GIULIO NATTA

Milano

Direttore dell'Istituto di Chimica industriale del Politecnico

3. Stereospecific polymerizations and catalysis

Two important branches of chemistry, namely kinetics and catalysis, assume particular aspects when applied to the macromolecules field.

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 the methods usually used in synthesizing low molecular weight substances.

Whilst for the latter, heterogeneous catalysis represented the most important and fertile branch of catalysis, leading to the most salient results in the synthesis of low molecular weight products, in the past, macromolecular synthesis had a higher devolopment through homogeneous catalysis 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 been the ones that, above all, 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 given life 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 difference. Natural products often respond to a precise arrangement, also sterically regular in their constitutive elements, whilst synthetic products, mostly, had a sterically irregular and disordered chemical structure. An exception, owing to the regularity of their structure, 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 some polymers, such as polyisobutylene, obtained by polyaddition of monomers having highly symmetric molecules. In other cases, polymers with a non-regular structure both obtained by polyaddition and by polycondensation are incapable of crystallizing.

The chemist, although having at his disposal stronger activation means (from very high temperatures to very high energy radiations) compared to the ones of natural biochemical processes, was 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 proteic substances, show, on the contrary, regular arrangements of their monomeric units. Such arrangement corresponds 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 reproduced model with the same configuration.

The difference between synthetic and natural products is evidently noticeable in the field of diolefin polymers.

Hevea rubber, on one side, and guttapercha, on the other, represent products in each of which monomeric units are repeated with the same steric configuration, 1-4 cis and 1-4 trans respectively. One is, at ordinary temperature, the best of elastomers, the other 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 higher.

Until 4 years ago all synthetic products obtained by diolefin polymerization were, on the contrary, amorphous.

Over 40 years of researches on diolefin polymerization had not made it possible to obtain polymers showing all the elastic properties of natural rubber.

Synthetic polymers having sterically regular structure.

A cause of irregularity in the structure of macromolecules is the steric configuration of their carbon atoms.

Whilst in nature there are polymers containing symmetric 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) contain, in their main chains, carbon atoms with different steric configurations succeeding in an irregular manner. They are incapable of crystallizing unless the size of R is only slightly different from the size of H (that is to say provided R is isomorphous with H). Only in the cationic polymerization of isobutyl-vinylether Schildknecht obtained mixtures containing two different types of polymers, one of which was crystalline and consequently structurally ordered [1].

(1) C. E. Schildknecht, S. T. Gross, H. R. Davidson, J. M. Lambert and A. O Zoss, Ind. Eng. Chem., *40*, 2104 (1948).

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

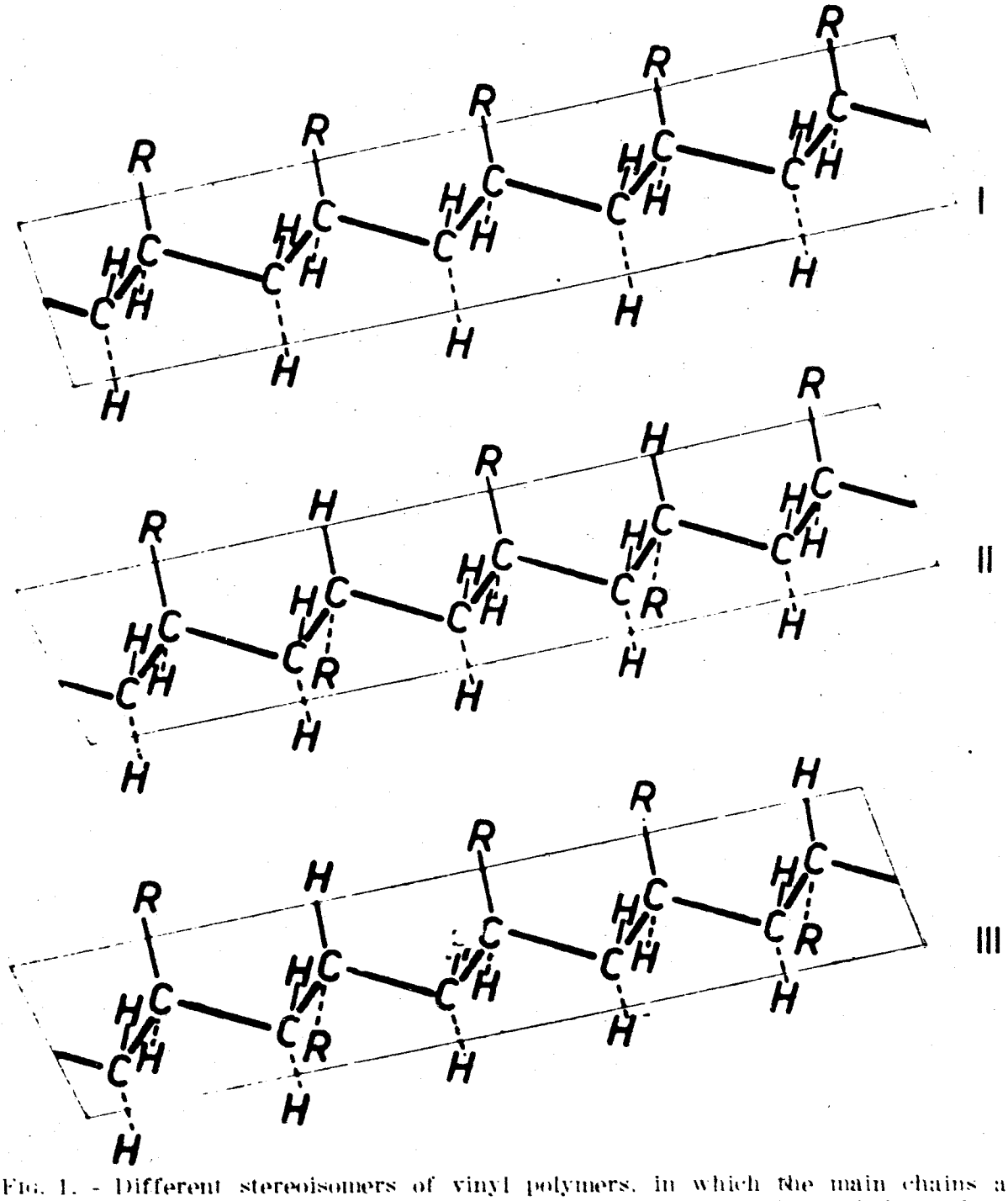


FIG. 1. - Different stereoisomers of vinyl polymers, in which the main chains are arbitrarily represented to be fully extended in a plane: I isotactic, II syndiotactic; III atactic.

both in case of alphaoletin and dioletin polymers (2). In the field of alpha oletin polymers, isotactics could be produced in which all the tertiary carbon atoms of long sections of chain show the same steric

(2) G. NATTA, Atti Accad. Lincei, Memorie, [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).

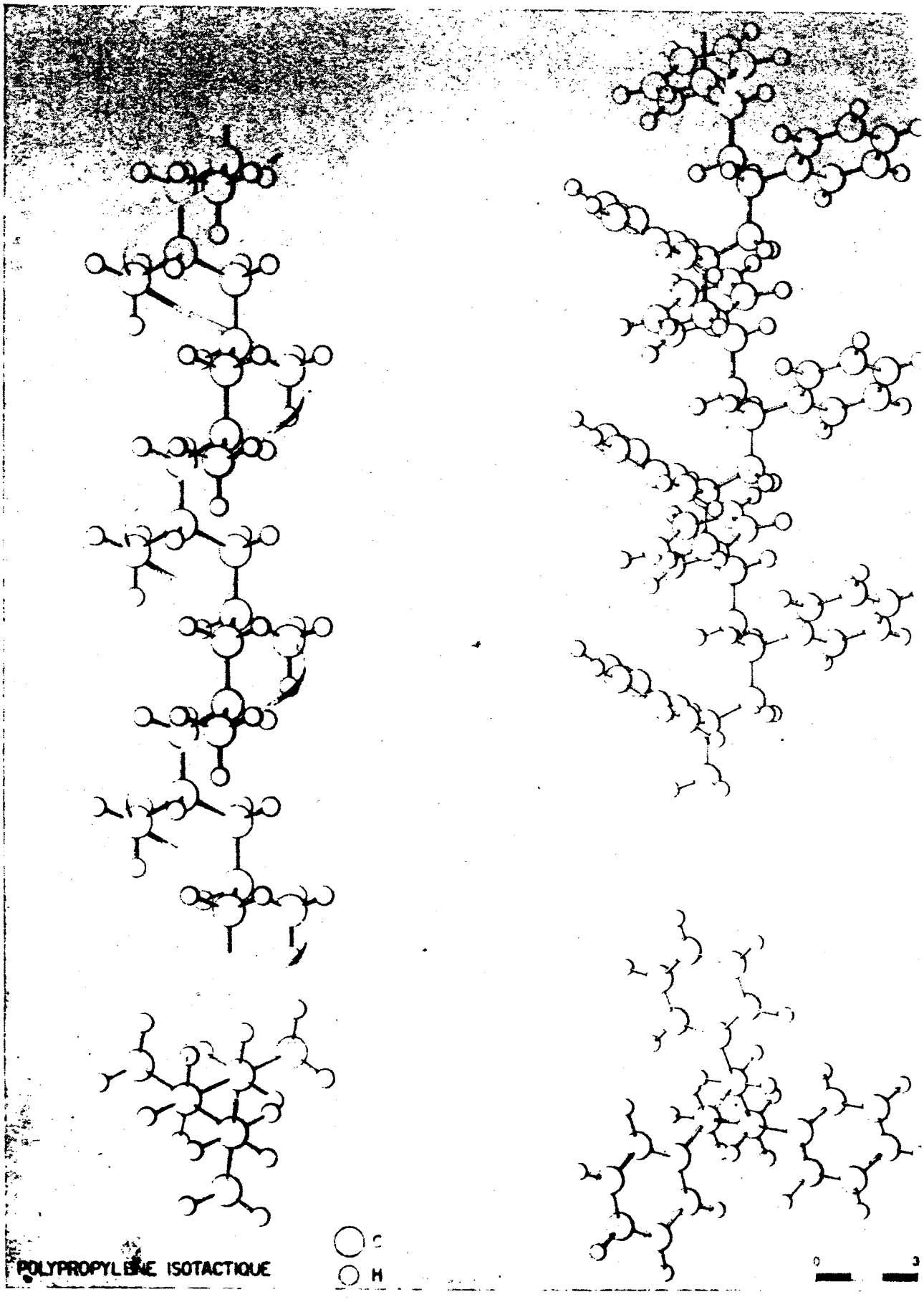


FIG. 2. - Chain structure of isotactic polypropylene and polystyrene as determined by X-Rays.

configuration. Perfectly linear crystalline products were thus obtained with high melting temperatures and with physical properties completely 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 opposed steric configuration.

I had to create 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 having opposed steric configurations, have been called atactic. Successively Mark proposed to use the name *cutactic*, which defines all regularly structured polymers regardless of their type of steric structure.

