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Properties of Isotactic, Atactic, and Stereoblock Homopolymers, Random and Block Copolymers of α-Olefins

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1. INTRODUCTION

In the paper submitted to the general section of this Symposium, I discussed the stereospecific polymerization of α-olefins. In particular, I examined the kinetics of the different chain-growth, chain-stop, and chain-transfer processes which determine the molecular weight of the polymers obtained in the presence of stereospecific catalysts. Such catalysts act through a mechanism which we have defined as coordinated anionic, and are more or less stereospecific according to their chemical composition, their physical state, and the different polymerization conditions.[1]

Our investigations on the nature of the catalysts and on the polymerization kinetics enabled us to produce an enormous variety of linear polymers, the properties of which differ among themselves to a remarkable extent, according to the type of the steric structure prevailing in the polymer. In the present paper I refer only to the different types of polymers obtainable by α-olefine polymerization and copolymerization.

The examination of polymers and copolymers of propylene suffices, by itself, to demonstrate the enormous variety of new products, now available to the macromolecular chemists, which include for instance, isotactic, atactic, and stereoblock homopolymers, random copolymers, block copolymers, and graft copolymers, which can all be obtained using the same monomers. I wish to emphasize that, until four years ago, no high polymer of propylene was known which had any practical interest.

2. MOLECULAR WEIGHT REGULATION IN THE ANIONIC COORDINATED POLYMERIZATION PROCESSES

The problem of the regulation of the average molecular weight in polymerization, without alteration of the stereoisomeric composition, is one of the most important problems, from the commercial point of view, in the polymerization of the α-olefins. In the case of isotactic polymers, excessively high molecular weights, corresponding to values of many hundreds of thousands, reduce the processability in the melted state and, in particular, hinder a high spinning speed in the production of textile fibers.

On the other hand, in the case of atactic polymers and of amorphous copolymers, the obtainment of very high molecular weights (over 100,000–200,000) appears necessary if one wishes to use the polymers for the production of elastic rubbers having high tensile strengths and low creep. The synthesis of crystalline, not-too-high molecular weight polymers and of amorphous high polymers requires particular working conditions, because, as a rule, the isotactic fractions, sterically purer, have relatively higher molecular weights, while the atactic fractions, obtained using similar polymerization conditions, show low molecular weights. We have thus been forced to elaborate the stereospecific processes to directly producing isotactic polymers with the desired not-too-high average molecular weight. Other processes have been developed to obtain atactic polymers having the highest possible average molecular weight. No data have been published before now on the different processes which have been used to this end in pilot plants as well as in commercial plants. In this paper I shall refer only to some processes of theoretical interest, since they lead to a better understanding of the nature of coordinated ionic catalysis.

Compounds containing bonds between carbon atoms and a different metallic or non-metallic atom, having a partial ionic character, are generally effective in lowering the molecular weight of the polymers, if they are able to transfer negative groups to the catalytic complex. The molecular weight, in particular, is lowered if one increases the concentration of a particular metal-alkyl in the polymerization medium. In the first paper of this Symposium I discussed the influence of the increase of aluminum

TABLE I

Lowering of the Molecular Weight of Isotactic Polypropylene in the Presence of Stopping on Transfer Agents

Reaction conditions: t = 70°C.; p = 1450 mm. Hg; α – $TiCl_3$ (containing traces of $TiCl_4$), 0.5 g.; $Al(C_2H_5)_3$, 1 ml.; polymerization time, 2½ hr.; solvent, 250 ml. *n*-heptane

Transfer agent		Polymer	Intrinsic viscosity of the ether insoluble polymer fraction	Polymer fraction		
Type	g.	Produced, g.	(II + III) (100 ml./g.)	I, extracted with boiling ether, %	II, extracted with boiling *n*-heptane, %	III, residual, %
—	—	15.7	3.05	14.8	5.5	79.7
HCl	0.12	12.5	1.68	20.5	10.0	69.5
$CH(C_6H_5)_3$	0.187	15.8	2.30	19.6	6.7	71.8
C_2H_5Br	0.10	8.8	2.15	22.8	6.7	70.5
$Zn(C_2H_5)_2$	0.12	16.5	1.43	12.4	8.8	79.0
$Zn(C_2H_5)_2$	0.38	17.0	1.15	15.0	8.3	75.8
$Zn(C_2H_5)_2$	0.9	16.2	0.69	12.5	11.5	76.0
$Zn(C_2H_5)_2$	1.40	16.8	0.59	12.6	11.2	76.5

alkyl concentration on molecular weight. The addition of other metal alkyls (*e.g.*, zinc) to the $Al(C_2H_5)_3$-$TiCl_3$ system does not influence the stereospecificity, but can exert an influence on the molecular weight by acting as an alkyl transfer agent (Table I).[2]

It has been possible to demonstrate that the molecular weight lowering is not due to a $TiCl_3$-$Zn(C_2H_5)_2$ catalytic system. In fact, the catalytic complexes containing zinc alkyls are less stable than the ones containing aluminum and show a very low stereospecificity. As is shown in Table I, the large decrease in the molecular weight is not accompanied by a corresponding decrease in the stereospecificity of the polymerization. Chain stopping and molecular weight reduction are shown by other compounds having a partial ionic character, such as the alkyl halides.

If, on the contrary, one adds traces of onium complexes to the normal catalytic system, there is no decrease but a slight increase in molecular weight (Table II). This fact can be explained by considering that in the dissociation of the oniom complexes no carbon ions are involed. The very high molecular weight of the amorphous α-olefin polymers obtained in the presence of oxygen-containing catalysts can be attributed to the formation of more stable complexes containing oxygen atoms chemisorbed on the surface of the solid support.[3]

According to the patent literature, a decrease of the molecular weight can be achieved by carrying out polymerization in the presence of hydro-

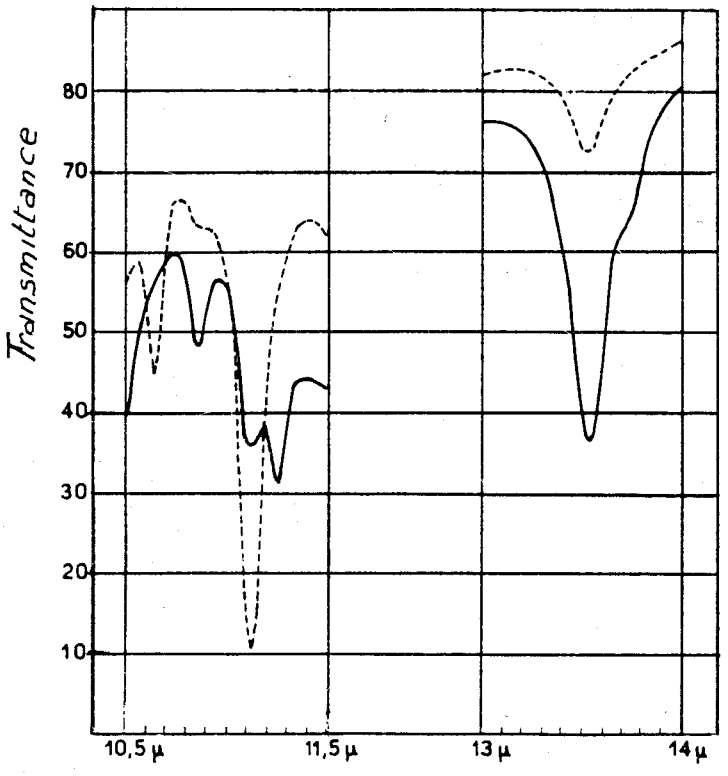

Fig. 1. Infrared spectra between 10.5 and 11.5 μ, and between 13 and 14 μ showing the vinylidene (11.27), isopropyl (10.88), and propyl (13.54) terminal groups of a low molecular weight amorphous (continuous line) and an isotactic (dotted line) polypropylene (m.p. 146°, viscosity MW <2000, crystallinity 70%) obtained in the presence of high hydrogen pressures.

