Progress in Five Years of Research in Stereospecific Polymerization

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Professor Giulio Natta received his degree in Chemical Engineering in 1924, and between 1926 and 1933 joined the faculty of the University of Pavia. During that time he became full Professor of General Chemistry. He was Professor of Physical Chemistry at the University of Rome and in 1938 joined the Institute of Industrial Chemistry at the Polytechnic Institute of Milan, of which he is now Director. Professor Natta is a member of the American Chemical Society, and the New York Academy of Science. He has authored more than 250 papers and holds a large number of patents.

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MORE THAN FOUR YEARS have elapsed since the first announcement of stereospecific polymerization of alpha olefins (Ref. 1). This discovery opened a new, immense field of research which attracted thousands of chemists and technicians in Europe, America and Asia.

This immense work has born 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 sterical regularity on the properties of the obtained polymers.

Progress in Stereospecific Catalysis

Alpha-olefins: in our initial work with these olefins we clearly indicated the conditions for obtaining highly stereospecific catalysts, and polymers having a remarkable sterical purity (Ref. 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 which yields complexes with the transition metal compounds: mole-

cules of these complexes are tenaciously adsorbed on some points of the surface of the solid, crystalline component (Ref. 3).

Many workers have put on the same plane stereospecificity in the polymerization of α-olefins with the production of linear polymers of ethylene with the aid of Ziegler catalysts. Someone has also erroneously spoken of "isotactic polyethylene," without considering that isotacticity is a particular regularity in steric arrangement, connected with the possibility of existance of enantiomorphous forms of the monomeric units, owing 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 e.g. the products of the reaction between transition metal alcoholates and aluminum alkyls (Ref. 4) and certain metal-organic soluble complexes, some of which have been isolated by us in pure crystalline form (Ref. 5), while on the other hand, it is not possible to obtain with the aid of such soluble catalysts, isotactic poly-α-olefins.

Progress in the field of α-olefin polymerization has been achieved in the sense of regulating molecular weights and their distribution. Besides the methods

TABLE I

Stereospecific Polymerization of Propylene
(Temperature 75°C; Propylene Pressure 2.8 at; Solvent n-Heptane)

Catalyst				
Metal-organic compounds		$TiCl_3$	Percentage of isotactic polymer*	$[\eta]$
mols		mols		
$Al(C_2H_5)_3$	6.2×10^{-3}	$.3.1 \times 10^{-3}$	84.5	2.9
$Be(C_2H_5)_2$	9.5×10^{-3}	3.2×10^{-3}	96.0	2.7
$Be(C_2H_5)_2$	5.4×10^{-3}	4.5×10^{-3}	92.8	3.4
$Be(C_2H_5)_2\,9.10^{-4} + Al(C_2H_5)_3 \cdot O(C_2H_5)_2$	4.2×10^{-3}	11.6×10^{-3}	96.0	2.5
$Be(C_2H_5)_2\,9.10^{-4} + Al(C_2H_5)_3 \cdot O(C_2H_5)_2$	4.2×10^{-3}	11.6×10^{-3}	94.5	2.9
$[(C_5H_5)_2\,TiAl(C_2H_5)_2]_2$	4.15×10^{-3}	3.7×10^{-3}	96.7	3.9

* As % of isotactic polypropylene we assume the % of polymer not extractable with boiling n-heptane.

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using hydrogen, many other processes have been found which are equally efficient, such as the one based on chain transfer with alkyl groups present in dissolved metal-organic compounds (Ref. 6).

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 that concentration) (Ref. 7). Kinetic studies (Ref. 8), which were first developed on the α-TiCl$_3$-Al(C$_2$H$_5$)$_3$ system, have been later extended to other systems. These studies allowed us to explain the mechanism of chain transfer and chain termination processes which regulate molecular weight (Ref. 9).

In the case, e.g., 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 practically independent from the monomer partial pressure when it is higher than 1 atmosphere (Ref. 10):

$$\overline{DP} = \frac{1}{K_1 + K_2\sqrt{C_{Alk}} + K_3\sqrt{P_{H2}}}$$

where C_{Alk} indicates the aluminum alkyl concentration and P_{H2} the hydrogen partial pressure.