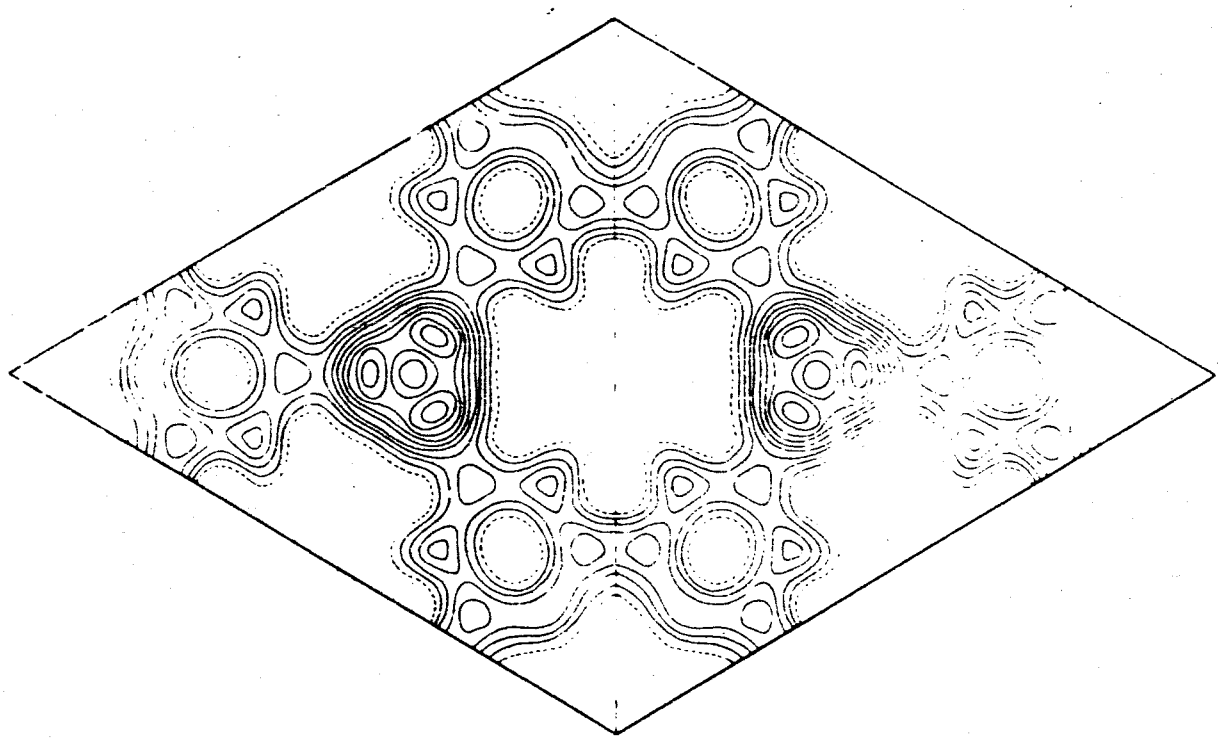


FIG. 3. - Projection of the electron density on a plane normal to c-axis, for polystyrene lattice.

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 and a specular reflection; so that adjacent monomeric units are structurally enantiomorphous.

([3]) G. NATTA and P. CORRADINI, Rend. Accad. Lincei, [8], *19*, 229 (1955).

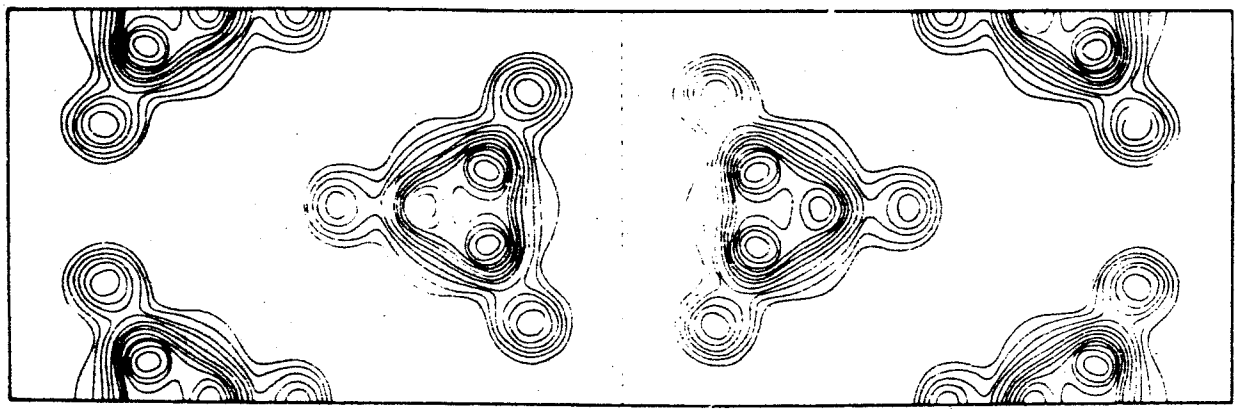


FIG. 4. - Projection of the electron density on a plane normal to c-axis, for polypropylene lattice.

Although in nature isotactic polyhydrocarbons do not exist, nevertheless a certain structural analogy is observed between certain crystalline proteins (alpha-keratin) (Fig. 6) and certain spiralised polysaccharides with isotactic polymers.

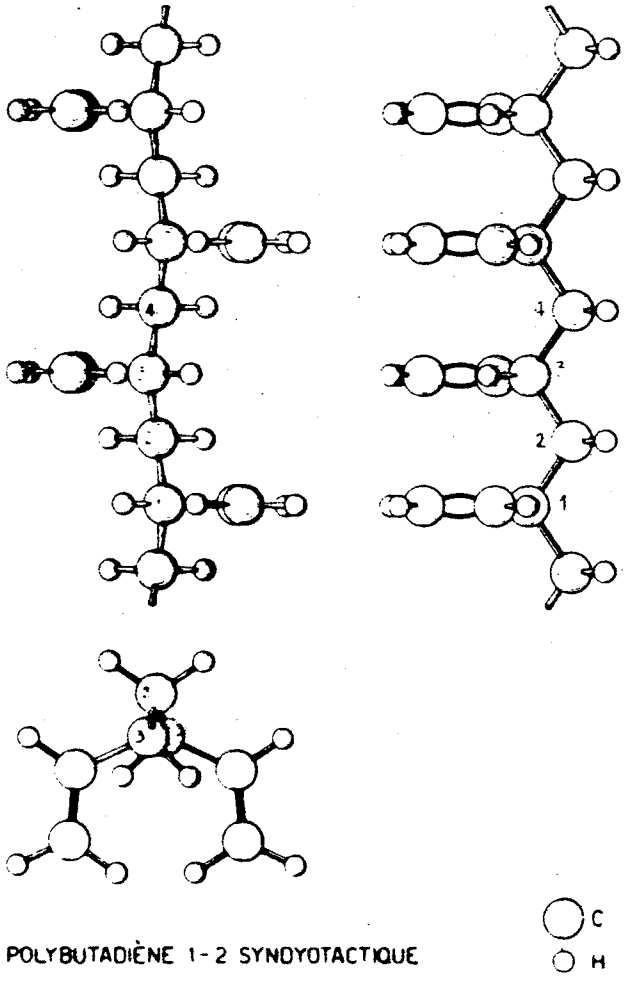


FIG. 5. - Conformation of the chain of crystallized 1.2-syndiotactic polybutadiene.

In such polymers, chains have a spiral 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.

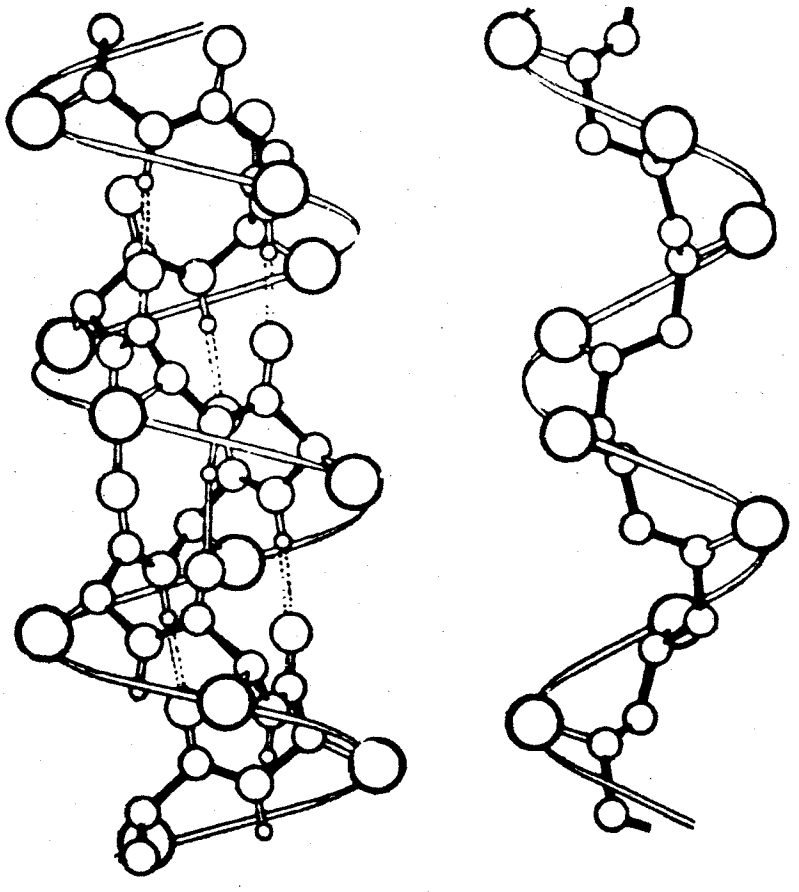


FIG. 6. - Comparison between the helix structure according to Pauling-Corey for the α-keratin (3.7 helice) and that according to Natta-Corradini for the isotactic poly-4-methyl-pentene (3.5 helice).

In very long macromolecules we can, in fact, 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. The first 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.

TABLE I.

MELTING POINTS AND CRYSTALLINITIES OF POLYPROPYLENES WITH DIFFERENT STEREOISOMERIC COMPOSITIONS

Solvent employed for the extraction	1°) Fractionation of polypropylene obtained with $TiCl_4$ and $Al(C_2H_5)_3$ catalyst; R = 2,5; T = 90°C; $[P_{INIT.}]$ = 21 ata			2°) Fractionation of polypropylene obtained with $TiCl_4$ and $Al(C_2H_5)_3$ R = 2,8; T = 35°C; Pcost = 3,3 ata			3°) Fractionation of polypropylene obtained with $TiCl_3$ and $Al(C_2H_5)_2$ Cl; R = 3; T = 70 °C; $[P_{INIT.}]$ = 21 ata			4°) Fractionation of polypropylene obtained with $TiCl_3$ and $Al(C_2H_5)$; R = 2,5; T = 80°C; Pcost = 6 ata		
	[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

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 sections of opposed configuration or with atactic sections, are called stereoblock polymers (Fig. 7).