TABLE II

Effect of Some Compounds Soluble Hydrocarbon on the Activity and Stereospecificity of α-$TiCl_3$ (containing traces of $TiCl_4$) in the Polymerization of Propylene
Reaction conditions: 70°C.; $P_{C_3H_6}$ = 1450 mm. Hg

$TiCl_3$, g.	$Al(C_2H_5)_3$, ml.	Polymerization time, min.	Solvent	Soluble compounds Type	Soluble compounds g.	Wt. of polymer, g.	Polymer fractions I, extracted with boiling ether, %	Polymer fractions II, extracted with boiling *n*-heptane, %	Polymer fractions III, residual, %	Intrinsic viscosity of the polymer fractions (II + III) (100 ml./g.)
0.5	1	150	*n*-Heptane	—	—	15.7	14.8	5.5	79.7	3.05
0.5	1	150	"	$(C_4H_9)_4.NI$	0.051	29.8	8.60	3.1	88.6	3.51
0.5	1	150	"	$Ti[O.CH(CH_3)_2]_4$	0.095	21.0	10.85	5.8	83.0	3.20
0.5	1	150	Benzene	$TiCl_2(C_5H_5)_2$	0.039	70.6	12.26	1.84	84.6	4.06
1.19	2	225	Toluene	—	—	8.0	13.8	4.5	81	3.38
1.19	2	225	"	$TiCl_2(C_5H_7O_2)_2$	0.31	10.8	13.0	5.2	82	3.75

gen, the decrease being dependent on the hydrogen partial pressure used. These processes are always accompanied by a certain decrease in the steric purity. We have attributed such a decrease of molecular weight to a process involving a heterolytic split of the hydrogen molecule, which is influenced by the nature of the metal alkyl, according to which a proton saturates the end of the growing polymeric chain and a hydride ion is attached to the catalyst, thus replacing the alkyl chain. Such a hydride ion, linked to the catalyst, reacts with propylene to form an alkyl group which can start a new polymeric chain. It follows that the polymers obtained are mainly saturated, and normal propyl terminal groups at one end (corresponding to the beginning of the chain), and isopropyl groups at the other end (corresponding to the termination of the chain). Such groups can be easily detected by infrared analysis (Fig. 1).

Under these conditions, the normal polymerization process is accompanied by a catalytic stepwise addition of α-olefin followed by an hydrogenation step:

$$mC_nH_{2n} + H_z \xrightarrow{[cat]^+H^-} C_{mn}H_{2mn+2}$$

which causes the production of saturated hydrocarbons.

By using different regulation factors it is now possible to obtain, at will, variable molecular weights within wide limits; for instance, it is possible, at very high H_2 pressure (50–150 atm.), to obtain highly crystalline low melting isotactic polymers soluble in ether and having an average molecular weight of about 1,000. High melting (175–176°C.) crystalline polymers, having a viscometric molecular weight between 30,000 and more than 500,000, can be obtained with different regulation agents.

3. INFLUENCE OF THE POLYMERIZATION CONDITIONS ON THE STERIC COMPOSITION OF THE POLYMERS

The properties of vinyl polymers depend, in a remarkable way, on their stereoisomeric composition. The first α-olefin polymers we obtained by coordinated anionic heterogeneous catalysis were complex mixtures of head-to-tail, linear polymers, containing isotactic and atactic molecules, as well as molecules which we found to be made up of stereoblocks, having intermediate properties between the isotactic and the atactic ones.[4] In Figure 2 the mechanical characteristics of isotactic, atactic, and stereoblock polymers of propylene are indicated.

Using well crystallized α (violet)-modification $TiCl_3$ and alkyl derivatives of highly electropositive metals having a very small radius, such as aluminum and beryllium, highly isotactic crude polymers have been produced.[3] The crude polymers contain more than 85%, and in some cases more than 95%, of polymer insoluble in boiling heptane, most of which is insoluble in boiling octane and has a melting temperature of 175°C. (Table III).

TABLE III

Fractionation by Boiling Solvents Extraction of Polypropylenes Obtained in the Presence of Different Catalysts at 70–80°C. and with a Constant Pressure of 2.4 Atm.

Catalyst	Acetone extractable fraction, %	Ether extractable fraction		Hexane extractable fraction				Heptane extractable fraction			
		%	[η]	%	[η]	Crystallinity, %	Melting point, °C.	%	[η]	Crystallinity, %	Melting point, °C.
$TiCl_4 + Al(C_2H_5)_3$	6.6	38.7	0.70	9.3	1.1	25	115	10.2	0.92	41	159
$TiCl_3 + Al(C_2H_5)_3$	1.50	6.5	0.42	4.0	0.52	32	125	3.3	0.65	52	159
$TiCl_3 + Be(C_2H_5)_3$	0.8	2.7	0.31	1.6	0.35	32	120	0.8	0.29	53	161

Catalyst	2-Ethyl hexane extractable fraction				*n*-Octane extractable fraction				Residue			
	%	[η]	Crystallinity, %	Melting point, °C.	%	[η]	Crystallinity, %	Melting point, °C.	%	[η]	Crystallinity, %	Melting point, °C.
$TiCl_4 + Al(C_2H_5)_3$	17.4	1.01	52	168	17.8	3.1	60	174	—	—	—	—
$TiCl_3 + Al(C_2H_5)_3$	18.0	0.90	62	170	16.20	1.3	64	175	50.5	3.0	66	175
$TiCl_3 + Be(C_2H_5)_3$	14.2	0.6	62	170	15.5	1.5	65	174	65	2.3	70	175

Polymers having a high steric purity, even if of comparatively low molecular weight, do not show viscous creep under prolonged loads at room temperature, being thus different from the crude polymers containing larger proportions of atactic and stereoblock polymers.

The most important factors influencing the formation of stereoblock polymers are the nature of the transition metal compound, its crystallinity, its ability to yield complexes with metallo-organic compounds, and the stability of the complexes produced. For instance, some vanadium compounds with a valence higher than 3 are more suitable than the titanium compounds to prepare poorly stereospecific catalysts. They give high yields of stereoblock polymers having very high molecular weight.