The regulation of molecular weight is of remarkable importance in particular applications of poly-α-olefins, in which melt viscosity plays an important role, e.g. for applications in the textile field. The use of highly pure and highly crystalline TiCl$_3$, and of metal-organic compounds yielding scarcely dissociable complexes permitted to obtain directly by polymerization, crude propylene polymers of remarkable sterical purity, containing more than 95% of macromolecules insoluble in boiling heptane, which are mostly insoluble also in boiling n-octane (Ref. 11).

The nature of the metal-organic compound has a remarkable influence on the sterical purity of the polymerizate. The more firmly the metal-organic compound is associated with the crystalline phase, the higher the stereospecificity.

If several metal-organic compounds are present at the same time, stereospecificity is determined by the one which is more strongly associated. This allows, for instance, to maintain the high stereospecificity

TABLE II

Physical Properties of Highly Isotactic Unoriented Polypropylene:

$[\eta] = (2\text{-}2.5)$ 100 cm³/g

Specific gravity	0.915-0.920 g/cm³
Crystallinity (X-rays methods)	80-85%
Melting point (crystallographic microscope)	175-176°C
Yield strength, ASTM D 412	400-410 kg/cmq
Elongation at break, ASTM D 412	25-50%
Stiffness, ASTM D 747	15,000-16,000 kg/cmq
Hardness (Rockwell) ASTM D 785	R 110-115
Vicat softening point (5 kg load), DIN 57302	125-135°C

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which is observed when employing beryllium alkyls alone, even adding to small amounts of Be comopunds an excess of an Al-trialkyl-etherate (Ref. 12). Recently we have obtained high stereospecificities by replacing simple metal-organic compounds with other complexes which are chemisorbed by the surface of the transition metal compound (Ref. 13). (See Table I).

The analytical method already proposed by us in our earlier work (Ref. 2), according to which highly isotactic propylene polymers were isolated as residue after extraction of the crude with boiling heptane, was confirmed as valid in practice also from successive studies. In fact, a further fractionation, for instance by boiling octane, does not lead practically to remarkable variations in melting temperature, and yields fractions having different molecular weights but having, in practice, the same sterical purity (Ref. 14).

In Table II the properties of high isotactic polymers are listed. The crystallinity of highly isotactic polymers, M.P. 175-176°C, determined by X-rays, can reach in case the molecular weights are not too high, values of 80-85%.
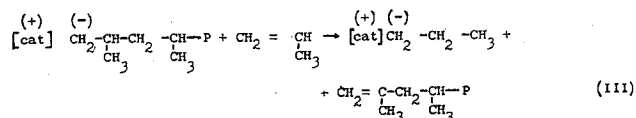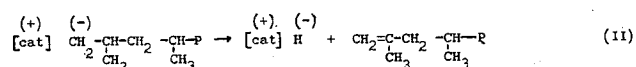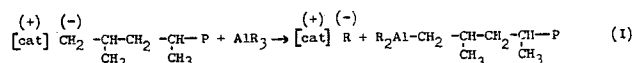
Analytical determinations made at Polytechnic Institute of Milan demonstrated that the polymeric chains obtained in the presence of aluminum-alkyls result mostly bound to aluminum, and this is because the most important processes limiting the molecular weight of the polymer, when operating at not too high temperature, are processes kinetically comparable to a chain trans-

TABLE III
Isotactic and Stereoblock Polypropylenes

Solubility		Melting Temperature	X-Ray Crystallinity	Irregularities*
Extractable with Boiling	**Non Extractable with Boiling**			
		°C	%	%
	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 units.
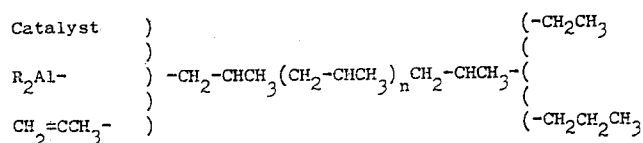
fer with the alkyl groups of the Al-alkyls in solution (I) and not the process of dissociation to hydride (II) and the chain transfer with the monomer (III). A great part of the chains remains therefore, during the whole polymerization, bound to the aluminum.

