

ISOTACTIC POLYMERS

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FIRST of all I would like to thank the Society of Chemical Industry, its Plastics and Polymer Group, and its London Section for inviting me to lecture on my work on isotactic polymers. It is a great honour for me to be asked to speak on crystalline poly- α -olefins in the country in which the first crystalline polymer of olefins—polyethylene—was discovered.

Other crystalline olefin polymers, belonging to the same family of ethylene, such as polypropylene and polybutylene, will shortly be produced commercially and will take their place beside polythene in large-scale industrial production. This is the fruit of a great deal of research carried out in my University laboratory with the help of one of the largest chemical combines of continental Europe, the Montecatini Company.¹

The subject being very vast, I will limit my lecture here to a short account of the new types of stereospecific catalysis which have permitted us to obtain new classes of stereoisomeric polymers: isotactic polymers, syndiotactic polymers and other new diolefin stereoisomers (for example, the four crystalline butadiene stereoisomers), and I will then describe some of the properties of these new polymers.

Before speaking of stereospecific catalysis, I would like to say a few words on the stereoisomerism in the field of macromolecules. The importance of the new processes lies in the possibility of obtaining macromolecules containing a given steric configuration, which are, in general, characterized by a high crystallinity. Before the discovery of stereospecific polymerization processes, only a relatively limited number of crystalline synthetic hydrocarbon polymers were known. Those obtained by polyaddition were derived from highly symmetric monomers, such as ethylene and vinylidene monomers (isobutylene).

All the synthetic polymers of α -olefins and of the vinyl monomers in general, and all the synthetic polymers of diolefins were generally amorphous. The lack of crystallinity depends on the random succession of their constituent units, having different steric structure.² Only the molecules of some typical natural polymers, and not those of vinyl polymers, correspond to an architectural model with a pre-determined steric arrangement.

To obtain crystalline polymers starting from vinyl monomers or from diolefins, the monomer units should be arranged regularly during polymerization into pre-established and not random configurations, and this was unobtainable synthetically before the discovery of stereoselective or stereospecific polymerization processes.

There are different types of stereoisomers in organic chemistry. The two best-known typical cases are:

geometric stereoisomerism, due to *cis* and *trans* configuration (for example, in compounds containing a double bond), optical stereoisomerism, generally due to the presence of carbon atoms which are linked to four different substituents. Both these cases are important in macromolecular chemistry.

A crystalline polymer can be obtained only when all the monomer units belonging to a long chain have the same configuration, or when opposing configurations follow one another in an orderly way. On the contrary, amorphous polymers are obtained when different configurations, for instance, *cis* and *trans*, or those "left" or "right", follow one another in a disorderly manner.

The new crystalline α -olefin polymers, which we have investigated, and the polypropylene oxides obtained by Price³ are examples of synthetic stereoisomeric polymers in which the crystallinity is due to

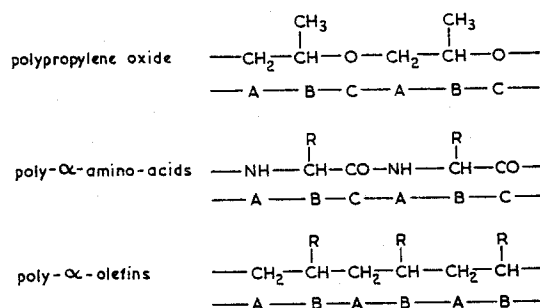


FIG. 1.—Polymers having asymmetric carbon atoms

the order assumed by the tertiary carbon atom configurations in the chain of each molecule. In the case of polypropylene oxide (Fig. 1) and in α -amino-acids condensation products, the tertiary carbon atoms are always asymmetric, even in the monomer before polymerization. In the case of poly- α -olefins, they become asymmetric only after polymerization, when the two parts of the chain on the sides of the tertiary atom have a different structure or length.

Fig. 2 illustrates molecules, supposedly placed on a plane, of α -olefin stereoisomeric polymers: the isotactic polymers in which the tertiary atoms show the same consequent steric configuration, syndiotactic polymers, in which each tertiary atom shows a steric configuration opposed to that of neighbouring atoms in the chain, atactic polymers in which the tertiary carbon atoms having different configurations are randomly distributed in the chain.