For each compound of a transition metal, the stereospecificity in polymerizing α-olefins depends on many factors, and particularly on the stability of the chemisorbed catalytic complexes. The stereospecificity is reduced by every factor which makes such complexes more easily desorbable or dissociable. The most important factors are: (*1*) An increase in the ionic radius of the metal linked to the metallo-organic compound[5]; (*2*) an increase in the length of the alkyls, having at least two carbon atoms, linked to the complex[6]; (*3*) an increase in temperature[7]; and (*4*) irregu-

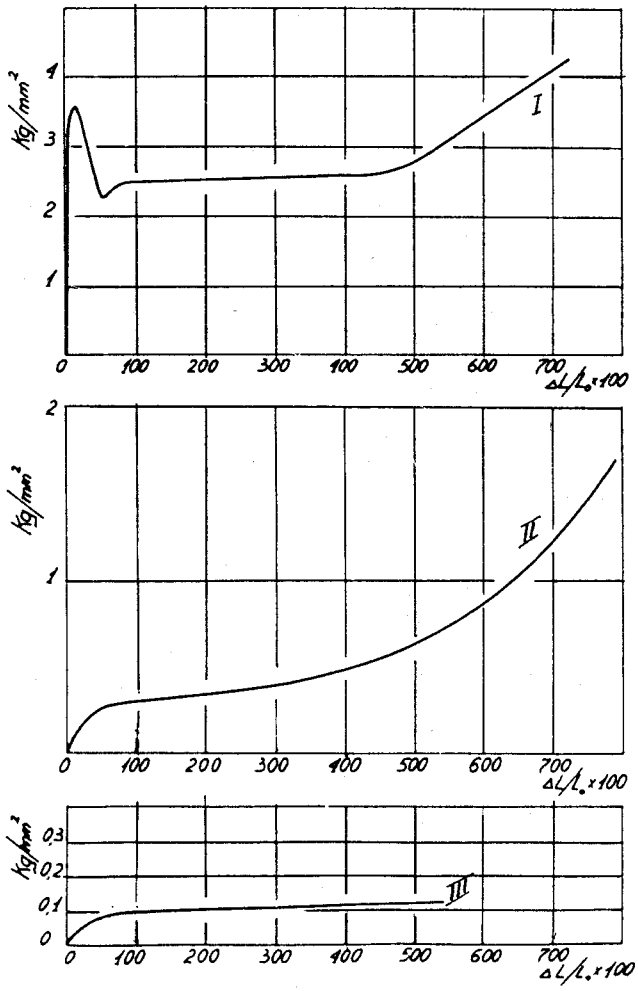

Fig. 2. Stress-strain curves of a highly isotactic (I), stereoblock (II), and atactic (III) propylene polymers.

larities and low cohesion force in the crystal lattice, which acts as a support to the chemisorbed catalytic complex.

Other factors reducing stereospecificity are connected with the exchange between compounds containing metal alkyls or components of non-chemisorbed complexes, also containing metal alkyls, with the corresponding components of the catalytically active chemisorbed complexes. Further, it has been observed that many factors which directly or indirectly influence the molecular weight (*e.g.*, ionic or ionizable compounds in solution, temperature) also have some influence on stereospecificity. It thus appears that the stereospecificity depends on different factors, but mainly on the nature of the catalytic complexes.

In general, increase of polymerization temperature reduces stereospecificity. The effect is reversible if the catalyst is used at a temperature which is much lower than the temperature at which the catalyst has been prepared. At higher temperatures the effect is generally not reversible, because an irreversible change of the chemical nature of the catalyst, containing transition metals, takes place. This effect depends on the chemical nature and in particular on the reducibility of the compound of the transition metal used, on the nature of the metallo-organic compound, and on the ratio between the different components used to prepare the catalysts. For instance an increase in the preparation temperature of the catalyst causes an increase in stereospecificity for catalysts prepared from $TiCl_4$ and a decrease for those prepared from $TiCl_3$. In the first case, an increase of temperature at which the catalyst is formed or employed causes the formation of a more highly crystalline precipitate (increase of stereospecificity). On the other hand, in the second case ($TiCl_3$), if the temperature is raised above 100°C., surface corrosion of the previously existing crystal occurs and results in a decrease of stereospecificity. In both cases the catalytic activity of the stereospecificity must be attributed to the formation of complexes containing transition metals and metallo-organic compounds which are chemisorbed on more or less crystalline solid phase.[6]

In some catalysts prepared at high temperature and thermally stabilized, one observes behavior which depends reversibly on the temperature, and reproducibility in experiments carried out at different temperatures at different times, provided the temperature is not allowed to exceed that at which the catalyst was stabilized. With such catalysts the stereoisomeric composition shows a regular variation which is almost linear with the temperature. This can be ascribed to the predominance of a single factor regulating both molecular weight and stereospecificity, most probably the dissociability of a chemisorbed complex.

A kinetic interpretation of the processes which regulate the stereoisomeric composition carried out on thermically stabilized catalysts allowed us to determine a very low activation energy corresponding to a process which causes an inversion in the steric configuration of the monomeric units in the growing chain.[7] The formation of stereoblock polymers de-

pends on the ratio between the growth rate and the rate of steric configuration inversion. The inversion rate is probably related to processes involving the dissociation and the reassociation processes in different active centers of the growing chains or of groups containing them. The rate of such dissociation processes also influences the molecular weight of the polymers, because other processes hindering the growth of the polymeric chains take place before the reassociation processes. To this cause can be attributed the diverse molecular weights of the different fractions of stereoblock polymers, simultaneously obtained and separated from the same crude polymer. The shorter the stereospecific blocks, the lower are

TABLE IV

Fractionation of Raw Polymers Obtained with Different Catalysts Prepared from Titanium Chlorides and Triethyl Aluminum at Temperatures from 35 to 90°C.

Fraction	Soluble in	Insoluble in	Crystallinity, %	Melting temperature, °C.	Irregularity, %[a]
I	—	Trichloroethylene	75–85	176	0
II	—	*n*-Octane	64–68	174–175	0.4–0.8
III	*n*-Octane	2-Ethyl hexane	60–66	174–175	0.4–0.8
IV	2-Ethyl hexane	*n*-Heptane	52–64	168–170	2.5–3.4
V	*n*-Heptane	*n*-Hexane	41–54	147–159	7.2–12.2
VI	*n*-Hexane	*n*-Pentane	25–37	110–135	17.3–27.8
VII	*n*-Pentane	Ethyl ether	15–27	106–114	26.1–29.5

[a] Supposing that ideal sterically pure crystalline polymer melts at 176°C.

