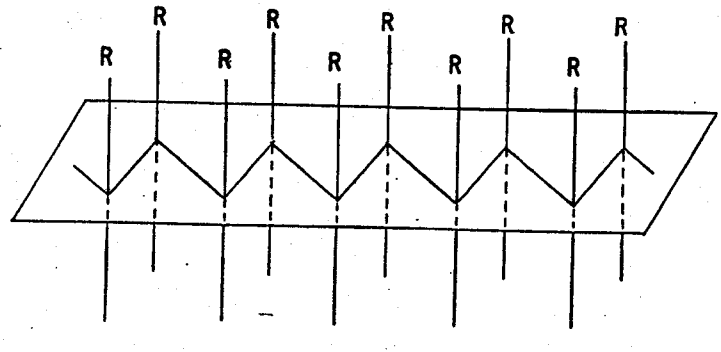


FIG. 15.

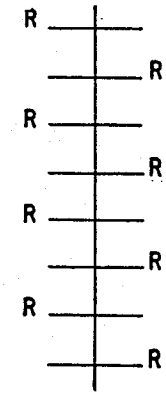


FIG. 16.

DI-ISOTACTIC POLYMERS

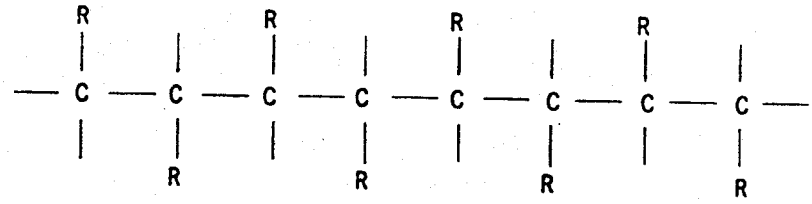


FIG. 17.

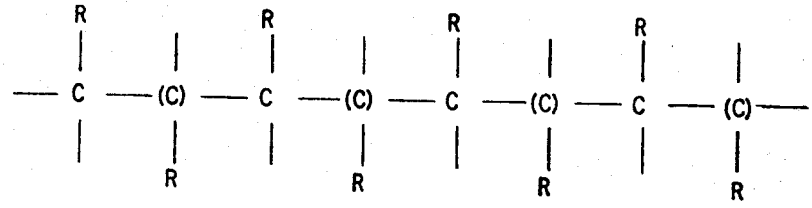


FIG. 18.

For instance, according to what we previously stated, the structure shown in Figs. 13 and 14 could be named erythro-di-isotactic poly (1,2-di (R) ethylene), while the structure shown in Figs. 15 and 16 could be named threo-di-isotactic poly (1,2-di (R) ethylene).

Referring to what has already been observed in connection with the possibility of confusion between the Fischer projection and the particular zigzag representation indicated, e.g. in Fig. 5, it is interesting to consider the example of an isotactic polyalkylidene. In this last representation its structure is drawn as in Fig. 17; the same drawing in the Fischer projection stands for a syndiotactic polyalkylidene. The confusion disappears when using the form of representation proposed in Fig. 18.

Briefly, we may say that the terms isotactic and syndiotactic can be used to define the steric relations between structural units, while the terms erythro and threo can be used to define the steric relations within a given structural unit.

The discovery of new stereoregular structures, which we have called di-isotactic, illustrates the general nature of the concepts of tacticity and isotacticity.

Finally, we believe that the proposed definitions can be extended also to non-olefinic linear polymers.

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COMPOSITION AND REACTIVITY IN THE STEREOSPECIFIC COPOLYMERIZATION OF VINYLAROMATIC MONOMERS

by D. SIANESI, G. PAJARO and F. DANUSSO

(9 Nov. 1959)

[*Chimica e Industria* **41**, 1176 (1959)]

ABSTRACT

The copolymerization of several vinylaromatic monomers with styrene has now been studied, by using stereospecific catalysts from Al $(iC_4H_9)_3$ and $TiCl_4$. Stereoregular isotactic copolymers were obtained, and composition curves and reactivity ratios were determined. The copolymerization appears to be essentially "ideal" ($r_1 \times r_2 = 1$), in agreement with evidences of a random distribution of the comonomer units in the copolymer chains.

The unique properties of these copolymers and the relationships between composition and crystallinity will be discussed in subsequent papers.

The monomer systems studied and reactivity ratios obtained are reported in Table 1.