$$[\text{cat}] \ \overset{(+)}{CH_2} - \overset{(-)}{\underset{CH_3}{CH}} - CH_2 \ - \underset{CH_3}{CH} - P + AlR_3 \rightarrow [\text{cat}] \ \overset{(+)}{R} \ \overset{(-)}{+} R_2Al - CH_2 \ - \underset{CH_3}{CH} - CH_2 - \underset{CH_3}{CH} - P \qquad (I)$$

$$[\text{cat}] \ \overset{(+)}{CH_2} - \overset{(-)}{\underset{CH_3}{CH}} - CH_2 - \underset{CH_3}{CH} - P \rightarrow [\text{cat}] \ \overset{(+)}{H} \ \overset{(-)}{+} CH_2 = C - CH_2 - \underset{CH_3}{CH} - R \qquad (II)$$

$$[\text{cat}] \ \overset{(+)}{CH_2} - \overset{(-)}{\underset{CH_3}{CH}} - CH_2 - \underset{CH_3}{CH} - P + CH_2 = \underset{CH_3}{CH} \rightarrow [\text{cat}] CH_2 - CH_2 - CH_3 +$$
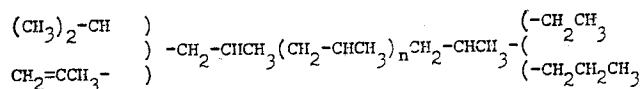$$\qquad \qquad + CH_2 = \underset{CH_3}{C} - CH_2 - \underset{CH_3}{CH} - P \qquad (III)$$

A characteristic feature of the polypropylenes, obtained with the aid of these catalysts after decomposition of the latter, 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 metalorganic compounds bound in the polymeric chains (Ref. 15).

In the polypropylenes produced with catalysts obtained from $TiCl_3 + Al(C_2H_5)_3$ the most frequent end groups are:

during the polymerization:

Catalyst $)$
R_2Al- $)$ $-CH_2-CHCH_3(CH_2-CHCH_3)_nCH_2-CHCH_3-$ $($ $-CH_2CH_3$
$CH_2=CCH_3-$ $)$ $($ $-CH_2CH_2CH_3$

and after decomposition of the catalyst with alcohol or water:

$(CH_3)_2-CH$ $)$
$CH_2=CCH_3-$ $)$ $-CH_2-CHCH_3(CH_2-CHCH_3)_nCH_2-CHCH_3-$ $($ $-CH_2CH_3$
$($ $-CH_2CH_2CH_3$

If the molecular weight is regulated employing a high alkyl concentration, or by means of hydrogen, the number of isopropyl end-groups in the total polymer increases.

If the catalytic complex is easily dissociable, with separation from the active center of compounds containing metal alkyls, the inversions of steric configuration in the polymeric chains are more frequent (Ref. 17). The stereoblock polymers possess properties quite different from those of highly isotactic polymers and of atactic polymers. The percentage of sterical irregularities of the different polypropylene fractions can be calculated on the basis of the heat of fusion (2600 cal/mol unit) (Ref. 16), recently determined in the Institute (See Table III).

To a decrease in crystallinity, deriving from an increase in the number of inversions, corresponds a decrease of the melting temperature, but no remarkable variations in the second order transition, which depends on the non-crystalline part. With an increasing crystallinity, the unfavorable effects exerted by the amorphous part on the dynamic characteristics at temperatures near 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 second order transition is presented by linear polyethylene.

Copolymerization leads to irregularities, which cause a reduction in crystallinity and in melting temperature, in a way quite similar to what happens for polymers containing sterical 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 (Ref. 18). While in random copolymers of α-olefins with ethylene crystallinity tends to disappear when the ethylene content is higher than 20% and less than 80%, quite different are the properties of heteroblock copolymers. The ethylene-propylene copolymers possess remarkable crystallinities even for ethylene contents which, in an ideal copolymer, would lead to a complete disappearance of crystallinity. The ethylene-propylene copolymers having long heteroblocks present not only a good crystallinity, but also better properties at low temperature and a temperature of complete melting only a few degrees lower than that of pure isotactic polypropylene (Ref. 19).
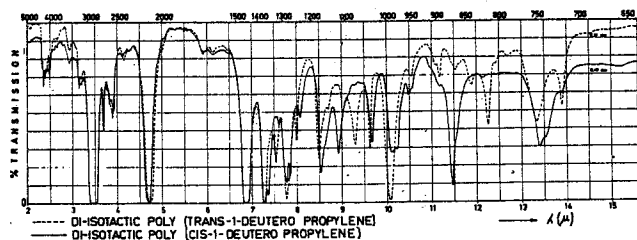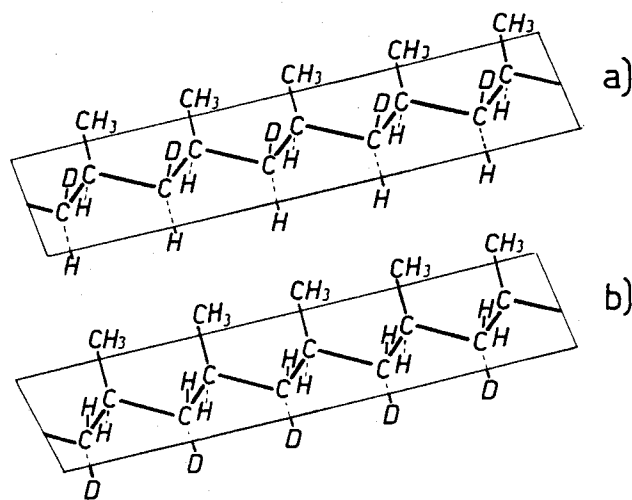
Figure 1.