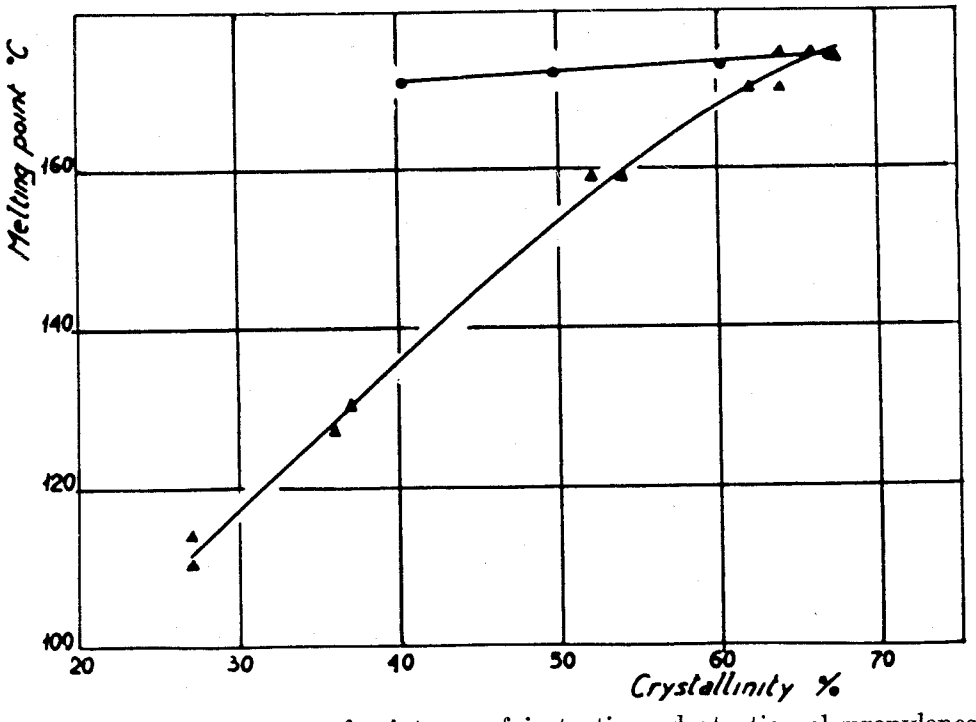

Fig. 3. Melting temperature of mixtures of isotactic and atactic polypropylenes (●) and of stereoblock polypropylenes (▲) having different crystallinity.

the crystallinity, the melting temperature, and also the molecular weight. On the same basis can be explained the even lower molecular weight of the amorphous fractions. These latter are produced by a different type of active center with a lower propagation rate and must be considered as very short stereoblock polymers, the formation of which is characterized by a low ratio between the propagation rate and the inversion rate.

Stereoblock polymers of propylene show a melting temperature and a crystallinity depending on the average lengths of the isotactic sections of

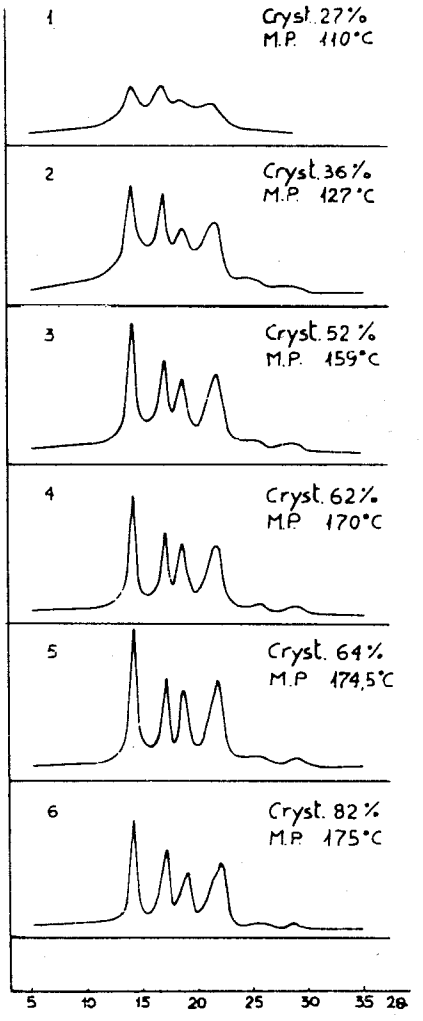

Fig. 4. Geiger counts of x-ray diffractions of stereoblock polypropylenes having different melting temperatures.

the chain. The theoretical decrease of the melting point was determined according to the Flory's theory for copolymers, assuming that the steric irregularities act like the irregularities due to the presence of different monomeric units (Table IV). In Figure 3 the lowering of crystallinity as a function of the melting temperature is shown for stereoblock polymers and for mechanical mixtures of isotactic and atactic high molecular weight polypropylenes.

Figure 4 shows the Geiger counts of x-ray spectra of stereoblock polymers, having increasing melting point, and of isotactic polymers.

4. PHYSICAL PROPERTIES OF STEREOBLOCK POLYMERS

The mechanical properties of stereoblock homopolymers confirm their characteristic structure. Very significant properties are observed on examining, in particular, block copolymers having 15–30% crystallinity (determined by x-rays). The stress-strain diagrams show that the initial elastic moduli are very low in comparison with those of highly isotactic polypropylene. The modulus increases with stretching. On the contrary, mixtures of amorphous and isotactic polymers, having the same crystallinity, show very rapid creep, even at a very low constant load.

The most interesting property of the block polymers is their high elasticity in the oriented state. The reversible elongation by stretching of