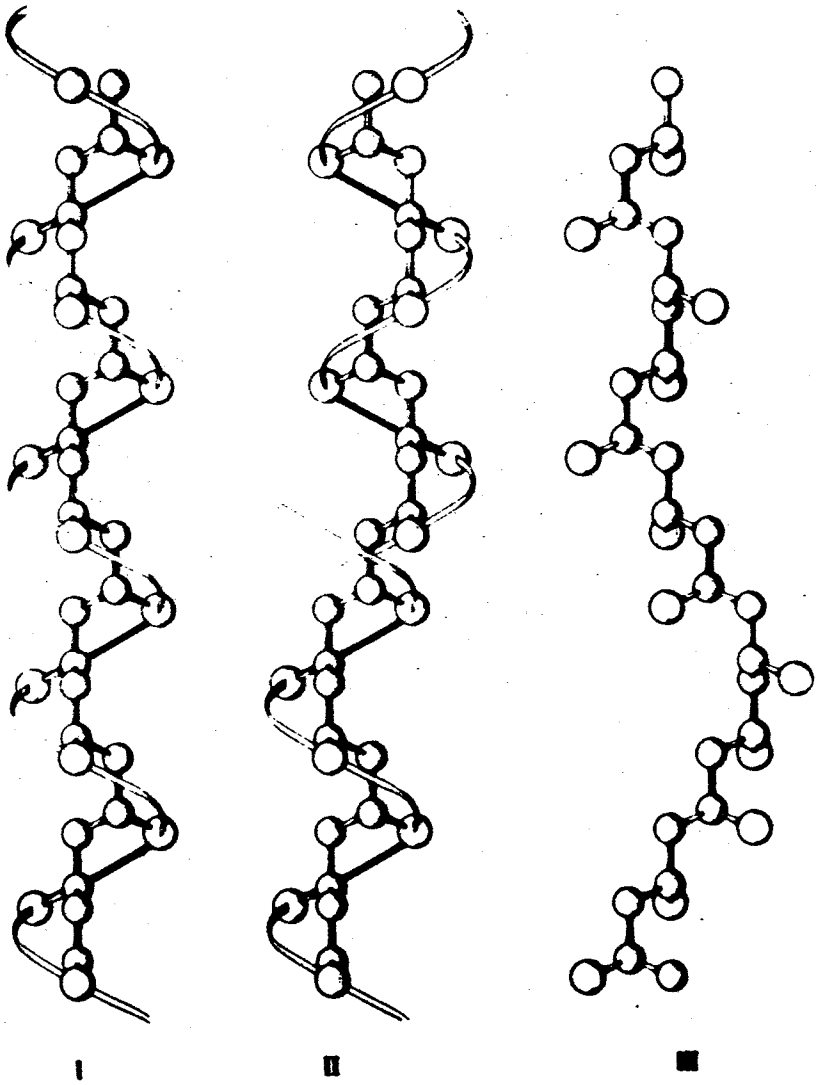


FIG. 7. - Comparison of an isotactic chain (I), with a section of stereoblock chain constituted from two isotactic portions having different configuration (II) and with an atactic chain (III).

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 I). For polymers having very high molecular weight the melting temperature may drop from 175° C for totally isotactic polypropylene to almost 100°, owing to

(4) G. NATTA, G. MAZZANTI, G. CRESPI and G. MORAGLIO, Chimica Industria, 39, 275 (1957).

the decrease of the average length of the individual isotactic sections present in stereoblock polymers (Tab. II).

TABLE II.

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 diminution of melting temperature. This is also valid for pure isotactic polymers, since the end groups cause irregularities in crystals. Such irregularities have an effect similar to the one caused by internal irregularities in stereoblock polymer chains.

Stereospecificity of polymerization processes.

Polyaddition processes more largely 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, dyazo 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 radic processes:

1) Irregularities of chemical nature such as branchings in poly meric chains, inversions in the head-to-tail structure, telomerizations d to chain transfer with solvent molecules or due to coupling with othe free radicals.

2) Steric irregularities due to the different possible steric co figurations of the asymmetric monomeric units.

The only obstacle to irregularities in steric configuration can deriv from the bulkiness of the functional groups. Functional groups can i the addition of each monomeric unit, foster its presentation with a opposed configuration with respect to the one of the previous unit. Th causes, in some vinyl polymers (polyvinyl chloride and polyacrylonitryle a greater probability of syndiotactic successions.

Cationic processes, in general, generate polymers having lo molecular weight and chemically and sterically irregular structure. Th is due to the facility with which chain transfers occur, unless one op rates at extremely low temperatures with particular monomers showin a certain symmetry (isobutylene).

A third polymerization mechanism is given by anionic catalysi processes which, in the past, had had a quite negligible importanc if one excludes the production of synthetic rubber in Russia before t war, by polymerization of butadiene with a sodium catalyst. Suc polymerization proved neither chemically nor sterically specific, sinc polymers thus obtained are constituted of monomeric units with diffe ent linkages, in part 1-2 and in part cis 1-4 and trans 1-4.

Processes of truly stereospecific catalyses of alpha-olefins and dioleti were discovered only at the beginning of 1954.

These processes (to which we attribute an anionic co-ordinate mechanism) taking place in the presence of catalytic complexes containin low valency transition metal compounds and metallorganic derivative of highly electropositive elements having small ionic radius enabled u to obtain in Italy the first isotactic and syndiotactic polymers and t four different pure, highly crystallin polybutadiene stereoisomers (tw with 1.2 linkage isotactic and syndiotactic, and two with 1.4 linka cis and trans).

Anionic processes, using metallorganic compounds of lithium, dev loped in U.S.A. allowed the preparation of the first synthetic rubbe from isoprene having prevailingly 1.4 cis configuration, like natur rubber.

Behavior of different monomers in stereo-specific 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 to the double bond determines its tendency to polymerize with a certain catalytic mechanism ([5]).

It is known that the monomers which react better to the cationic polymerization contain electron-releasing substituents.

The data concerning the classical polymerizations of anionic type were rather scarse and concerned a small number of monomers. This data shows 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 polarisability, 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 alpha-olefines) 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 catalyst.

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 metallorganic electron-deficient complexes, blocking their catalytic activity. The consequence is that the most typical monomers, which are polymerized by catalysts considered as basic or nucleophilic (acrylonitrile, methyl metacrylate, 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 stereospecifily (Tab. III).

([5]) C. E. SCHILDKNECHT. Ind. Eng. Chem., *50*, 107 (1958); C. C. PRICE. Reactions at Carbon Carbon Double Bond, Interscience, N. Y. (1946).

TABLE III.

Monomers	Substituent action		Respondence 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
$CH_2=CH-CROOR_1$				
$CH_2=CH-F$				
$CH_2=CH-Cl$				
$CH_2=CH-Br$				
$CH_2=CH-O-CH_3$				
$CH_2=CH-O-CH(CH_3)_2$				
$CH_2=CH-O-CH_2CH(CH_3)_2$				
$CH_2=CH-CR=CH_2$		conjugative effect		anionic co-ordinated polymerization with very electron deficient complexes
$CH_2=CH-C_6H_4-F$				
$CH_2=CH-C_6H_5$				
$CH_2=CH-C_6H_4-CH_3$				
$CH_2=CH-C_6H_4OCH_3$				
$CH_2=CH_2$	electron attracting		cationic polymerization	possible co-ordinated polymerization not anionic
$CH_2=CH-CH_3$		inductive effect		
$CH_2=CH-CH_2-CH_3$				
$CH_2=CH-CH(CH_3)_2$				
$CH_2=C(CH_3)_2$				highly stereospecific polymerizations
$CH_2=CR(CH_3)$				

Schemes in which monomers are arranged according to their respondence to the different types of catalysts (cationic and ionic) or to radicalic initiators were proposed by various authors. In the scheme reported in the table, we 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 Craft cationic catalysts. The alpha-olefins and the vinylidene 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 electro-deficient catalysts with substances containing lone electron pairs, etc.).

The first partially stereospecific polymerization of vinyl monomers had been carried out by Schildknecht with catalysts of cationic type by complexing BF_3 with ether and operating at low temperature.

The alpha-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 this catalyst 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 alpha-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 polymerisation of such monomers also. 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 (Tab IV).

TABLE IV.

I.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 enable us to clarify stereospecific catalysis as well as the possible causes of stereospecificity.

Co-ordinated anionic polymerization occurs when the metallorganic complex contains very electro-positive atoms linked to carbon atoms and at least one transition metal atom.

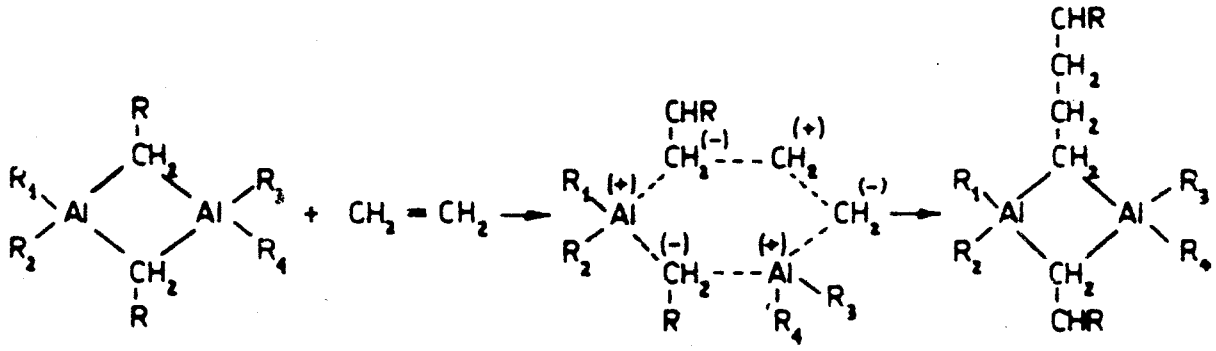
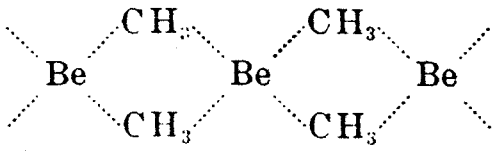
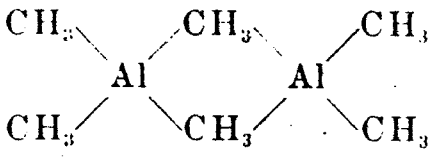
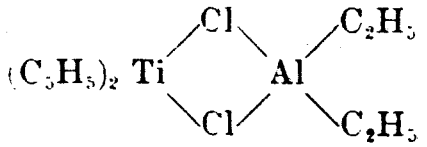


FIG. 8. - Catalytic polymerization of ethylene with soluble metallorganic complexes.

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 electro-positive metal and the more substituted carbon towards the negative group previously linked to the metal complex.

TABLE V.

	Angle M—C—M	Distance C—M Å	
		bridge	terminal
	66°	1.93	—
	70°	2.24	1.99
	90°	~ 2.5 (Ti—Cl)	—

All stereospecific catalysts are constituted by electron-deficient bi metallic complexes. In these catalysts electro-negative atoms constitut bridge bonds between very electro-positive metal atoms of very smal diameter.