TABLE 1. REACTIVITY RATIOS OF THE VINYLAROMATIC MONOMERS IN THE STEREOSPECIFIC COPOLYMERIZATION WITH STYRENE, AT 40°C

(monomer 1 = styrene)

Monomer 2	r_1	r_2	$r_1 \times r_2$
o-methylstyrene	12·5 (±1)	0·10(±0·1)	1·25
m-methylstyrene	2·00(±0·1)	0·50(±0·1)	1·00
p-methylstyrene	0·90(±0·08)	1·15(±0·08)	1·05
p-ethylstyrene	0·95(±0·1)	1·05(±0·1)	1·00
p-fluorostyrene	1·50(±0·1)	0·60(±0·1)	0·90
p-chlorostyrene	2·20(±0·2)	0·50(±0·1)	1·10
p-bromostyrene	1·75(±0·1)	0·55(±0·1)	0·95
1-vinylnaphthalene	3·3 (±0·5)	0·35(±0·2)	1·15

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IONIC COMPLEXES BETWEEN ALUMINUM ALKYLS AND AMMONIUM SALTS

by M. FARINA

(9 Nov. 1959)

[*Gazz. Chim. Ital.* **89**, 1532 (1959)]

ABSTRACT

Compounds having a high electric conductivity are formed from the reaction of aluminum alkyls with quaternary ammonium salts. These compounds are slightly soluble in hydrocarbons. Such a reaction takes place without substitutions of groups or other secondary reactions. It has also been demonstrated that three moles of ethane are produced per every aluminum atom by decomposition with alcohol of the complex formed from $Al(C_2H_5)_3$ and $N(C_4H_9)_4I$. Moreover, it has been observed that the optical activity of the complex obtained by the reaction between an optically active ammonium salt and aluminum tri-isobutyl was kept constant. The ammonium salt can be regenerated without racemization.

Due to the high electric conductivity and analogously with the many complexes obtained by the reaction of aluminum compounds of the type AlX_3 or A_2lX_6 with alkaline salts, with organometallic compounds and with acid halides, we have proposed for these compounds an ionic formula of the type $[R_4N]^+[(AlR_3)_nX]^-$. This formula was proved for those soluble complexes by experiments of electrolysis. The complete interpretation of our results requires, however, the existence of at least two complexes, one of which contains the two components in a 1:1 ratio, whereas the other (or others) shows a molar ratio of Al/I = 2 (or higher).

In the case of insoluble complexes, the study of the change in composition of the phases with respect to the change of the ratios among the components has proved our interpretation. In fact a particular behaviour in the composition of the phase is observed in the Al/I ratio ranging from 1 to 2.

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SYNTHESIS OF SOME METAL AMIDE COMPOUNDS OF ALUMINUM AND BERYLLIUM

by P. LONGI, G. MAZZANTI and F. BERNARDINI

(16 Nov. 1959)

[*Gazz. Chim. It.* **90**, 180 (1960)]

ABSTRACT

Metal amide compounds of aluminum and beryllium were prepared under suitable conditions by the reaction of the corresponding organometallic compounds with secondary amines.

It was observed that the addition of an aluminum or beryllium organometallic compound to a secondary amine produces first at room temperature a complex without any elimination of hydrocarbons:

$$(CH_3)_2NH + AlR_3 \rightarrow (CH_3)_2\overset{H}{\underset{|}{N}} \rightarrow AlR_3$$

Only at higher temperatures does a reaction take place which proceeds to the substitution of one alkyl and to the formation of a metal–nitrogen bond:

$$[(CH_3)_2\overset{H}{\underset{|}{N}} \rightarrow AlR_3] \rightarrow RH + (CH_3)_2N{-}AlR_2$$

By operating with a sufficient excess of amine and at even higher temperatures, one can obtain reactions with successive substitutions for the other two alkyl groups followed by the final formation of a compound containing exclusively metal–nitrogen bonds.

The metal amide compounds of aluminum obtained are solid, crystalline, colourless, soluble in hydrocarbons and highly associated.

Starting from lithium aluminum hydride and secondary amines, complex metal amide compounds are obtained which contain, even when operating with a considerable excess of amine, in addition to the $—NR_2$ groups, also a hydrogen atom bound as a hydride.