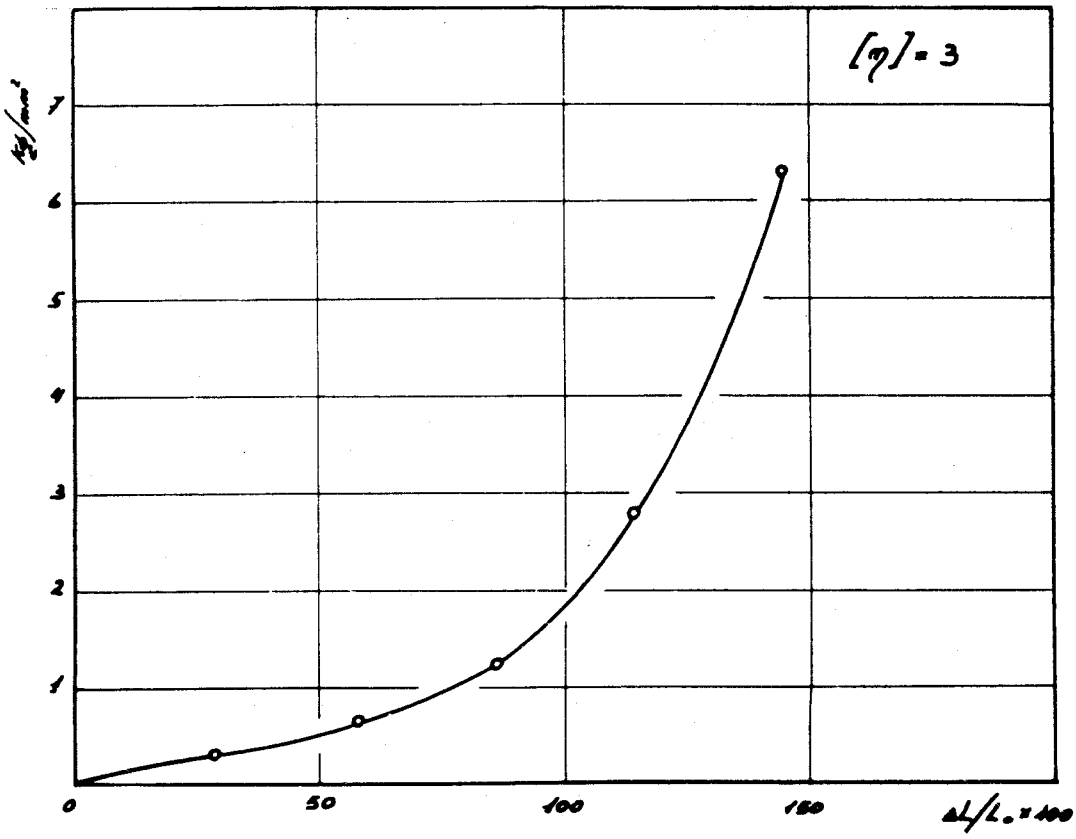

Fig. 5. Stress-strain curve of a stereoblock polypropylene (intrinsic viscosity 3) prestretched to 700%.

oriented block polymers, having a crystallinity of about 25%, reaches values between about 100% and 200% (for stereoblock having intrinsic viscosities between about 1 and 1.5).[4] From this point of view, certain oriented propylene stereoblock polymers may be considered true elastomers, as they fall within the definition normally accepted for such materials. Their elastomeric behavior becomes evident if one examines the stress-strain diagram of a stereoblock polymer previously oriented by 700% stretching (Fig. 5). The diagram shows that such polymers have initial low elastic modulus, reversible elongation, and relative high tensile strength. The creep diagram at constant load is very similar to that of a

vulcanized elastomer (Fig. 6). The creep is very small for products of very high molecular weight. This behavior can be attributed to the fact that in the oriented products the chains tend to dispose themselves parallel to the stretching direction, their isotactic sections being associated into crystals whose lattice energy opposes the flow of the chain. The crystallinity exerts an action similar to that observed in natural rubber when rapidly stretched. Its effect is similar to that of a thermolabile vulcanization.

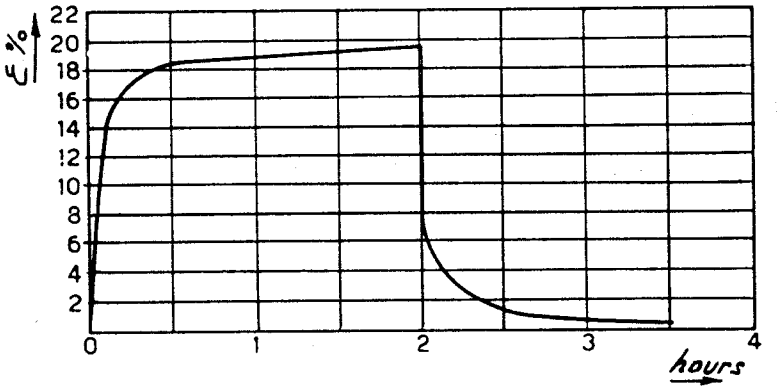

Fig. 6. Creep curve at constant load (10 kg./cm.^{2}) prolonged for 2 hours and successive recovery curve of a stereoblock polypropylene.

The stereoblock polymers having a higher crystallinity (40–50%) show higher initial elastic modulus, higher tensile strength, and in general, rather lower elastic elongation (in the order of 10–20%).

5. BLOCK COPOLYMERS: HETEROBLOCK POLYMERS OF α-OLEFINS

By alternating the introduction of different monomers in the reaction medium we succeeded in lengthening a growing polymeric chain with long successive homogeneous sections of monomeric units in the same macromolecule, obtaining block polymers of the type:

...AAAAAAABBBBBBBAAAAAAABBBBBBB...

In order to achieve this result, we operated with catalysts containing catalytic centers active for both monomers and at temperatures at which the average life of each macromolecule was sufficiently long.[8]

In operating at room temperature with highly stereospecific catalysts based on α-$TiCl_3$, we employed the following polymerization steps: (*1*) Polymerization of monomer A for a short time (τ'); (*2*) complete elimination of the unreacted monomer A from the system (*e.g.*, by evacuating or stripping with an inert gas); (*3*) introduction of monomer B and polymerization for a time τ''; and (*4*) complete elimination of unreacted monomer B.

These four steps can be repeated at will with the same or with different monomers. The average length of each block of monomeric units A (or B) depends on the time τ' (or τ'') and on the polymerization rate

r' (or r''). Equal length blocks can be obtained by adjusting the concentration of the monomers and the time in order to obtain $r'/r'' = \tau''/\tau'$.

The crude polymers obtained by successive polymerization of ethylene and propylene show, by x-ray examination, the presence of crystals, some of them having the structure of polyethylene, others having the structure of polypropylene. Fractionation enables us to separate the crude polymers into many fractions which possess different total crystallinity but about the same ratio of crystalline polyethylene content to crystalline polypropylene content.

In Table V 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 polymerizations and evacuation steps but operating with only one monomer). The melting temperatures of the polyethylene crystals and of the isotactic polypropylene crystals present in the heteroblock copolymers are lower than that of the pure homopolymer.

TABLE V

Comparison between the Fractionations of an Ethylene–Propylene Heteroblock Copolymer, Ethylene and Propylene Homopolymers Obtained with the Same Catalytic System [α-$TiCl_3$ + $Al(C_2H_5)_3$], and a Random Copolymer

Polymer	% by weight of fraction extractable with different boiling solvents			
	Ether	*n*-Heptane	*n*-Octane	Residual
Heteroblock copolymer, $C_2:C_3$ = 1:1 mole	0.9	17	30.5	51.6
Random copolymer, 1:1 mole	48.9	51.1	—	—
Polyethylene	Traces	4.6	65.0	30.4
Polypropylene	14.4	6.5	22.8	56.6

The study of block copolymers of α-olefins with more or less long sections of homopolymers with a regular structure is a new field of research showing some very interesting aspects from the theoretical and in particular from stereochemical viewpoints.

6. RANDOM COPOLYMERS OF α-OLEFINS

The properties of the random copolymers of α-olefins present some analogies with those of stereoblock homopolymers. Small quantities of a different monomer introduced into an isotactic polymer reduce its crystallinity and lower the melting point, as does the presence of sterically different units in stereoblock homopolymers. Larger quantities (*e.g.*, more than 20%) make the copolymers amorphous.

Although the physical properties of the α-olefin amorphous copolymers should be practically independent of the relative configurations of the

monomeric units when the sequences of each monomeric unit are very short, the production of random copolymers is made easier by using highly dispersed catalysts which, in the homopolymerization of α-olefins, yield mainly atactic homopolymers. While, as a rule, by using certain Ziegler-type catalysts one obtains products containing mixtures of macromolecules including homopolymers, and copolymers having a very large range of composition, the products obtained continuously, either with certain catalysts containing only one type of highly stereospecific active centers, or with no stereospecific catalysts (for instance, obtained from VCl_4 and triethyl aluminum), consist entirely of copolymers and are free from homopolymers.