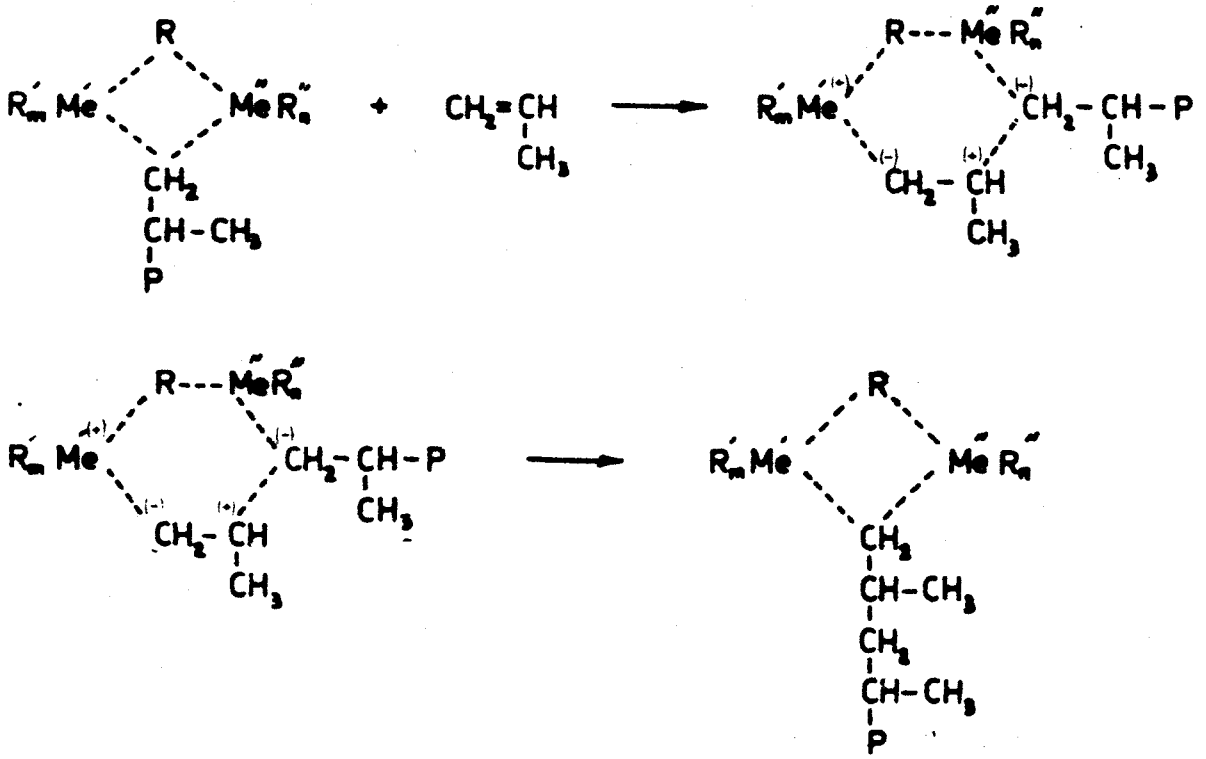
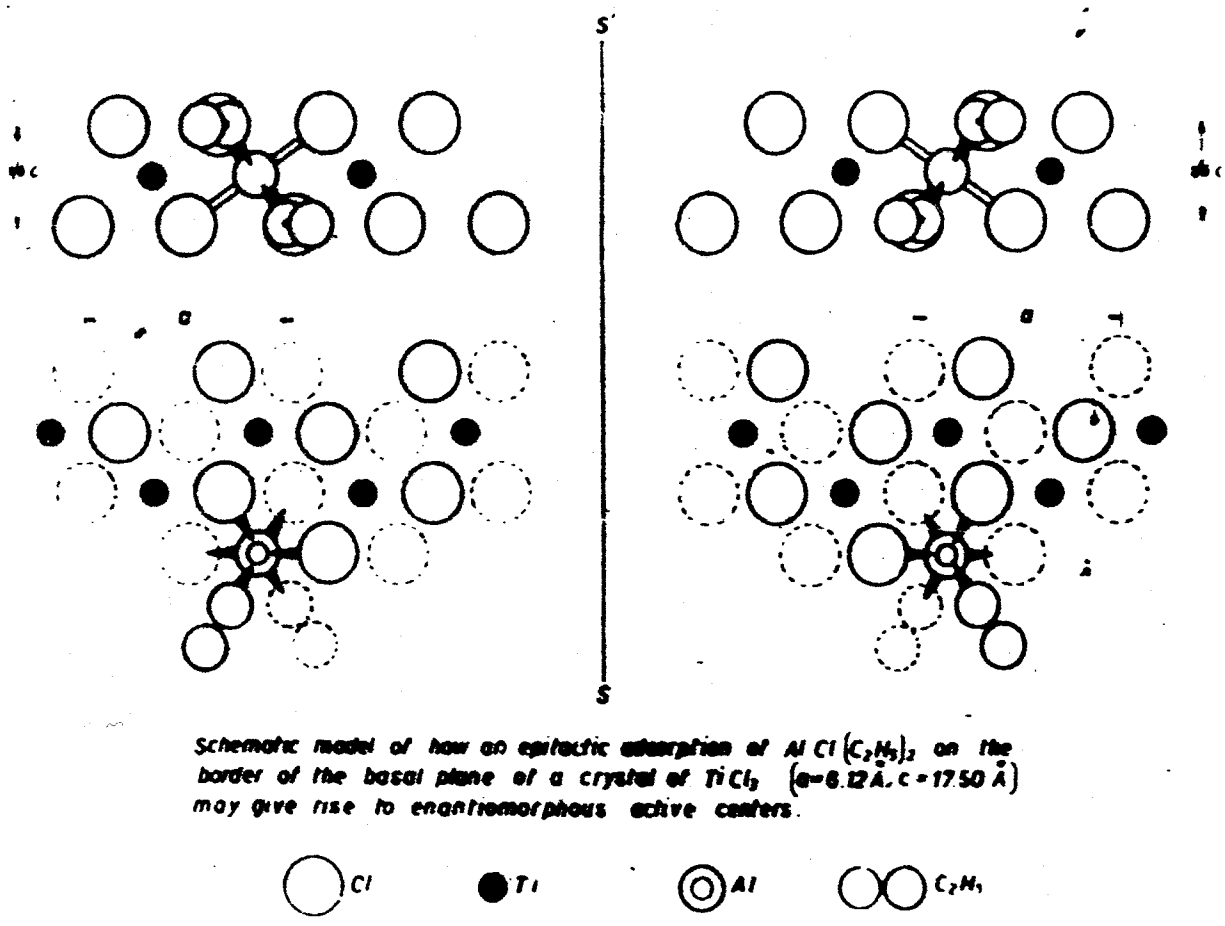


FIG. 9. - Catalytic polymerization of propylene with metallorganic insoluble complexes, containing two kind of metals.

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 lac of symmetry in the complex, which causes a determined orientation i the monomer molecule in the instant of its transformation in monomeri unit.



Schematic model of how an epitactic absorption of $Al\,Cl(C_2H_5)_2$ on the border of the basal plane of a crystal of $TiCl_3$ (a=6.12 Å. c=17.50 Å) may give rise to enantiomorphous active centers.

FIG. 10.

In our stereospecific catalysts the stereospecificity is in relatio with the ionic diameter of the metal. Each active center causes th synthesis of macromolecules containing sequences of hundreds o thousands of monomeric units having the same relative steric confi guration.

Each active center causes therefore an asymmetric synthesis.

In the case of α-olefins polymers, isotactic chains thus obtained assu me, with regard to crystals, regular helical conformations. It is possibl 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 left hand or in right hand sense. The lack of optical activity is due to the fact that the effect of the two spiralization senses are mutually compensated.

TABLE VI.

DEPENDENCE OF THE STEREOSPECIFICITY ON THE IONIC RADIUS OF THE METAL CONTAINED IN THE CATALYTIC COMLEXES

Metal of the metal organic compound	Ionic radii of the metal	% of polypropylene not extractable by boiling n-heptane
Be	0.35 Å	94-96%
Al	0.51 Å	80-92%
Mg	0.66 Å	78-83%
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 (Tab. VII).

TABLE VII.

INTRINSIC VISCOSITY IN TETRALINE OF ISOTACTIC POLYMERS, PREPARED WITH CATALYSTS OBTAINED FROM $Al(C_2H_5)_3$ AND TITANIUM CHLORIDES AT 60-80° C

Monomers	Titanium chloride	$\frac{\text{moles } Al(C_2H_5)_3}{\text{moles } TiCl_n}$	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

(6) G. NATTA, Opening lecture of the XVI Congress of International Pure and Applied Chemistry, Experientia Supplementum VII, 21 (1957).

Nature of the surface of the solid catalysts.

One of the more intensively studied problems in heterogeneo catalysis is the determination of the number and nature of active cente on the catalyst surfaces.

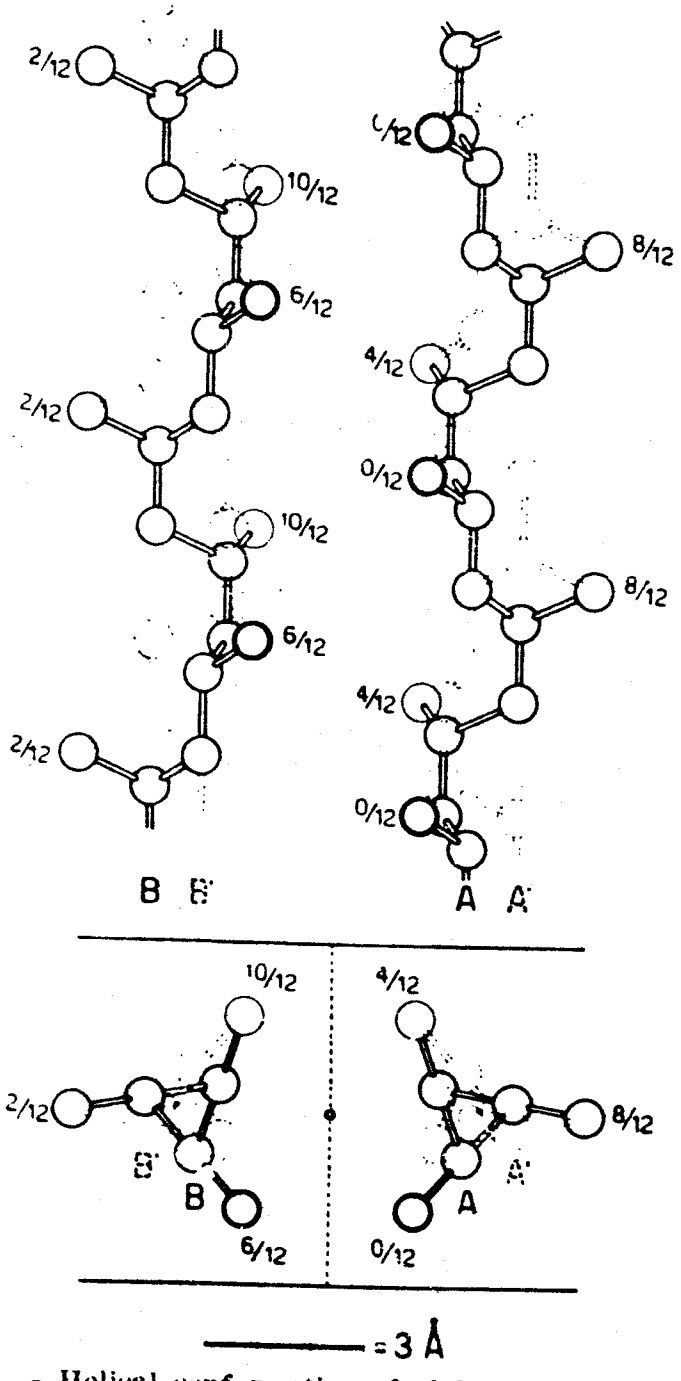


FIG. 11. - Helical conformation of alpha-olefins polymers.