In the field of diolefin polymers other stereoisomeric phenomena of geometric nature appear. Natural polyisoprene stereoisomers with 1:4 linkage are

well known, and of these natural rubber has nearly a complete *cis* structure (97%); guttapercha, instead, is *trans*. Other new stereoisomers of diolefins with 1:2 linkage, not existing in nature, have been synthesized by us in the last few years.⁴

The polymerization processes previously used before, most of them using free radicals, are unable to produce chains having a regular steric structure. Only during the last three years have new processes, employing stereospecific catalysts, permitted us to produce different types of stereo-unitary polydiolefins, and also synthetic macromolecules having the same structure as natural rubber and guttapercha.⁵

In Fig. 3, pure polybutadiene isomers, with 1:4 *cis*, 1:4 *trans*, 1:2 isotactic and 1:2 syndiotactic linkages, which we have prepared synthetically in my laboratory, are shown. The lattice structure has been determined by us for the different stereoisomers.^{4, 6}

Isoprene could give, in theory, by polymerization, three types of linkage, namely 1:4, 1:2 and 3:4, each in different stereoisomeric forms. Six stereoisomers can have regular steric structure: two with 1:4 linkage, one *cis*, the other *trans*; two with 3:4 linkage, and two with 1:2 linkage, respectively isotactic and syndiotactic. Only the first two exist in nature. Besides that, two types of amorphous atactic stereoisomers (with 1:2 and 3:4 linkage) and the amorphous 1:4 stereoisomers with random *cis* and *trans* configurations are possible. The two stereoisomers which exist in nature, and others besides, have now been prepared synthetically.

The most interesting physical and technological properties of isotactic polymers of α -olefins in the field of plastics and textile fibres, and of some new stereoisomers of diolefins are due to the great linearity of the chain and to the crystallinity of these polymers.

Atactic stereoisomers of α -olefins cannot crystallize and are completely different in their properties. Their practical interest is limited to very high molecular weight products, giving a particular type of elastomer.

The properties connected with the crystallinity (such as the configuration of the chain in the crystalline state, the relative position of the chains in the crystals, the degree of freedom of rotation of lateral groups, the rate of crystallization, the size, the distribution and the orientation of the crystals, etc.) determine the most interesting technical characteristics of these polymers, namely hardness; the mechanical properties like modulus, ultimate tensile strength and elasticity; the range of the melting temperatures; the moulding properties; and the ability to give high tenacity fibres.

The crystalline structure will be described before discussing the technical properties of these isotactic polymers. Isotactic polypropylene, polystyrene, polybutene, etc., having asymmetric carbon atom sequences with the same configuration, present a characteristic structure. The principle that, in a crystal monomer, units of a macromolecule must have equivalent positions, referred to the axis of a chain, imposes a helical configuration on the main chain, as in some crystalline proteins. Polypropylene, for instance, has a helical structure with threefold symmetry,

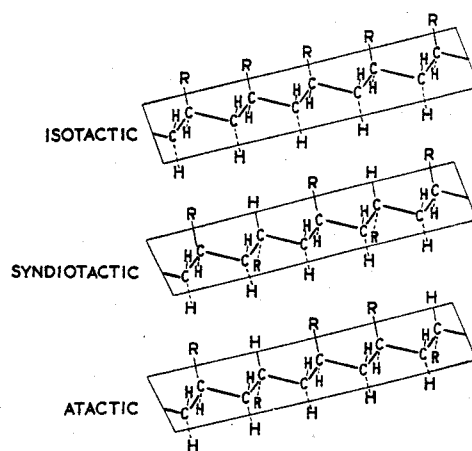


FIG. 2.—Poly- α -olefin stereoisomers

which respects the principle of staggered bonds.⁷ Polystyrene and the most stable modification of polybutene have an analogous structure, with a small deformation of the angle formed by the linkage of the principal chain (respectively 116° and 114°).⁸ Sometimes, steric obstacles may cause the main chain to assume other types of helix structure.

The helix of poly-3-methylbutene-1 has a fourfold symmetry and the helices of branched α -olefins in positions 4 have a sevenfold symmetry. Naturally, in most cases, the symmetry of the chain axis does not correspond to the crystallographic symmetry of the same axis.

The symmetry, the freedom of rotation, the mobility of the side chain and the steric hindrance have a great influence on the melting temperature of the polymers. Some polymers, having side isopropyl or isobutyl groups, such as poly-3-methylbutene-1 and poly-4:4-dimethylpentene-1, show very high melting points. Also polyorthomethylstyrene shows a very high melting point (over 300°C).⁹