a) IHREO POLY(I-DEUTERO PROPYLENE)   b) ERYTHRO POLY(I-DEUTERO PROPYLENE)

○ • C
○ • H
● • D

Figure 3.

DI - ISOTACTIC POLYMER

a) threo poly (1-deutero propylene)

b) erythro poly (1-deutero propylene)

Figure 2.

The use of polymers having a high sterical purity is particularly important in the fiber field.

Four years of research in the laboratory were accompanied in Italy by the gradual development of a series of pilot plants of increasing capacity. These will be followed, in a short time, by commercial production of 10-million lb./year of textile fibers, which will be easily doubled. Staple fibers of different types will be produced and high-tenacity continuous yarns. They will be produced in a plant of the Montecatini Co. at Terni, whereas polypropylene for use as a plastic material is produced at Ferrara.

The Italian Industry early recognized the importance and vastness of the new fields which were 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 other research centers which have shared the tasks connected with the study of the stereospecific polymerization of α-olefins and of other monomers, of the preparation of copolymers, of the properties of the polymers and of the nature of the catalytic complexes. Besides the scientific studies in the University Laboratories of Milan, Pisa and others, the Research Institutes of the Montecatini Co., particularly those of Ferrara, Terni and Novara, are studying the commercial development of the new processes.
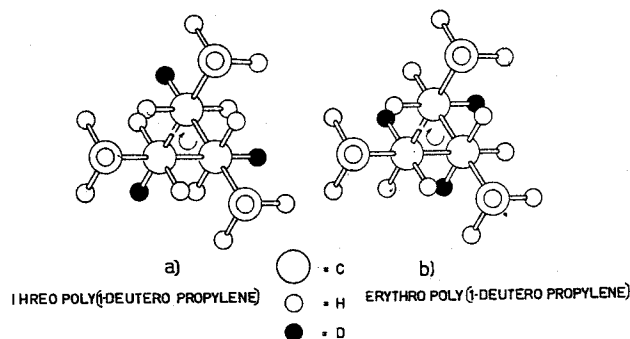
Optical Active Isotactic Polymers

Very interesting results from the scientific viewpoint, have been achieved by Professor 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 crystallinity than those 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-methyl-hexene-1, the optical activity is more than 100 times the optical activity 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 with results of scientific interest which will form the object of 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 are polymers having 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 (Ref. 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 from the attached drawings (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 occur in two different configurations. Suppose the chain stretched on a plane, we can, in the case of isotactic polymerization, have the two types of structure indicated in Fig. 2.

In Fig. 3 the projections of the spiral chains of the two stereoisomeric di-isotactic polymers, in the crystalline state, on a plane perpendicular to the c chain axis are represented. In Fig. 3 the left hand spiralized chains (up configuration) are represented; the right hand chains, which are also present in the crystals are different, being enantiomorphic (specular reflection).

In the projections shown in Fig. 3 the carbon atoms of the -CH⌐ groups are not visible, because they are covered (by the tertiary carbon atoms of the -CHCH₃ groups).

We propose the following nomenclature: "threo-di-isotactic" for the polymers of one of the two types indicated in Fig. 3, for which, suppose the chain stretched on a plane, all the substituting groups are on the same side of the plane; and "erytro-di-isotactic" for those in which one substituting group is on one side, while the other is on the other side. Both these isomers were isolated by us, as well as the mono-isotactic polymers obtained by random copolymerizantion of a mixture of the cis and trans isomers of the monomer.

of different crystallinity having dimensions greater than the wave length of light.