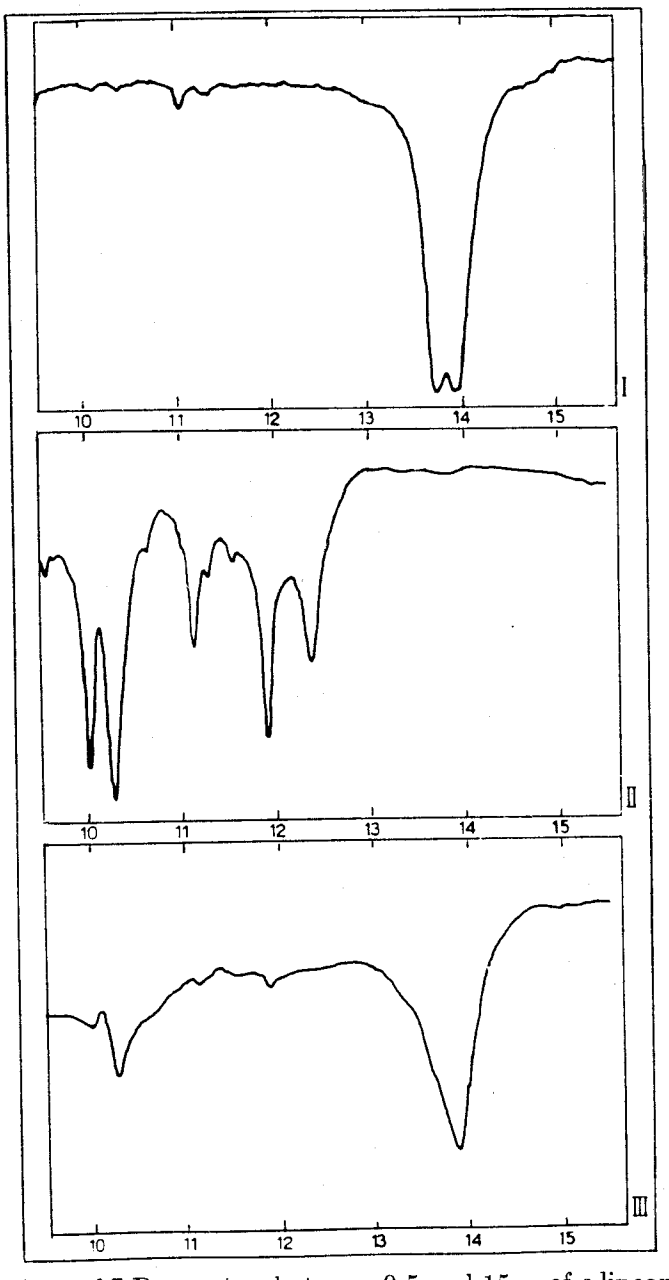

Fig. 7. Comparison of I.R. spectra, between 9.5 and 15 μ, of a linear polyethylene (I), of a fraction of polypropylene insoluble in ether but extractable in n-hexane (II), and of a corresponding fraction of ethylene–propylene copolymer containing 60 mole-% of ethylene (III). Thickness of the samples, 0.1 mm.

The above mentioned facts have been demonstrated by us by carrying out some accurate fractionations of the copolymerization products and examining the properties of different fractions.[9,10]

The amorphous copolymers of ethylene with propylene [obtained with VCl_4 and $Al(C_2H_5)_2$] are completely soluble in boiling *n*-heptane. On the contrary, the polyethylene obtained using the same catalyst is almost completely insoluble, and also polypropylene is partially insoluble in boiling *n*-heptane.

The infrared spectra of the copolymer fractions isolated by solvent extraction differ remarkably from the spectra of the corresponding fractions obtained from propylene homopolymers, from the spectrum of pure polyethylene, and from the spectra of their mechanical mixtures (Fig. 7). The infrared spectra of all the copolymer fractions show absorption bands between 13.4 and 13.8 μ. These can be attributed to the presence of sequences of methylene groups having different lengths.

X-ray examination also confirms the nature of the copolymers prepared by us. The fractions which can be isolated by ether extraction are amorphous, and the maximum diffraction intensity appears in the spectra at an angle which is different from the angles corresponding to the maximum of amorphous linear polypropylene and from the maxima which can be

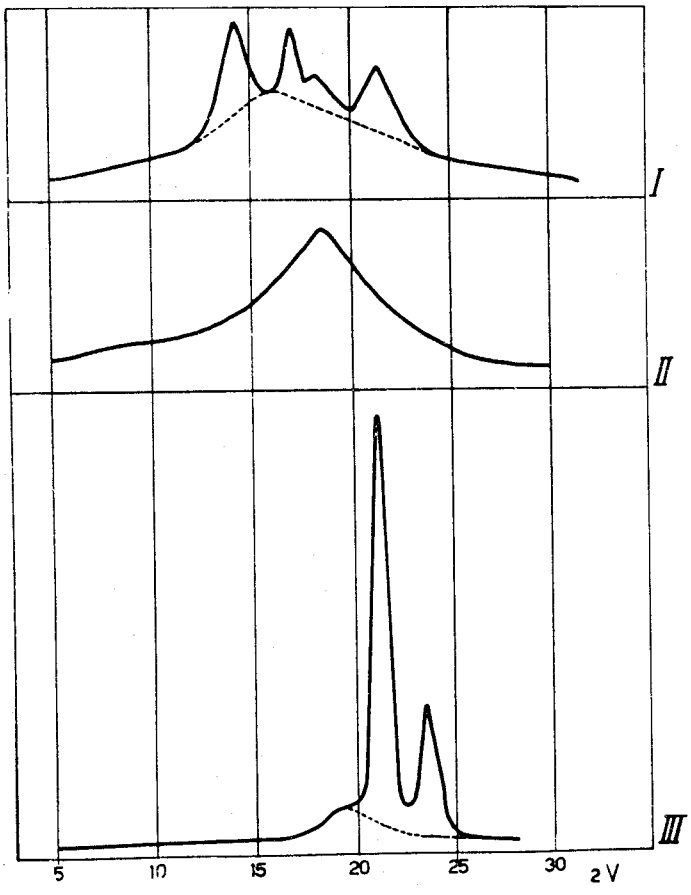

Fig. 8. Comparison of x-ray diffraction of a fraction of polypropylene insoluble in ether, but extractable with boiling hexane (I), with a corresponding fraction of ethylene–propylene copolymer containing 60% ethylene (II), and a linear polyethylene (III).

foreseen for an amorphous polyethylene and for the mixture of both the amorphous polymers. Also the fractions successively extractable by hexane and by boiling heptane prove, in general, amorphous to x-rays, contrary to the analogous fractions obtainable from the propylene homopolymers which show remarkable crystallinity (between 30 and 50%). As an example, we report in Figure 8 a comparison between the x-ray examination of a linear polyethylene, an ethylene–propylene copolymer fraction insoluble in ether but extractable by hexane, and a corresponding fraction obtained from pure polypropylene.