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THERMODYNAMICS AND MOLECULAR CONFIGURATION OF ATACTIC POLYPROPYLENE IN SOLUTION

by F. Danusso and G. Moraglio

(19 Nov. 1959)

[*Rend. Ist. Lomb. Sci. e Lettere* **93**A, 666 (1959)]

ABSTRACT

The intrinsic viscosity of atactic polypropylene fractions was determined in two Θ solvents at 34°C in isoamylacetate and at 58°C in isobutylacetate, and in a series of different solvents, in the whole range of temperatures from 20° to 70°C. The results are discussed according to Fox and Flory's theory. The average statistical dimensions of the unperturbed macromolecules decrease with the increase in temperature. The expansion coefficients $[\alpha]$ in the different solvents were calculated; from these values the thermodynamic interaction parameters, reported in Table 1, were also calculated.

Table 1. Parameters of Thermodynamic Interaction between Atactic Polypropylene Units and Different Solvents

Solvent	Θ	ψ_1	κ_1 *at 30°C*	$(\psi_1-\kappa_1)\ 10^3$ *at 30°C*
isoamyl acetate	307	0·473	0·479	—6
benzene	281	0·624	0·579	45
chlorobenzene	231	0·393	0·300	93
toluene	239	0·533	0·420	113
n-heptane	105	0·346	0·119	227
iso-octane	85	0·337	0·094	243
cyclohexane	(123)	(0·440)	(0·179)	(261)

The entropy contributions to the interaction have a fairly uniform value; on the contrary the enthalpy contributions appear rather different. The scale of solvent-polymer affinities, which appears clearly connected with the structures of the solvents examined, is expressed by the overall interaction.

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ATACTIC POLYBUTENE: FRACTIONATION AND OSMOTIC PRESSURE

by G. MORAGLIO and G. GIANOTTI

(19 Nov. 1959)

[*Rend. Ist. Lomb. Sci. e Lettere* **93**A, 683 (1959)]

ABSTRACT

The fractionation of atactic polybutene by fractional precipitation is described here. The dispersity of fractions was controlled by both viscometric and osmotic measurements.

Accurate osmotic measurements on some narrow fractions have allowed us to calculate the value of the interaction affinity for polybutene solutions in benzene at 30°C; this value is discussed and compared, using the same solvent, with that of known polymers having a different structure.

The relationship between $[\eta]$ and M is reported:

$$[\eta] = 1{\cdot}55 \times 10^{-4} M^{0.725}$$

for viscosity determinations in toluene at 30°C.

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DEPENDENCE OF THE DISTRIBUTION OF THE MOLECULAR WEIGHTS OF POLYPROPYLENE ON THE DISTRIBUTION OF CATALYTIC ACTIVE CENTRES. NOTE I

by M. PEGORARO

(19 Nov. 1959)

[*Rend. Ist. Lomb. Sci. e Lettere* **93**A, 695 (1959)]

ABSTRACT

This note reports on the type of distribution curve of the molecular weights, the so-called "most probable" one, according to the known reaction mechanisms of the anionic coordinated polymerization of propylene.

The practical behaviour of the distribution curves obtained experimentally by the fractionation of polymers obtained at constant temperature and at constant partial pressure of the monomer, shows, however, that it is impossible to justify the distribution, by just taking into account one statistical parameter, p_i; this can be attributed to the fact that various types of active centres exist, each being characterized by a different probability parameter.

By a statistical reasoning, we can get to know how the formation of the polymer is distributed among the different types of active centres and, for each of such fractions, how the molecular weights are distributed.

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VISCOMETRIC AND CONFIGURATIONAL PROPERTIES OF ATACTIC POLYBUTENE

by G. MORAGLIO and G. GIANOTTI

(12 Dec. 1959)

[*Rend. Accad. Naz. Lincei* (8) **27**, 374 (1959)]

ABSTRACT

We have determined the relationships between molecular weight and intrinsic viscosity for fractions of atactic polybutene, using various solvents, at different temperatures.

$$[\eta] = 1{\cdot}68 \times 10^{-4} M^{0.735} \text{ (in decalin at 30°C)}$$
$$[\eta] = 1{\cdot}55 \times 10^{-4} M^{0.725} \text{ (in toluene at 30°C)}$$
$$[\eta] = 2{\cdot}15 \times 10^{-4} M^{0.685} \text{ (in benzene at 30°C)}$$
$$[\eta] = 11{\cdot}33 \times 10^{-4} M^{0.500} \text{ (in isoamylacetate at 23°C)}$$

Since isoamylacetate at 23°C proved to be a pseudo-ideal solvent, we were able to calculate the statistical average dimensions of the molecules of atactic polybutene in the unperturbed state. These average dimensions are compared with those of other known polymers with particular reference to the relationships between configurational properties and chain structure.