Research work recently performed at the Milan Polytechnic Institute, and the results of which are in press, have demonstrated that the crystallinity bands in the 2-15 microns field 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 ternary helix conformation of the macromolecule and not to the interactions between monomeric units of different chains.

Crystallinity of Isotactic Polymers

Isotacticity is a property depending only on the steric structure of the main chain and is not necessarily connected 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, having different lattice structure and low density (0.88). This modification presents approximately the same infrared spectrum, and shows a crystallinity which is only slightly lower than for 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 helical chain structure and the same identity period along the chain as the stable modification, but a different (random) packing of the enanthiomorphous chains in the tridimensional lattice (Ref. 21). This explains the possibility of obtaining from highly isotactic polypropylene, films which are more transparent 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
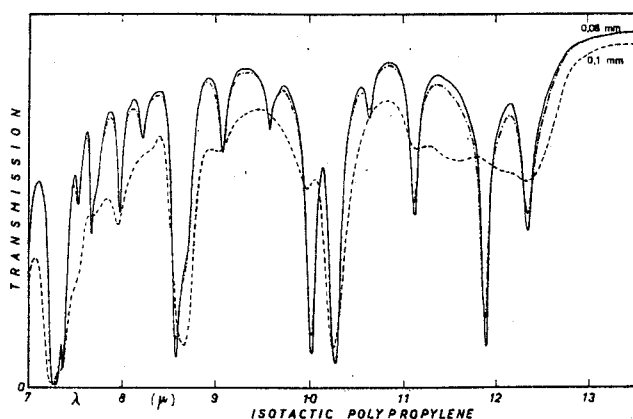

Figure 4.

POLYPROPYLENE

Isotactic Modification I

Isotactic Modification II

(CuKα)

Atactic

Figure 5.

TABLE IV
Isotactic, Crystalline Aromatic Polymers.

Monomer	Intrinsic Viscosity	Melting Point °C
styrene	3.5	240
o-methyl-styrene	—	>360
m- " "	3.9	215
2-4 dimethyl-styrene	3.5	310
2-5 " "	3.5	330
3-4 " "	3.2	240
3-5 " "	2.6	290
o-fluoro-styrene	2.3	270
p- " "	2.0	265
2-methyl-fluoro-styrene	—	>360
3-vinyl-naphtalene	2.3	360

Figure 6.

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 are crystalline by X-rays, but where different "isomorphous" (e.g. vicariable in the chain) monomeric units follow each other along the chain, the infrared bands of crystallinity disappear (Ref. 22).

The absence of a crystallinity, depending on the structure of the main chain, 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 to the crystallinity, according to the type of monomers employed and the operating conditions.

Monomeric units having shape and dimension only silghtly different from each other can vicariate along the chain in a quite similar way to what occurs 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 linear spiralized 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 spiralized chain. Phenomena of iso-dimorphism 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 monomeric units which is copolymerized, is small; 2. When copolymerization does not occur randomly, but forming long isotactic blocks.

The melting temperature of isotactic homopolymers depends, first of all, on steric factors and is not related with the melting point of the monomers. Branched olefins have melting temperatures lower than those of linear olefins having the same number of carbon atoms, but the isotactic polymers of many branched olefins
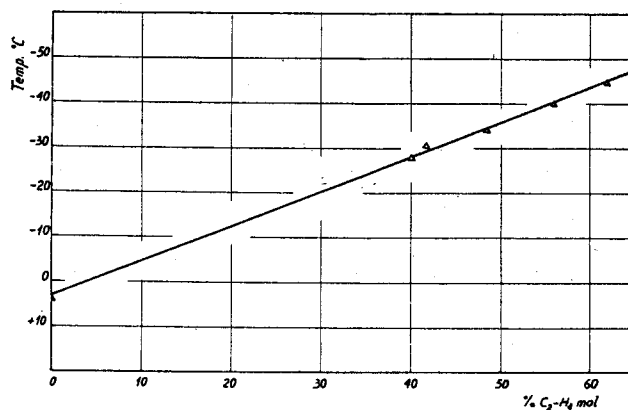
have melting points much higher than those of the corresponding linear olefins (Ref. 23).