The mechanical properties of the copolymers prepared by us are different from those of the homopolymers and from those of their physical mixtures, and can be used as raw materials for the production of good elastomers.[9] Ethylene–propylene copolymers are made up of long linear hydrocarbon chains containing short sequences of methylene groups, having no tendency to crystallize when unstretched. The amorphous sequences of methylene groups confer a great mobility to the chain due to the low energy barrier contrasting small rotations of chain segments around the CH_2—CH_2 bond. The non-vulcanized polymers show, in fact, a viscoelastic behavior which is very similar to the polyhydrocarbon rubber having a low second-order transition temperature. They show low initial elastic moduli, high ultimate elongations, and low hardness. The temperature at which the resilience passes through a minimum is near to the one shown by natural rubber (Fig. 9).

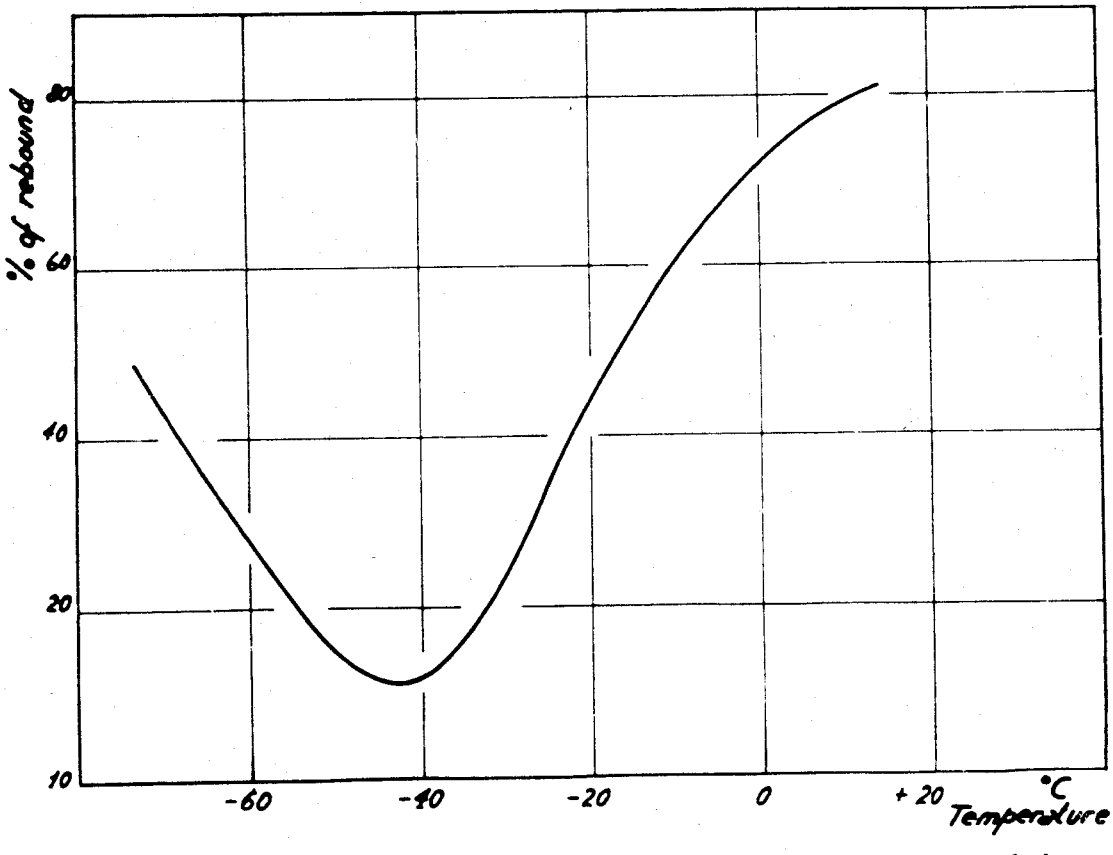

Fig. 9. Per cent rebound with Pirelli-pendulum *vs.* temperature for an ethylene–propylene copolymer.

The crosslinking of the ethylene–propylene copolymers can be suitably achieved by different methods and leads to vulcanized products having excellent chemical resistance, high tensile strength, and good elastic properties[11] (Fig. 10). They can be reinforced with active fillers, such as carbon-black or silica, and mixed with conventional plasticizers (Fig. 11).

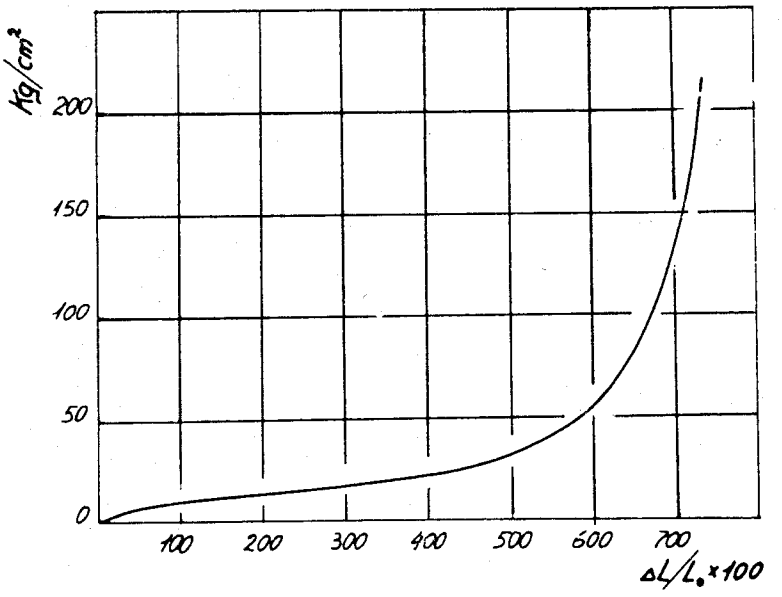

Fig. 10. Stress-strain curve of a vulcanized ethylene–propylene (1:1 mole) copolymer without reinforcing agents.

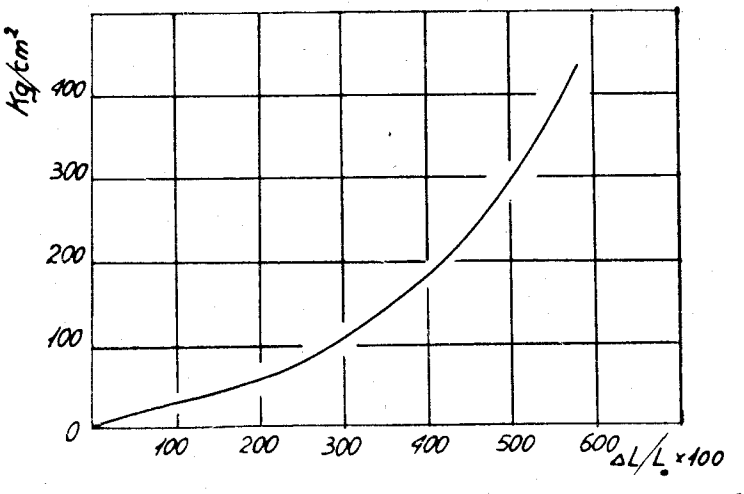

Fig. 11. Stress-strain curve of a vulcanized ethylene–propylene (1:1 mole) copolymer with 45 parts of EPC black.