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ENTHALPY AND ENTROPY OF FUSION OF ISOTACTIC POLYSTYRENE

by F. DANUSSO and G. MORAGLIO

(12 Dec. 1959)

[*Rend. Accad. Naz. Lincei* (8) **27**, 381 (1959)]

ABSTRACT

The enthalpy of fusion ΔH_u of isotactic polystyrene, determined from measurements of the depression of the melting point of the polymer in the presence of diluents by the dilatometric method at equilibrium, was 2150 cal/structural unit (± 100). It has been observed that, if one determines the melting temperatures by the optical method, instead of the dilatometric one, even if the measurements are performed at limited heating rates, but obviously not at equilibrium, a value of ΔH_u which is lower by 14 per cent than the more reliable one reported above, is obtained.

The heat of fusion of isotactic polystyrene, if referred to a gram, is far lower than that of linear polyethylene and of isotactic polypropylene.

From the melting temperature of isotactic polystyrene and from ΔH_u it was possible to calculate the entropy of fusion $\Delta S_u = 4{\cdot}2$ cal/°K units ($\pm 0{\cdot}2$).

From it, by applying the corrections for the change in volume at melting and by suitable comparisons with other polymers, it can be deduced that isotactic polystyrene on melting acquires very limited configurational possibilities, likely to be connected, at least in part, to the fairly high stiffness of its macromolecular chains.

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THE ACTION OF TERTIARY AMINES ON THE $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$ COMPLEX

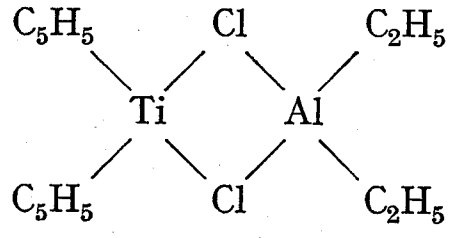
by P. Pino, G. Mazzanti, U. Giannini and S. Cesca

(12 Dec. 1959)

[*Rend. Accad. Naz. Lincei* (8) **27**, 392 (1959)]

ABSTRACT

The structure of the complex:



(I)

was determined by the degradation reaction with trimethylamine.

By using trimethylamine on a solution of complex I, we were able to isolate *bis*-cyclopentadienyl titanium monochloride and the complex formed by trimethylamine and aluminum diethylmonochloride: $(CH_3)_3N \rightarrow AlCl(C_2H_5)_2$

The structure of complex (I) was further proved by its synthesis from aluminum diethylmonochloride and *bis*-cyclopentadienyl titanium monochloride, obtained from sodium cyclopentadienyl and titanium trichloride.

Analogously, the complexes with formula $(C_5H_5)_2TiCl_2AlClC_2H_5$ and $(C_5H_5)_2TiCl_2AlCl_2$ can be prepared from *bis*-cyclopentadienyl titanium monochloride and aluminum dichloro-monoethyl and aluminum trichloride, respectively.

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DEPENDENCE OF THE DISTRIBUTION OF THE MOLECULAR WEIGHTS OF POLYPROPYLENE ON THE DISTRIBUTION OF CATALYTIC CENTRES. NOTE II

by M. PEGORARO

(17 Dec. 1959)

[*Rend. Ist. Lomb. Sci. e Lettere* **93**A, 707 (1959)]

ABSTRACT

With reference to the Note I, we demonstrated that it is possible, by using an original graphic procedure, to elaborate the fractionation data of polypropylene obtained by anionic coordinated catalysis at constant temperature and pressure. This finding affords a knowledge of the function $\xi_i = \xi_i(p_i)$, which explains how the formation of the polymer is distributed on the various types of the active centres.

From fractionation runs it is thus possible to obtain important kinetic information, such as for instance the distribution of the rate constants of various types of active centres and the distribution of the mean lifetime of the molecules.

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COPOLYMERIZATION OF ETHYLENE WITH ALIPHATIC α-OLEFINS. NOTE VII: DISTRIBUTION OF MONOMERIC UNITS IN THE ETHYLENE-PROPYLENE COPOLYMERS

by G. NATTA, G. MAZZANTI, A. VALVASSORI, G. SARTORI and D. MORERO

(18 Dec. 1959)

[*Chimicae Industria* **42**, 125 (1960)]

ABSTRACT

The distribution of the monomeric units in the ethylene–propylene copolymers obtained by copolymerization of mixtures of the two monomers in the presence of a catalyst prepared from trialkyl aluminum and vanadium tetrachloride is reported here.