In the literature one can find hundreds of papers on the determination of the number and nature of active centers, their variations with respect to temperature and their behavior in catalysis.

Since a long time ago, 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 inter sting aspect in catalysis, namely its stereospecificity. Moreover, sinc every active center presents the property of producing a chain of rea tions of a given type, it is now possible to differentiate the active center in terms of the composition and structure of the produced polymers

The fact that a layer lattice crystalline catalyst is activated by th action of a metallorganic compound raises the problem whether th activation is due to a reversible or irreversible adsorption of the latte or to a true reaction with irreversible modification of the superficia structure of the support.

The problem has been faced, as for heterogeneous systems including a solid phase having a laver lattice, by using metallorganic compound containing labelled carbon. In Table VIII the quantity of alkyls fixe at different temperatures is indicated.

From the data of Table VIII it is thus proved that only part of th fixed alkyls are efficient in catalysis.

The ratio between the absorbed quantity according to the two adsor ption types seems to correspond, approximately, to the ratio betwee the surface of the base of the crystals and the surface of the mor irregular lateral facets of the hexagonal prisms.

We believe that also chemiosorption is connected to the formatio 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 o active centers 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 C_{14}.

Such 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, at low temperature, is not reversible and which can be considered as due to a surface chemical reaction, is the one which determines the active centers in the catalysis (observed in the order of magnitude of some units 10^{-3} active centers $TiCl_3$).

3) Each active center maintains in the absence of poisons an activity which is constant with time.

TABLE VIII.

DETERMINATION OF THE NUMBER OF ACTIVE CENTERS ON A GROUND SAMPLE OF α-$TiCl_3$, FROM ADSORPTION DATA OF LABELLED C^{14} ALUMINUM ALKYL COMPOUNDS, FOLLOWED BY POLYMERIZATION OF PROPYLENE

($TiCl_3$: 0,5 g; aluminum alkyl compound: 0.5 cm³; solvent: 30 cm³ 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 preadsorbed alkyl groups remaining on $TiCl_3$ after washing	Number of alkyl groups adsorbed on active centers (preadsorbed alkyl groups found in the polymer)
$Al(C_2H_5)_3$	— 18	1/2	n-heptane	— 18	17.0×10^{-3}	n.d.
$Al(C_2H_5)_3$	— 18	3	n-heptane	— 18	45.0×10^{-3}	9.3×10^{-3}
$Al(C_2H_5)_3$	20	1/2	benzene	20	48.2×10^{-3}	10.1×10^{-3}
$Al(C_2H_5)_3$	46	1/2	benzene	46	17.7×10^{-3}	10.5×10^{-3}
$Al(C_2H_5)_3$	70	1/2	benzene	20	10.5×10^{-3}	10.8×10^{-3}
$Al(C_2H_5)_3$	70	1/2	benzene	70	6.2×10^{-3}	6.7×10^{-3}
$Al(C_2H_5)_3$	100	1/2	toluene	100	3.0×10^{-3}	3.0×10^{-3}
$Al(C_2H_5)_2Cl$	70	1/2	n-heptane	20	3.0×10^{-3}	3.1×10^{-3}

4) The first polymeric chain which is formed on an active center starts with an alkyl deriving from $AlEt_3$, but 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 center, are formed as a consequence of successive processes of chain termination and of chain transfer.

5) The molecular weight of the polymer depends on several processes:

a) a termination process which takes place at high temperature by dissociation of the catalytic complex to hydride, succeeded 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 through one of two possible catalytic mechanisms. One of them is independent from 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 (Tab. IX). In Tab. IX the catalytic complex was written in a simplified ionic form. It is an electron-deficient complex in which the R group is crosslinked between two metals (i.e. Ti and Al) ([7]).

The chain transfer processes connected with alkyls exchange become prevailing, when operating with relatively high concentrations of alkyls in solution, and in such a case the rate of these processes may represent more than 50% of the total chain transfer and termination processes.

In other conditions (low concentration of alkyls and high temperature), the other termination processes are prevailing.

The determination of the number of the active centers has made it possible to determine also the average life of each macromolecule which is of the order of minutes. Since each molecule contains, as an average, hundreds of monomeric units, it follows that the polymerization, considered as an addition (through successive « stepwise addition » stages), corresponds under certain conditions to times of hundredths of a second for each addition of a monomeric unit ([8,9]).

([7]) G. NATTA. Introductory Lecture at the International Symposium on the Chemistry of the Coordination Compounds. « La Ricerca Sci ». Suppl., *28* (1958).

([8]) G. NATTA, G. PAJARO, I. PASQUON and V. STELLACI. Rend Accad. Naz. Lincei, [8]. *24*, 479 (1958).

([9]) G. NATTA, I. PASQUON, G. PAJARO and E. GIACHETTI, Chimica Industria, *40*, 556 (1958).

The formation of an entire macromolecule thus results in a relatively slow process with respect to the normal formation of macromolecules by free radical processes.

TABLE IX.

REACTION SCHEMES FOR THE PROPYLENE POLYMERIZATION PROCESS WITH STEREOSPECIFIC CATALYSTS

a) *Initiation and propagation*

$$[Cat]^{(+)(-)}—R + CH_2 = CHCH_3 \rightarrow [Cat]^{(+)(-)}—CH_2CHCH_3R$$

$$[Cat]^{(+)(-)}—CH_2CHCH_3(CH_2CHCH_3)_{n-1}\ R + CH_2 = CHCH_3 \rightarrow$$
$$\rightarrow [Cat]^{(+)(-)}—CH_2CHCH_3\,(CH_2CHCH_3)_nR$$

where: R = H, C_2H_5, C_3H_7 or other polymeric alkyl groups

b) *Chain transfer and termination*

1° Monomolecular termination process

$$[Cat]^{(+)(-)}—CH_2CHCH_3(CH_2CHCH_3)_n\ R \rightarrow$$
$$\rightarrow [Cat]^{(+)(-)}—H + CH_2 = CCH_3\,(CH_2CHCH_3)_n\ R$$

2° First order chain transfer process with respect to the monomer

$$[Cat]^{(+)(-)}—CH_2CHCH_3(CH_2CHCH_3)\ R + CH_2 = CHCH_3 \rightarrow$$
$$\rightarrow [Cat]^{(-)(-)}—CH_2CH_2CH_3 + CH_2 = CCH_3(CH_2CHCH_3)_n\ R$$

3° Chain transfer process depending on aluminum alkyl concentration

$$[Cat]^{(+)(-)}—CH_2CHCH_3(CH_2CHCH_3)_n\ R + R_2AlR_2 \rightarrow$$
$$\rightarrow [Cat]—R_2 + R_2AlCH_2CHCH_3(CH_2CHCH_3)_n\ R$$

or:

$$TiCl_n\text{-}AlY_2P + AlR_3 \rightarrow TiCl_nAlR_3 + AlY_2P$$

where Y = alkyl and P = polymeric chain

Since the catalytic activity is constant in time, it follows that when one uses very pure reagents, each active center in the course of a polymerization protracted for some days, can lead to thousands of macromolecules, containing altogether millions of monomeric units.

Heteroblock copolymers of alpha-olefins.

By alternative introduction of different monomers in the growth reaction we succeeded in obtaining macromolecules consisting of a succes-

sion 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 centers active for both monomers and at a temperature at which the average life 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 minutes);

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 of 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 x 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 from the steric view point also which shows some very interesting aspects.

Random copolymers of alpha-olefins.

The properties of the random copolymers of alpha-olefins present some analogies with those of stereoblock homopolymers.

(10) G. Natta, I. Pasquon and E. Giachetti, in press.

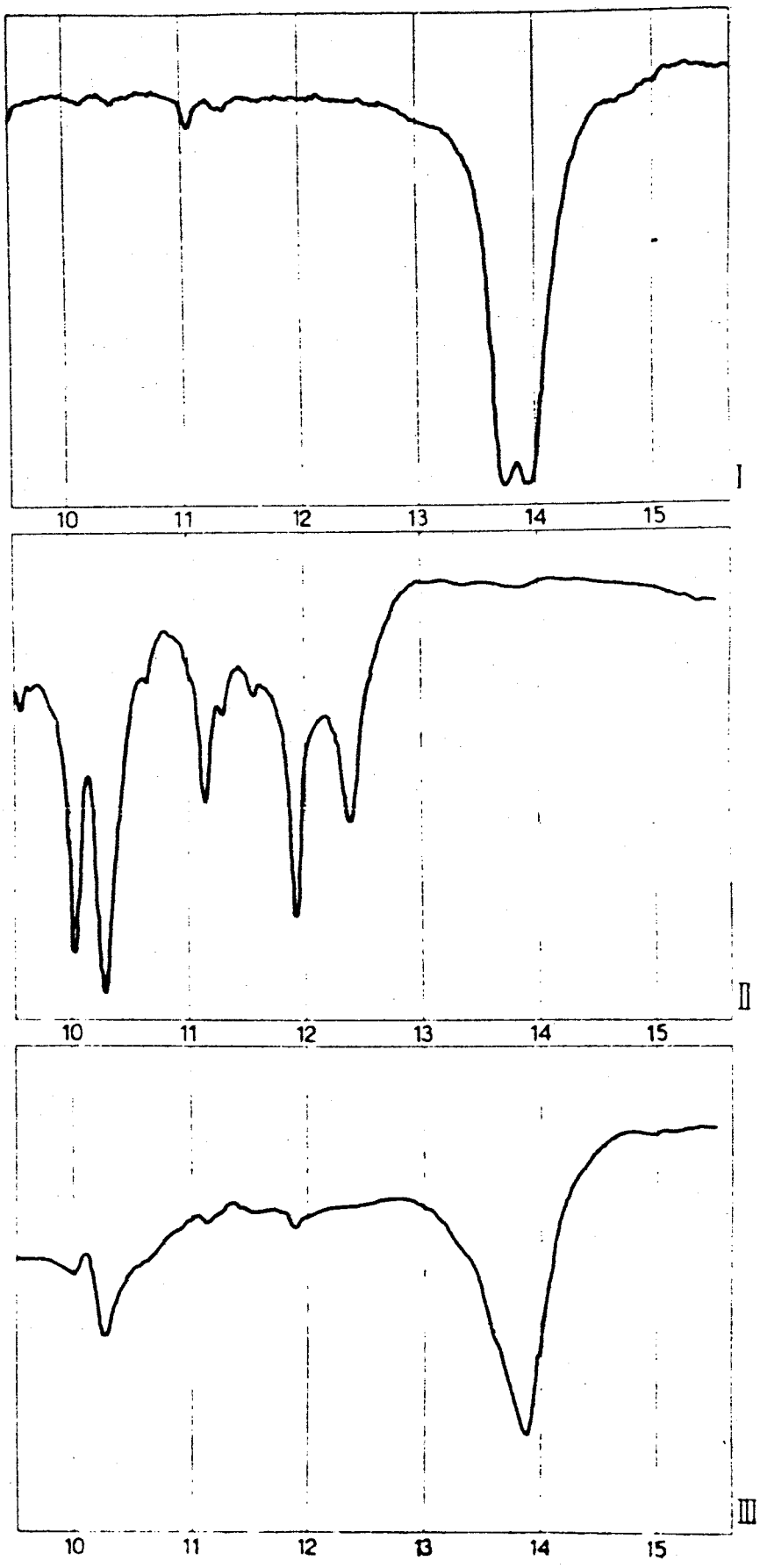


FIG. 12. - Comparison of I.R. spectra, between 9.5 and 15 μ, of a linear polyethylene (I), of a fraction of polypropylene insoluble in ether but extractable in n-hexane (II), and of a corresponding fraction of ethylene-propylene copolymer containing 60 mols % of ethylene (III). Thickeness of the samples 0,1 mm.