A similar behavior is noted also with certain isotactic aromatic polymers (See Table IV). Isotactic polymers having high crystallinity were obtained also from certain aromatic monomers; some of these polymers possess the advantage, in respect of normal isotactic polystyrene, of a higher crystallinity and a higher crystallization rate (Ref. 24). Crystallinity in isotactic polymers is hindered in those cases in which the side chains are very mobile or when, even if not mobile, they present a bulk which does not permit of a good, compact packing, without large bond deformations or a too close approaching of the atoms to each other in contrast with Van der Waals distances.

It can be affirmed that in all cases in which hydrogen bridges or attractions of a chemical nature favoring the packing of chains are absent, a polymer cannot crystallize when the possible packings of the chains, taking into account the distances permitted by Van der Waals forces, 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 is why many isotactic polymers do not crystallize at all, or crystallize only with difficulty.

We must, however, distinguish between the impossibility to crystallize and the difficulty to crystallize. The latter can be due to sterical hindrances, such as interactions between the main chain and side groups. The difficulties encountered 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 sterical 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 behavior, as far as the second order transition is concerned. An atactic polymer possesses approximately the same second order transition as 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 monomers. This explains the variation of the mechanical properties of ethylene-propylene copolymers with composition. Fig. 6 shows the minimum rebound temperature of the random copolymers. This is the reason of the great interest presented in the field of elastomers by copolymers containing ethylene, presenting, as said, a very low second order transition.
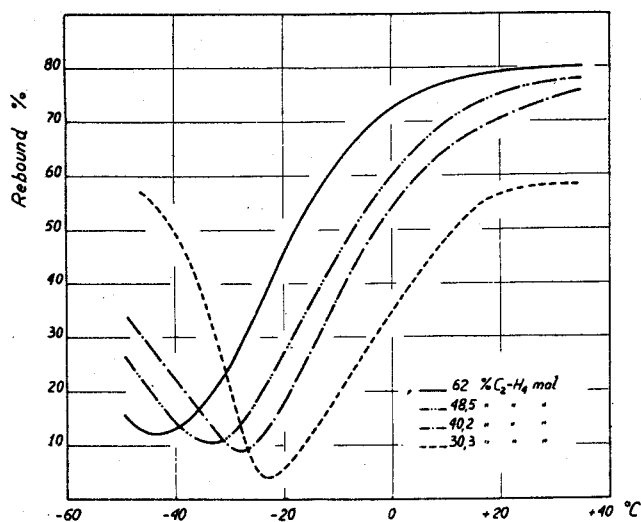
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Figure 7.

Fig. 7 shows the rebound properties of the random C_2—C_3 copolymers having different composition, as a function of temperature. It is important to note that when the copolymer obtained with the aid of highly stereospecific catalysts contains such a number of irregularities as to hinder crystallization, many of its properties (particularly the mechanical properties) are practically identical to 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.

When working with stereospecific catalysts, the monomer's reactivity ratios are nearer to each other and this is an advantage in the polymerization process, making it easier to obtain homogeneous copolymers (Ref. 25). (See Table V).

A characteristic feature of coordinated, anionic copolymerization, as well as of other ionic polymerizations, is the fact that the product of reactivity ratios presents a value of 1 or near 1. This has been verified also in the case of copolymerization of aromatic monomers (Ref. 26). (See Table VI).

Isotactic Polymers of Various Non-Hydrocarbon Monomers

The same catalysts which polymerize in a stereospecific way α-olefins, behave similarly with vinyl monomers containing silicon or tin in the side chain (Ref. 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 sterical orientation of the monomeric units is probably related with 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 constance in the type of opening of the double bond are related with a sterically univocal chemisorption of the monomer on an active center formed by an asymmetric metal-organic 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·CH₃

TABLE V

Ethylene and Propylene Reactivity Ratios in Copolymerization in the Presence of Catalysts Prepared from Trialkyl Aluminum and Different Transition Metal Halides.