The values of the distribution functions for these copolymers (shown in Table 1) are compared with those foreseeable for the ideal case in which the product of the reactivity ratios is equal to one, and moreover with those foreseeable for values of this product equal to 10 and to 0·1 respectively*.

When $r_1 r_2 = 1$, the distribution of the monomeric units is completely random and it corresponds to that foreseeable in the case in which the relative rate of the addition of a monomer to the growing chain is not influenced by the nature of the monomeric unit which previously entered the chain.

(*) The distribution of the monomeric units in a copolymer having a certain composition depends only on the value of the product of the reactivity ratios of the two monomers and it does not depend on the single values of the reactivity ratios.

TABLE 1. DISTRIBUTION OF THE SEQUENCES FOR ETHYLENE–PROPYLENE COPOLYMERS OF DIFFERENT COMPOSITION, PREPARED IN N– HEPTANE WITH A CATALYST OBTAINED FROM $Al(C_6H_{13})_3$ AND VCl_4

molar % of m_x *in the copolymer*	% $P\ (m_x)_n$										
	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$	$n = 9$		$n > 15$
85	15·80	13·20	11·20	9·430	7·941	6·687	5·630	4·741	3·992	for n from 10 to 14 $P(m_X)_n =$ 12·271 %	9·006
74	27·07	19·74	14·40	10·50	7·658	5·584	4·073	2·970	2·166	for n from 10 to 14 $P(m_X)_n =$ 4·631 %	1·204
60	44·47	24·69	13·71	7·614	4·228	2·347	1·303	0·274		for n from 9 to 14 $P(m_X)_n =$ 0·762 %	0·142
50	55·89	24·65	10·87	4·796	2·116	0·933	0·412			for n from 8 to 14 $P(m_X)_n =$ 0·324 %	0·003
40	66·70	22·21	7·398	2·464	0·820	0·273				for n from 7 to 14 $P(m_X)_n =$ 0·136 %	$<1\cdot10^{-3}$
25	81·20	15·27	2·871	0·540	0·101					for n from 6 to 14 $P(m_X)_n =$ 0·023 %	$<1\cdot10^{-3}$
15	89·53	9·377	0·982	0·103						for n from 5 to 14 $P(m_X)_n =$ 0·012 %	$<1\cdot10^{-3}$

$\%P(m_X)_n$ = percentage of ethylene (or propylene, respectively) sequences, of length n.
n = number of monomeric units forming the sequences.

For values of the r_1r_2 ratio less than one, the alternation of the two monomers is favoured, and since the composition remains the same, those sequences that contain the same monomeric units become shorter and shorter.

When the r_1r_2 product is greater than one, the formation of a relatively long chain portion containing the same monomeric unit is favoured. As a consequence of this, it follows that if one wants to obtain amorphous copolymers, by the introduction of monomeric units of α-olefins in a polyethylenic chain, it is convenient to carry out the copolymerization in the presence of catalysts for which the r_1r_2 product is equal to or less than one.

From the values of the distribution functions of the ethylene–propylene copolymers reported in the table, it can obviously be seen that the probability of having long ethylene (or propylene) sequences increases with the increase of the monomer content present in the copolymer.

The highest distribution in the length of sequences of both monomers occurs in those copolymers that contain equimolecular amounts of ethylene and of propylene.

From values given in the table one can observe that the ethylene sequences which are sufficiently long to be crystallizable, containing at least 15 monomeric units, can exist in practice, only for ethylene contents in the copolymer of the order of 85 mol.%.

In agreement with this hypothesis, we have experimentally found that copolymers can be obtained containing up to 80 mol.% of ethylene, which when examined by X-rays do not show a crystallinity due to the long sequences of methylene groups.

The theoretical predictions on the distribution of the sequences of different lengths of the ethylene–propylene copolymers agree with the values of the length of sequences of methylene groups, determined by I.R. analysis, within the limits of accuracy of this method.

A formula is then developed, which allows us to foresee the distribution of the monomeric units in sequences of different length.

Finally, some considerations have been proposed to predict the degree of alternation of the monomeric units in the copolymers vs. the reactivity ratio and the composition of the mixture of the reacting monomers.

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