TABLE X.

EXTRACTION OF A NON-RANDOM COPOLYMER COMPARED WITH THE EXTRACTIONS OF HOMOPOLYMER

Polymer	Fraction extractable by boiling ethylether %	Fraction extractable by boiling n-heptane %	Fraction extractable by boiling 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%) make the copolymers amorphous.

Whilst, as a rule, by using some of typical Ziegler catalysts one obtains products containing mixtures of macromolecules comprising copolymers having a very large range of composition, together with homopolymers, the products obtained by continuous polymerization, either with certain catalysts containing only one type of highly stereospecific, active centers, or with certain non-stereospecific catalysts (*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 $Al(C_8H_{17})_3$) are completely soluble in boiling n-heptane. On the contrary, the polyethylene obtained using the same catalyst is almost completely insoluble and the 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

(11) G. NATTA, G. MAZZANTI, A. VALVASSORI and G. PAJARO, Chimica Industria, 39, 733 (1957); G. MAZZANTI, A. VALVASSORI and G. PAJARO, ibid., 39, 743 (1957); G. MAZZANTI, A. VALVASSORI and G. PAJARO, ibid., 39, 825 (1957).

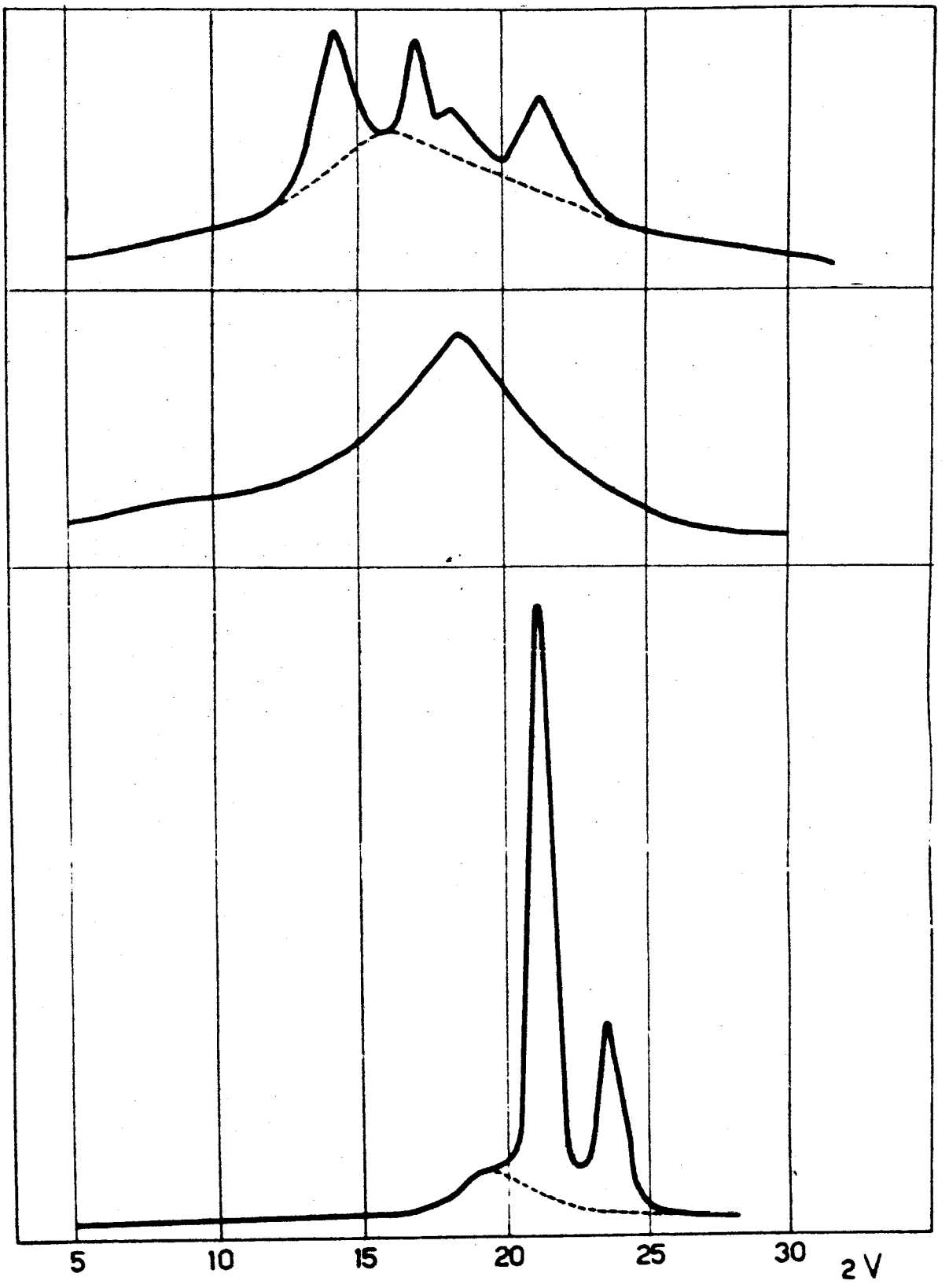


FIG. 13. - Comparison of X ray diffraction of fraction of polypropylene insolubl in ether, but extractabie with boiling hexane (I), of a corresponding fra tion of ethylene-propylene copolymer containing 60% of ethylene (II), an of a linear polyethylene (III).

fractions obtained by extraction of propylene homopolymers and from the spectrum of pure polyethylene (Fig. 12).

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 and the maximum in the diffraction intensity appears in the spectra in correspondence with a value of the diffraction angle which is different from the one corresponding to the maximum for amorphous linear polypropylene, and, respectively, to the maximum value which can be predicted for an amorphous polyethylene.

Also the fractions successively extractable by boiling hexane and by heptane prove, in general, amorphous with X-rays, contrary to the analogous fractions obtainable from the propylene homopolymers which present a remarkable crystallinity (between 30 and 50%).

As an example, we report in fig. 13 a comparison between the X-ray examination 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 to the chain. At 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 opposed only by a low energy barrier.

The non-vulcanized polymers show, in fact, a viscoelastic behavior which is very similar to the natural rubber one and have a low second order transition temperature. They show low initial elastic moduli and high ultimate elongations. The temperatures at which the resilience decreases, reaching a minimum, is near to the one shown by natural rubber (Fig. 14).

[12] G. Natta, Rubber Plastics Age, *38*, 6 (1957).

The crosslinking of the ethylene-propylene copolymers can be suitably achieved by different methods and leads to vulcanized products having

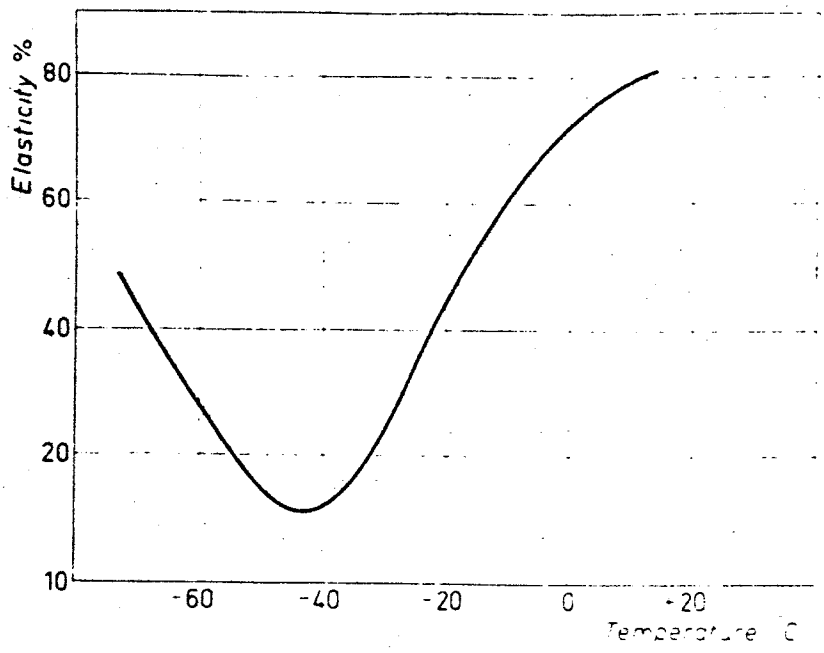


FIG. 14. - % of rebound versus temperature of a ethylene-propylene copolymer.

excellent chemical resistance, high tensile strength and good elastic properties (Fig. 15) ([13]).

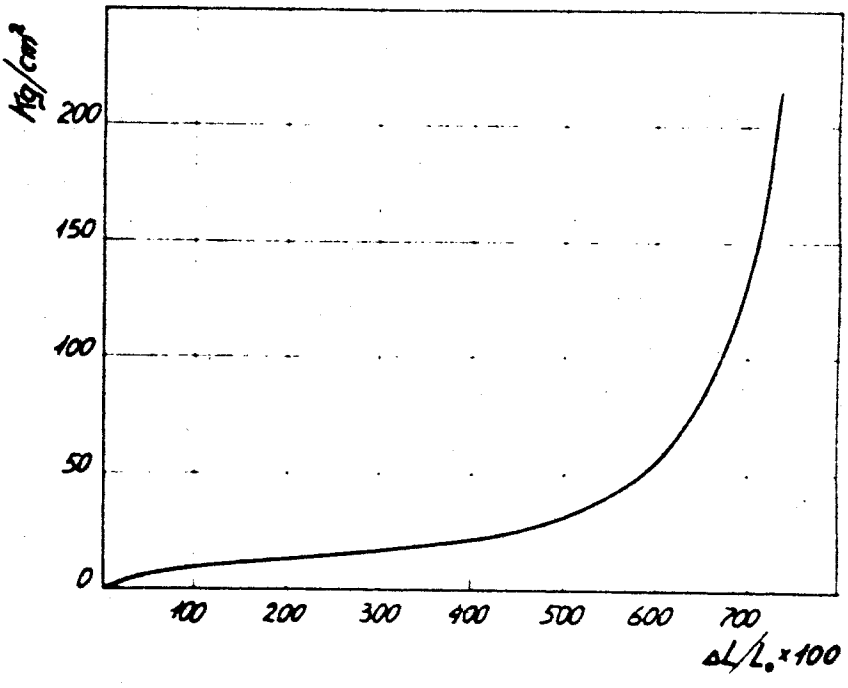


FIG. 15. - Stress-strain curve of vulcanized ethylene-propylene copolymer without reinforcing agents.