Metal halide	$^rC_2H_4$	$^rC_3H_6$	$^rC_2H_4 \cdot {^rC_3H_6}$
VOCl₃	17.95	0.065	1.17
VCl₄	7.08	0.088	0.63
VCl₃	5.61	0.145	0.81
TiCl₄	33.36	0.032	1.07
TiCl₃	15.72	0.110	1.73
TiCl₂	15.72	0.110	1.73

TABLE VI

Reactivity Ratios of Some Vinyl Aromatic Monomers in Copolymerization in the Presence of Catalysts Prepared from TiCl₄ and Al(C₂H₅)₃

Monomers	r_1	r_2	$r_1 \cdot r_2$
styrene-p-methylstyrene	0.82	1.15	0.95
" m-methylstyrene	2.0	0.5	1.0
" p-ethylstyrene	1.0	1.0	1.0
" p-chlorostyrene	2.2	0.5	1.1

monomers, forming "di-isotactic" polymers, makes it possible to affirm 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·CH₃ groups, is determined. Quite different can be the behavior of monomers which, besides a vinyl double bond, contain another double bond conjugated with the first, or an atom having a lone electron pair able to associate itself chemically with the catalytic complex.

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 given by the other group or atom conjugated with the first (Ref. 28). These interactions impose a particular structure to the intermediate activated complex. This is why it is possible in these cases to have stereospecific polymerizations also with the aid of soluble catalysts.

In our early investigation we had obtained by homogeneous catalysis crystalline isotactic and syndiotactic polymers, with 1-2 enchainment, and atactic, amorphous polymers of diolefins (Ref. 29).

Recently, T. G. Fox and coworkers of the Rohm & Haas Co. have disclosed the preparation of isotactic and syndiotactic polymers of methacrylates, by means of anionic polymerization using soluble catalysts, formed by metal-organic compounds of lithium (Ref. 30). J. D. Stroupe and H. E. Hughes have established the structure of the isotactic polymers thus obtained (Ref. 31). Isotactic polymers of vinyl ethers were prepared by us (Ref. 28) with the aid of various soluble catalysts of a more or less cationic type, different from those initially used by Schildknecht (Ref. 32) (See Table VII). In many cases we obtained higher crystallinity.

The knowledge of these new types of stereospecific catalysts permits us to explain better the mechanism of stereospecific polymerization. In a preceding paper, I had defined as anionic, coordinated polymerization the one based on the use of catalysts formed by complexes in which metal-organic compounds of strongly electro-

positive metals and low-valence compounds of transition metals are contained (Ref. 33). In the United States there is a tendency to call this type of polymerization "coordinated," eliminating the term "anionic."

Such a simplification may lead to some misunderstandings, since there are processes of cationic polymerization which should be considered as coordinated, owing to the fact that the catalysts 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 put in relationship with 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 it presents, on the contrary, a positive polarity, the catalysis should be considered of the cationic, coordinated type.

The α-olefin polymers obtained in conditions in which a chain transfer with the monomer takes place, 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.

There are typically cationic complexes, such as those obtained from $AlCl_3$ or $TiCl_4$ and an alkyl-halide, and typically anionic complexes, 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 present intermediate properties. Some of those complexes show stereospecific properties. For instance, the $AlCl_3$-$Ti(Cp)_2Cl$ complex polymerizes vinyl ethers to crystalline polymers (Ref. 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 VIII). Complexes richer in alkyl groups do polymerize also α-olefins, if a suitable crystalline support is present.

Stereoisomeric Polymers of Diolefins

Our research work in the field of diolefin polymerization by catalysts containing aluminum metal-organic compounds began with a study of butadiene polymerization by means of a catalyst formed 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 enchained 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%) trans, 1-4 polymers (Ref. 35). Using catalysts formed by soluble complexes containing O, N, etc., we similarly obtained isotactic, syndiotactic, and atactic polymers having a 1-2 enchainment (Ref. 29).

We also succeeded in obtaining high yields of crystalline butadiene polymers having a high content of cis, 1-4 units. The metal-organic catalysts containing titanium, prepared by us in our early work, even if

TABLE VII

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, [η] in toluene at 30°C = 2.1
$Al(C_2H_5)Cl_2$	crystalline, substantially insoluble in boiling acetone, [η] in toluene at 30°C = 2.3
$AlBr_3$	almost completely amorphous, soluble in boiling acetone, [η] in toluene at 30°C = 0.9

TABLE VIII

Catalytic Activity of Dimetallic Complexes in the Polymerization of Ethylene and of Isobutyl-Vinyl-Ether.

Catalyst	Polymerization of isobutyl-vinyl-ether					Polymerization of ethylene			
	Mols of monomer Mols of catalyst	Temp.	Time	Yield	[η] in toluene at 30°C	Polymers 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%
** B = Crystalline polymer. Fraction insoluble in boiling acetone = 55%

TABLE IX

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 stress, 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-naphtylamine)	1

Cure: 145°C x 45 min.