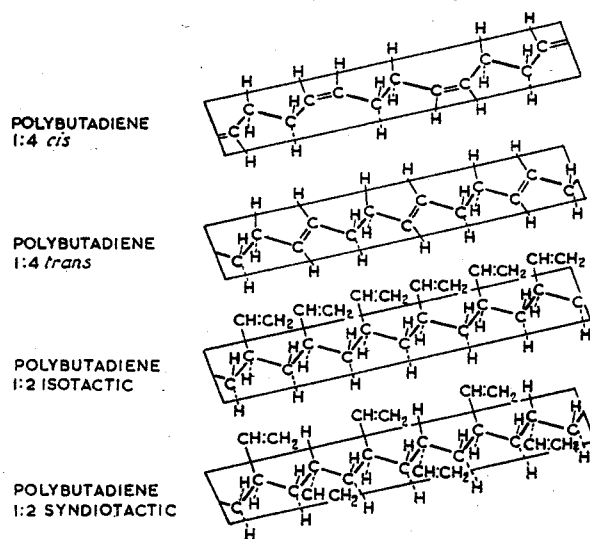


FIG. 3.—Polybutadiene isomers

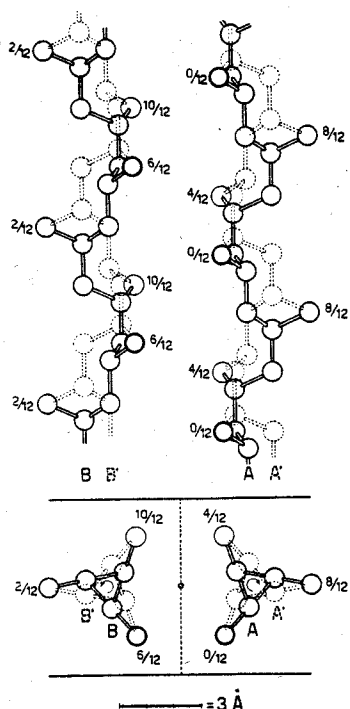


FIG. 4.—Arrangement of isotactic polypropylene chains in a crystal

In isotactic polymers the linkages of the lateral groups with the tertiary carbon atoms of the principal chain are always inclined relatively to the chain axis. In a part of an isotactic chain contained in a crystal all the bonds are inclined in the same sense (isoclined). We can have right-hand and left-hand helices; therefore when we consider the inclination of the lateral groups we find two types of congruent right-handed helices with opposite inclinations (anticlined helices), and two types of left-handed helices. All four types can be present in the crystals of synthetic polymers which contain racemic mixtures of macromolecules.⁷

In a crystal, two anticlined isomorphous chains occupy about the same space; we consider them capable of being substituted for one another and distributed at random in the same site. The symmetry of isotactic synthetic crystals (racemic) is in accord with a distribution of helices in such a way that each right helix is facing a left-handed one, and vice versa.

Figs. 4 and 5 show how two enantiomorphous chains of isotactic polypropylene and polybutene respectively are associated in a crystal.

Crystallinity of isotactic polymers

Crystallization rate depends on the viscosity of the system which increases with the molecular weight of the polymer. For high molecular weights it is very slow. Even if the crystals are very often smaller than the wavelength of light (in general some hundreds of Angström units), the presence of crystallites may, however, be demonstrated by optical methods, as they gather into spherulites, which sometimes are very large, up to a tenth of a millimetre or of the order of a millimetre (polybutene-1). Some very good photo-

graphs of spherulites have been taken at the Castellanza laboratories of the Montecatini Company. Fig. 6 shows polypropylene spherulites obtained by cooling the melted polymer. In Fig. 6A the same spherulites seen by polarized light are shown.

In certain cases, for example with polybutene-1, the spherulites can be of the order of hundreds and even thousands of microns. Fig. 7 shows part of a crystallite examined under the electron microscope in the Novara laboratories of the Montecatini Co.

In the case of polymers having a very low molecular weight it is possible to see crystalline aggregates under the microscope which confirm the symmetry previously seen by X-ray examination.

Isotactic polystyrene aggregates, with a molecular weight of about 10,000 can be seen in Fig. 8. Hexagonal lamellae are visible; when these are well oriented they do not seem to be birefringent under polarized light.

The formation of spherulites by crystallization of a solution in appropriate solvents is more evident. In this way polybutylene spherulites are very well developed. The presence of small quantities of amorphous products of low molecular weight, which reduce the viscosity of the raw polymer and occupy the intercrystalline spaces, facilitates the formation of large spherulites separated one from another and easily distinguishable under the microscope.