([13]) G. NATTA, G. CRESPI, M. BRUZZONE and G. BORSINI, in press in « Chimica Industria ».

They can be reinforced with active fillers (such as carbon-black, and silica) or mixed with conventional plasticizers (Fig. 16). A 50% propylene — 50% ethylene copolymer having an intrinsic viscosity about

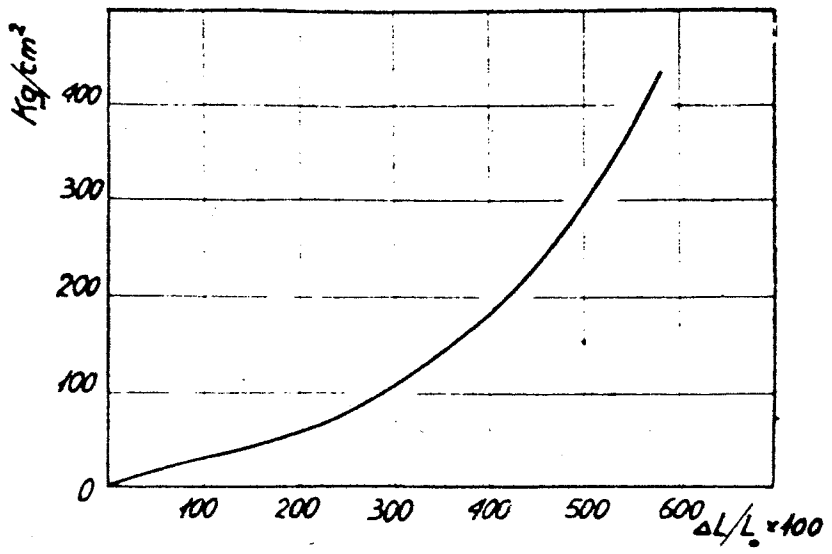


FIG. 16. - Stress-strain curve of vulcanized ethylene-propylene copolymer with 45 part of EPC black.

4, reinforced with 45 parts of carbon-black, shows, after vulcanisation, tensile strengths of 300-400 kg/cm², ultimate elongations of 500-600%, hardness of 60-70 degrees (Shore A) and a rebound, at room temperature, of 60-70%.

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 higher number of the possible isomers and the great influence of the sterical purity on the mechanical properties of the polymers enable us to better understand the great importance of stereoisomery in the field of macromolecular chemistry (Tab. XI).

By stereospecific polymerization of butadiene we have been able to obtain, with different catalysts, the isotactic and syndiotactic polymers with 1.2 linkage. 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 con-

figuration for the syndiotactic polymers of butylene 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 group.

Decreasing 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 having both crystallinity and melting point decreasing according to the diminution of the steric regularity.

Generally both the prevailingly isotactic or syndiotactic crude polybutadienes contain amorphous parts separable by ether extraction. It

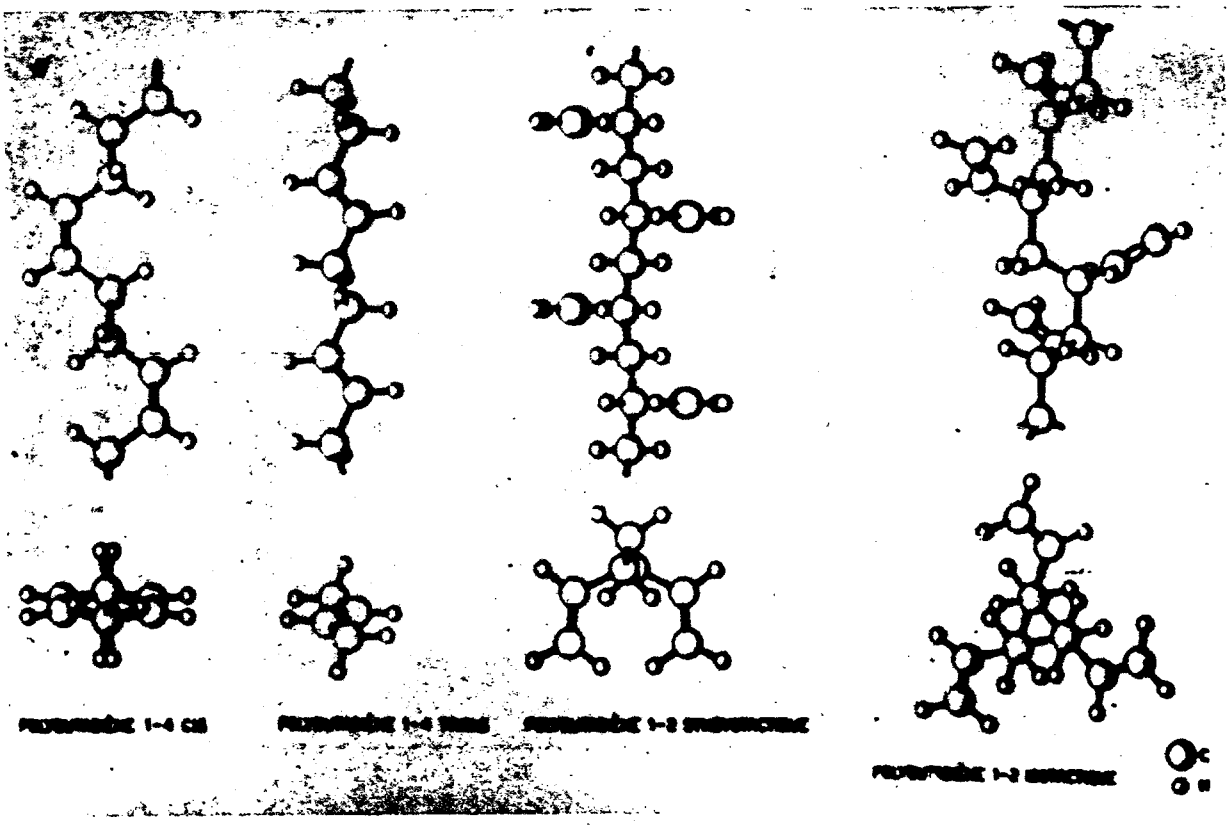


FIG. 17. - Chain structure of the polybutadiene chains, determined by Natta-Corradini by X-Rays for the four crystalline stereoisomers.

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 linkage. In fact, an ideal atactic polymer corresponds to an ideal statistical distribution of the equally probable sterically opposed units. It may be considered as an intermediate case between the ideal isotactic polymer (ratio between inversion rate and chain growing rate equal to zero) and syndiotactic polymers (ratio equal to 1).

The atactic polymers with 1-2 linkage are rubbers presenting a lower resilience than 1-4 linkage rubbers, obtained from 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 polymers with 1-2 linkage are those obtained from chromium soluble complexes having a coordinated bulky group containing oxygen (acetylacetonate) or nitrogen (carbylammines). The formation of isotactic and syndiotactic polymers depends on the ratio between the mols of aluminum alkyl and the mols of the chromium complexes 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, proves very interesting.

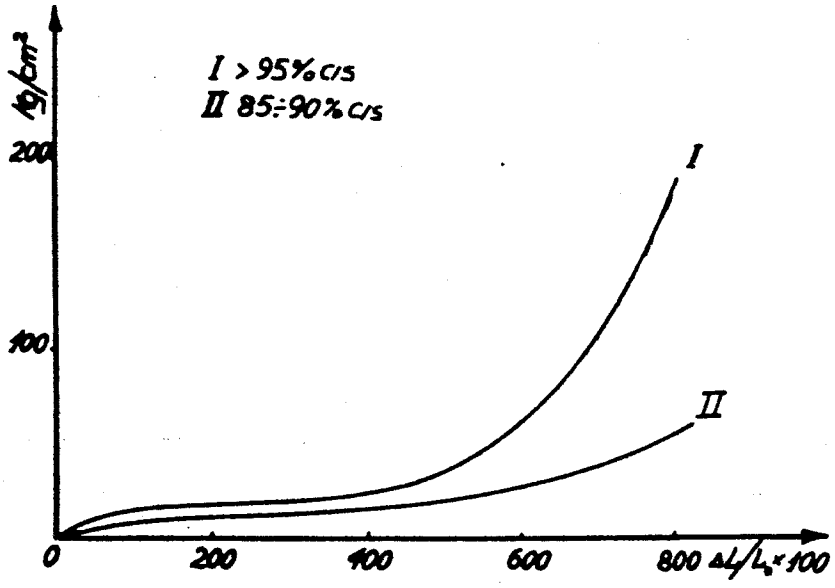


FIG. 18. - Stress-strain curve of two vulcanized 1,4 cis polybutadienes.

Trans 1-4 polybutadiene which can be obtained in the state of very 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 polybuta-

([14]) G. NATTA, L. PORRI, P. CORRADINI and D. MORERO, Rend. Accad. Lincei, [8], *20*, 560 (1956).

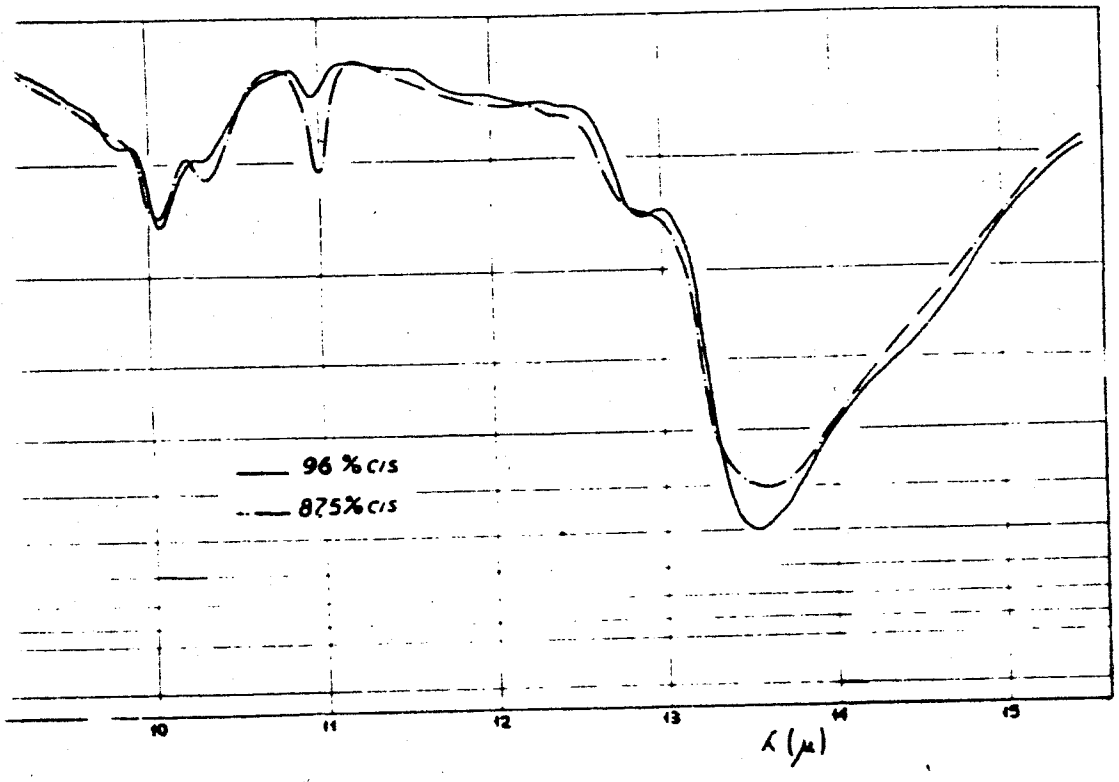
([15]) G. NATTA, L. PORRI, P. CORRADINI and D. MORERO, Chimica Industria, *40*, 362 (1958).