A 50% propylene–50% ethylene copolymer having an intrinsic viscosity of about 4, reinforced with 45 parts of carbon-black shows, after vulcanization, a tensile strength of 300–400 kg./cm.^{2}, an ultimate elongation of 500–600%, a hardness of 60–70 degrees shore A, and a resilience, at room temperature, of 60–70%. In comparison with other elastomers, the ethylene–propylene copolymers, being substantially saturated, have a high resistance to oxidation and aging; furthermore, they resist quite well the attack of many chemical reagents such as sulfuric acid and nitric acid.

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Synopsis

The study of several methods of controlling the molecular weight in the stereospecific polymerization of α-olefins leads us to a better understanding of the nature of coordinated ionic catalysis. Some physical and chemical factors that influence the steric composition of polymers have been examined and a kinetic interpretation of stereoblock polymers is proposed. A continuous variation of physical properties, particularly of crystallinity, melting point, and densities, and mechanical properties is observed as functions of the length of the sterically homogeneous section in stereoblock polymers. This length is related to the number of steric irregularities of the chain. A new method to prepare block copolymers of different monomers is described; these copolymers show evidence of crystallinity due to long sequences of the same monomeric units, but properties different from those of physical mixtures of homopolymers and from those of random copolymers. The production of random copolymers has been examined, particularly of amorphous ethylene-propylene copolymers having interesting elastomeric properties.

Résumé

L'étude de diverses méthodes de mesure des poids moléculaires dans la polymérisation stéréospécifique des α-oléfines, nous a conduit à un meilleure compréhension de la nature de la catalyse par ion coordonné. On a examiné quelques facteurs physiques et chimiques qui influencent la composition stérique des polymères et on a avancé une interprétation cinétique de polymères a stéréoblocs. On constate une variation continue dans les propriétés physiques, particulièrement dans la cristallinité, le point de fusion, la densité et les propriétés mécaniques en fonction de la longueur de la section stériquement homogène dans les polymères à stéréoblocs. Cette longueur est liée au nombre d'irrégularités stériques de la chaîne. On décrit une nouvelle méthode pour préparer les copolymères à blocs de différents monomères. Ces copolymères présentent des caractéristiques cristallines en raison des longues séquences d'unités monomériques identiques mais présentent des propriétés différentes de celles de mélanges physiques d'homopolymères et de celles des copolymères statistiques. On a examiné la production de copolymères statistiques, particulièrement de copolymères amorphes éthylène-propylène ayant des propriétés intéressantes d'élastomères.

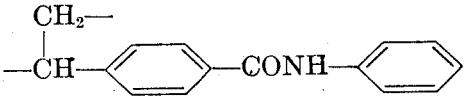
Zusammenfassung

Die Untersuchung mehrerer Methoden zur Kontrolle des Molekulargewichts bei der, stereospezifischen Polymerisation führte uns zu einem besseren Verständnis der Natur der ionischen koordinativen Katalyse. Einige physikalische und chemische Faktoren die den sterischen Aufbau der Polymeren beeinflussen, wurden untersucht und eine kinetische Deutung für die Stereoblockpolymeren wird vorgeschlagen. Eine kontinuierliche Änderung der physikalischen Eigenschaften, besonders der Kristallinität,

des Schmelzpunktes, der Dichte und der mechanischen Eigenschaften in Abhängigkeit von der Länge sterisch homogener Abschnitte wird bei den Stereoblockpolymeren beobachtet. Diese Länge wird zur Zahl der sterischen Unregelmässigkeiten in der Kette in Beziehung gebracht. Eine neue Methode zur Darstellung von Blockpolymeren wird beschrieben; diese Copolymeren weisen Anzeichen von Kristallinität als Folge der Anwesenheit langer Sequenzen des gleichen Monomeren auf; ihre Eigenschaften unterscheiden sich aber sowohl von denen einer physikalischen Mischung von Homopolymeren als auch von denen statistisch aufgebauter Copolymerer. Die Herstellung von statistisch aufgebauten Copolymeren, besonders von amorphen Äthylen-Propylen-copolymeren mit interessanten elastischen Eigenschaften, wurde untersucht.

Discussion

H. P. Frank (*Illinois Institute of Technology*): The solubility of any polymer depends on both molecular weight and structure. Accordingly, a fractionation procedure based on solubility will not clearly distinguish between these two factors. In order to carry out a systemic fractionation of essentially isotactic polypropylene the polymer was deposited on very finely dispersed Celite and fractions were extracted at increasing temperatures by a comparatively poor solvent such as α-chloronaphthalene or didecylphthalate. Complications due to crystallinity and crystallite size were minimized by the high extraction temperature (up to 160°). Fractions which are soluble at comparatively low temperatures represent polymeric material of comparatively high molecular weight and low crystallinity and could be considered as "stereoblocks." The results are not unlike those reported by Professor Natta in Table III. Inasmuch as it is only reasonable to assume that there exists a complete range of tacticity from entirely atactic to isotactic, we would prefer to consider these species as polymers of reduced tacticity rather than as block polymers. In order to establish a measure for the degree of tacticity in the case of polystyrene, it is possible to convert atactic and isotactic polystyrene into the corresponding polyvinyl benzanilide:



The hydrolysis kinetics of these polymers are being studied; distinct differences between the two species are observed. It is hopeful that this effect can be developed to serve as a suitable measure for the degree of tacticity.

G. Natta (*Milan*): The principal evidence of the existence of steric irregularities in the same macromolecule, which we call stereoblocks, is given by their melting temperatures, which are lower than those of the sterically pure isotactic polymer. A mixture of isotactic and atactic polymers shows completely different properties from those of the stereoblock polymers.

We consider as isotactic polymers those polymers which by further solvent extraction can be separated into fractions which differ only in molecular weight, but show practically the same melting temperature. From this point of view the polypropylene not extractable by boiling normal heptane can be considered as a substantially isotactic polymer [*Chim. e ind.*, **39**, 275 (1957)].

Recently (G. Natta and M. Pegozaro, *Ricerca sci.*, in press) we have refractionated a fraction of stereoblock polypropylene, obtained by solvent extraction. The refractionation was carried out by adsorbing the stereoblock polymer on highly crystalline high molecular weight polypropylene precipitated on a porous support. By elution with solvents, in which the highly crystalline polypropylene is insoluble, we obtained at first fractions of stereoblock polymers having lower crystallinity and higher molecular weight than the corresponding average values of the molecular weight and of crystallinity of the starting material. Later fractions had a higher crystallinity, but most of the fractions are constituted by macromolecules having not very different crystallinity but different molecular weight. The competitive effect of the molecular weight and of the crystallinity on the polymer solubility is important only in the case of fractions having low molecular weight.