TABLE X

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 stress, 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 x 45 min.

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. (Ref. 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 an 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, by means of fractional crystallization at −30 to −40°C. crystalline cis, 1-4 butadiene polymers, to establish their lattice structure and to observe their ability to crystallize, as does natural rubber, under stretch at room temperature or higher (Ref. 37).

Using catalysts of a particular type, containing only one type of active center, crude butadiene polymers having a cis, 1-4 content higher than 97% were obtained, both at the Donegani Institute of Novara and at Milan. The influence of steric purity on the properties is enormous (See Tables IX and X).

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 able to acquire high crystallinity under stretch. Cis, 1-4 highly pure polybutadiene is the product nearest to cis, 1-4 polyisoprene (i.e. to natural rubber) in elastic properties. One of the difficulties encountered in the use of polybutadiene was the fact 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 planned distribution of the molecular weights.

The infrared spectra of isotactic and syndiotactic 1, 2 and of trans-1, 4 polybutadienes are reported in Figs. 8, 9 and 10 respectively. We think it useful to report these infrared spectra here since, examining the literature, one sees that different coefficients have been used in the United States and in Europe to determine the
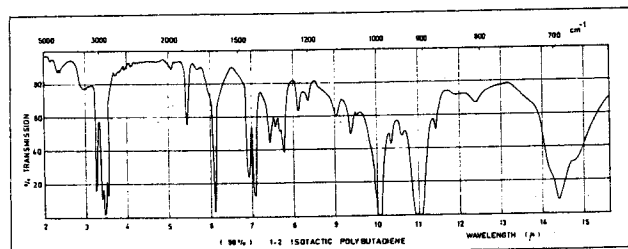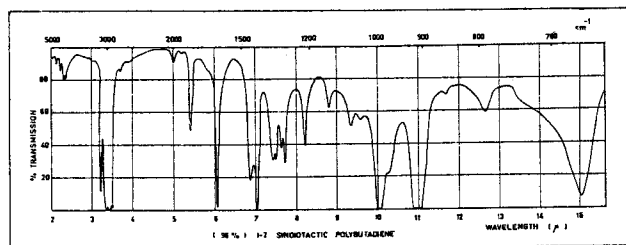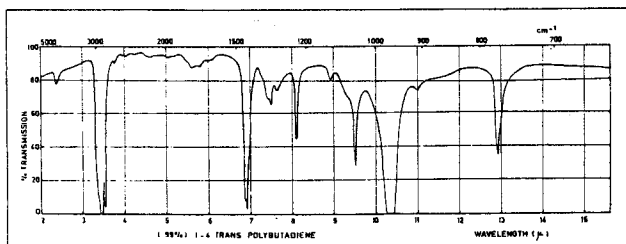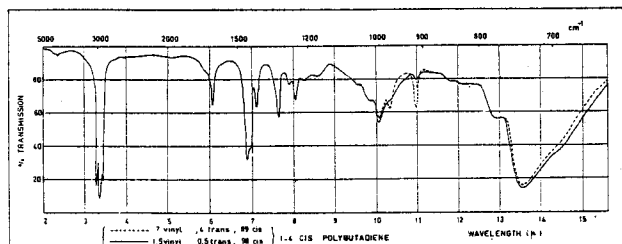

Figure 8.

Figure 9.

Figure 10.

Figure 11.

stereoisomeric purity of the polybutadienes by infrared methods. Thus, infrared spectra of butadiene polymers have been reported (Ref. 38), from which the authors have concluded to a *cis*, 1-4 content of 95%; when interpreting said spectra according to our coefficients, a *cis*, 1-4 content of only about 88% 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 maximum practical interest is shown by 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 resiliency even at low temperature.

The study of the polymerization of diolefins and of other monomers, with the production of crystalline polymers of different steric structure, demonstrates that the difference in properties between various polymers of different structure is due not only to the fact that they present crystallinity or not, but depends in a determining way on the specific type of steric structure.

In all cases where 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 necessary to establish the type of sterical regularity and its sterical purity.

The same polymer having a given sterical configuration and a given sterical purity, and which can be obtained in different crystalline modifications, can show different properties in dependence of 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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