en extruded into filaments can be cold-stretched. The highly
ıe and oriented filaments thus obtained present properties which
ır, from some points of view, to those of the protein fibers of
les. In fact the reversibe transformation of the crystals into
ıally oriented crystals by heating at a temperature of 65° C, is
ıied by contraction in the length of the chains identity period
sequently, of the length of the fibers and may be accompanied
roduction of mechanical work.

ples of 1,4 cis polybutadiene with a steric purity of 95-97% have
g temperature of about 0° C; crystallize under stretch (400%)
still crystalline at a temperature of 80° C. They show properties
'e very similar to those of natural rubber
. pure polymers melt at lower temperatures.

variations of elastic properties in function of the stereoisome-
ty, prove very interesting.

Fig. 18 are reported the stress-strain curves, for two polybuta-
ne having a purity of 96%, the other of 87,5%. We reproduce
ared spectra of the two polymers (Fig. 19) The coefficients used



19. - Infrared spectra of two polybutadienes having high 1.4 cis content.

ıe determination of the composition are different from coefficients
)y other researches (16). When adopting these last with the polymer
red by us, a cis 1-4 percentage of 95 would result for the 87,5%
4 polymer.

16) G. Kraus and coworkers, Rubber Plastics Age, 38, 880 (1957).

The different mechanical behavior and the high tensile strength are due to the higher stereoisomeric purity which allows a higher crystallinity under stretching and 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 highy crystalline polymers, unknown until now.

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 2nd order transition temperature and are rubblerlike above this temperatures. The crystalline polymers maintain high mechanical characteristics over the range between the 1st order transition temperature and 2nd order transition temperature and, when oriented, even below this last temperature (Fig. 20).

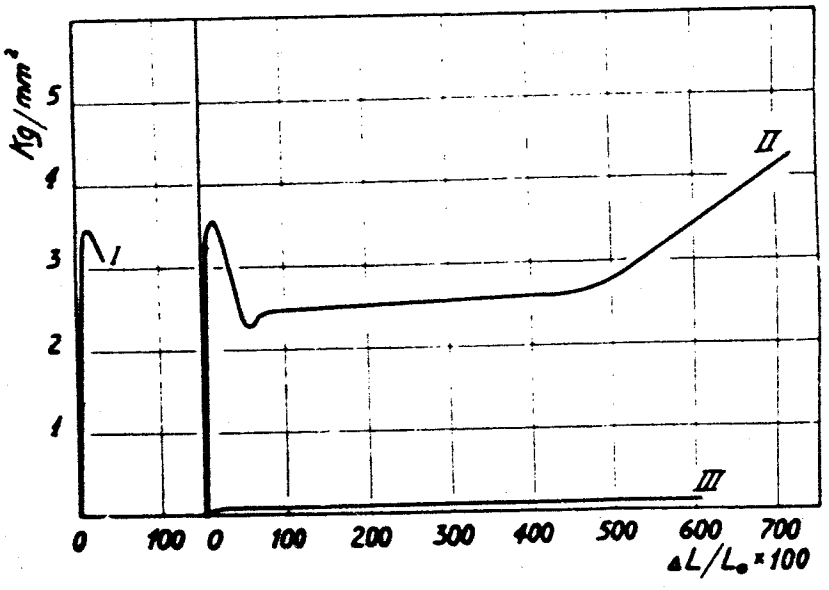


FIG. 20. - Stress-strain curves of three polypropylenes: I $[\eta] = \sim 1$ II $[\eta] > 2{,}5$. III atactis.

From the practical point of view the most interesting polymers are highly crystalline polypropylene (m.p. 175° C) and poly-1-butene (m.p 136-140°C), because of the low cost of the monomers, immense amounts of which are available in the petroleum craking gases, or cheaply available by pyrolysis of petroleum fractions or of natural gases.

Certain linear isotactic and low crystalline stereoblock polymer having high molecular weight are of particular interest, owing to thei higher elasticity compared with that of the highly crystalline polymers

They consist of macromolecules containing isotactic chain section interspersed with atactic sections or with isotactic sections of opposit steric configuration and show properties which can be varied graduall depending on their stereoisomeric composition, from the propertie of a hard, highly crystalline thermoplastic material, having a high tena

TABLE XI.

X-RAY DATA ON CRYSTALLINE POLYBUTADIENE-STEREOISOMERS

Polymer	Space group	Number of monomers per unit cell	Cell. dimensions Å		Chain axis c Å	α	β	γ	X-Ray density	X-Ray melting point
			a	b						
1-4 trans	(pseudohexagonal)	(1)	(4.54)		4.9				1.02	148 °C
1-4 cis	C2/c (monoclinic)	4	4.60	9.50	8.60	90°	109°	90°	1.01	0 °C
1-2 syndiotactic	Pacm (rhombic)	4	10.98	6.60	5.14	90°	90°	90°	0.96	155 °C
1-2 isotactic	R $\bar{3}$c (hexagonal)	13	17.3	17.3	6.50	90°	90°	120°	0.96	125 °C

city, to less crystalline materials, having mechanical properties simila to those of leather, and thence to still more elastic rubberlike material (Fig. 21).

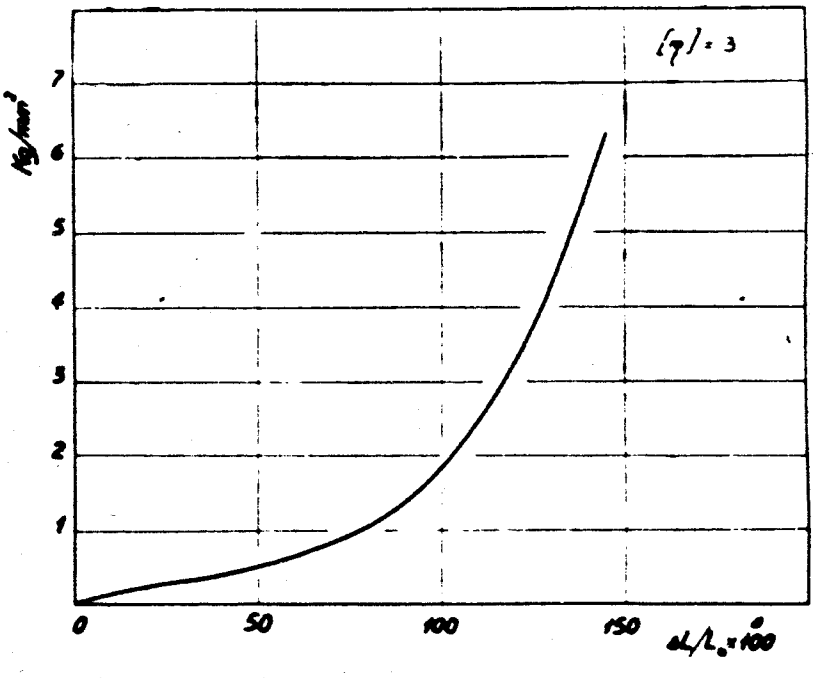


FIG. 21. - Stress-strain curve of a stereoblock polypropylene (having intrinsic v scosity of 3) preoriented by cold stretching to an elongation of 700%.

It is to be expected that, among the infinite 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.

In the field of films, transparent crystalline products, both in the non-oriented and in the oriented state, which is rather unusual for crystalline materials, were obtained.

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 creep 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).

The low cost of propylene, which is probably lower 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 low count and a high strength, all these factor will make possible the production on a com-

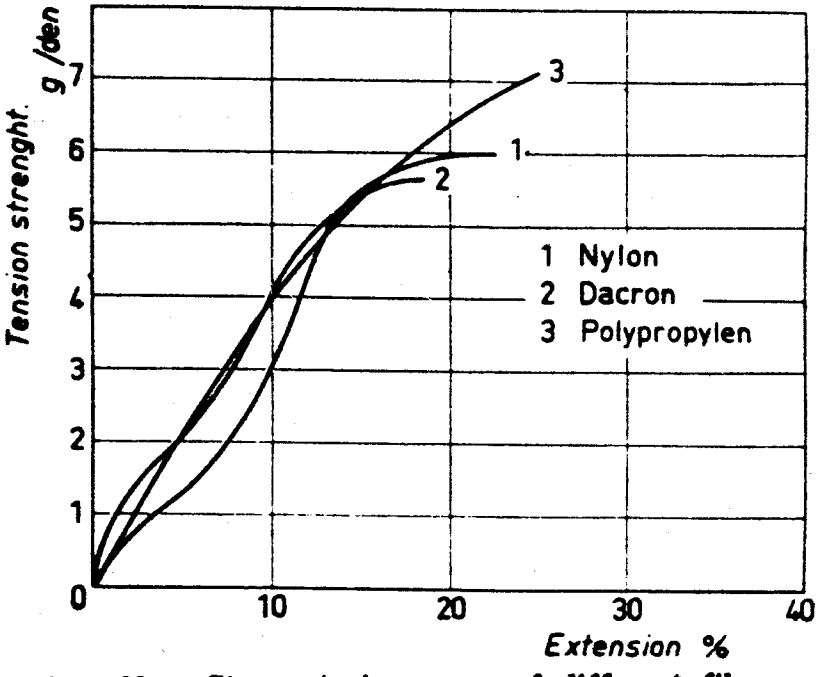


FIG. 22. - Stress-strain curves of different fibers.

mercial scale of textile fibres whose production cost is likely to become, in the future, lower than that of any other synthetic textile fibre, and also below that 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.

An other important applicative field of the anionic coordinated polymerization processes concerns, as already mentioned, the production of new synthetic rubbers.

The diolefin polymers with 1-4 cis linkage may give rise to rubbers having very good elastic properties, and high resilience: 1-4 cis polyisoprene, synthesized in U.S.A., is practically equal to natural rubber. 1,4 cis polybutadiene stereoisomers which crystallize under stretch, as does natural rubber, were prepared long since at the Polytechnic of Milan. Successively 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 have surely a great future, is the one of the ethylene-propylene copolymers. Rubbers prepared from these copolymers show very low elastic hysteresis values which approach very much those shown by natural rubber, 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 remarkable interest for the production of synthetic rubbers.