Stereospecific processes of catalysis

In these last few years a great deal of work has been done by us on stereospecific catalysis and a great number and variety of catalysts have been found that can be used to obtain given steric configurations in

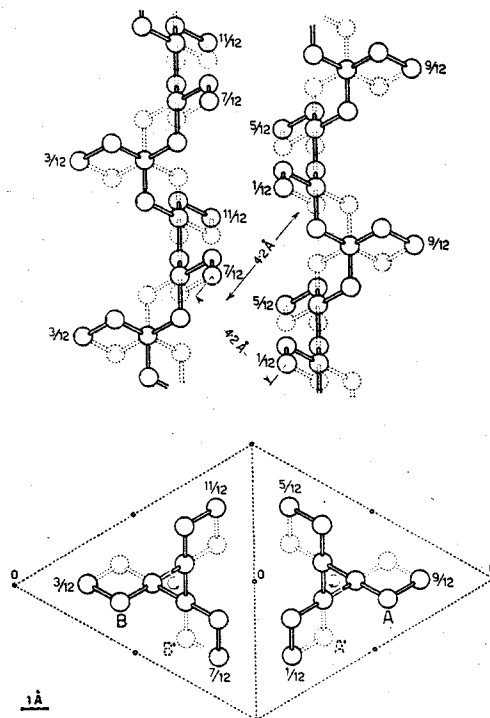


FIG. 5.—Arrangement of isotactic polybutene chains in a crystal

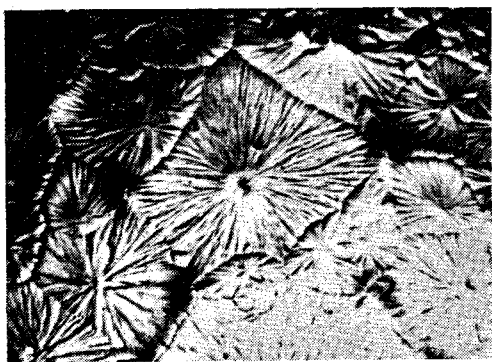


FIG. 6.—Polypropylene spherulites

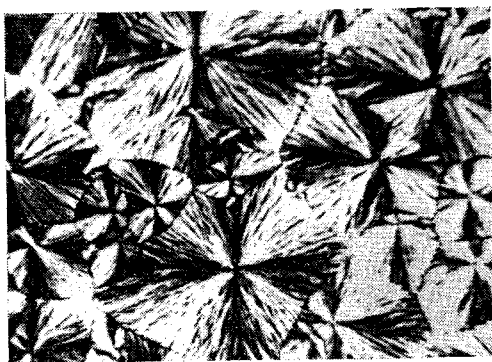


FIG. 6A.—Polypropylene spherulites viewed with polarized light

macromolecules of polyolefins. These catalysts contain compounds of strongly electropositive transition metals having valency inferior to maximum valency and act in the presence of organo-metallic compounds, preferably belonging to the first, second and third group of the periodic system. From the possible combinations of the various transition metals and metal-alkyl compounds which are also highly electropositive (lithium, beryllium, aluminium, magnesium, zinc, etc.) we can obtain a great number and variety of catalysts to which we attribute a polymerization mechanism of anionic type.¹⁰ These catalysts derive from the important research on organo-metallic compounds carried out by Prof. Ziegler.¹¹ The numerous catalysts described by Ziegler can be used in ethylene polymerization, but only a few of them, prepared under particular conditions, can be employed practically in polymerizing the higher α -olefins. In general, however, they are not really stereospecific, because they produce complex mixtures containing various stereoisomers, mostly atactic, and in certain cases a limited quantity of only partly crystallizable stereoisomers.¹²

Our research has not only established conditions for the polymerization of propylene and other α -olefins (styrene and other aromatic vinyl hydrocarbons) to high molecular weight linear polymers. We have also found really stereoselective catalysts for the production of highly isotactic polymers having high crystallinity, and other catalysts for the produc-

tion of completely atactic polymers, i.e. completely amorphous.¹³

It is interesting to observe that the completely amorphous products obtained by these new processes differ from the poly- α -olefins previously known. This is due to the fact that the new processes (even when not stereospecific) can produce high molecular weight polymers, which are completely linear head-to-tail, without long branchings.

In the case of ethylene, polymerization already takes place with aluminium alkyl or lithium alkyl alone, and the addition of small quantities of transition metal compounds, able to give complexes with the organo-metallic compound, causes very high polymers to form.

In order to obtain crystalline polymers from other α -olefins, it is necessary that an asymmetric metal-alkylic complex be part of the surface of a solid catalyst, able to impart a particular orientation to the reacting monomer units. The monomer inserts itself in the metal-alkylic link, polarized in the sense of an electropositive metallic cation and of an electro-negative carbon ion ($\bar{C}H_2$). Our recent research on a large class of monomers has enabled us to understand the nature of these complexes better and the cause of their catalytic activity.

One of the most interesting characteristics of some of the highly stereospecific polymerization processes is the simplicity of their kinetic mechanism. Some catalysts obtained from dichloride or trichloride of V, Ti, etc., are characterized by the presence of a crystalline support consisting of a stratified lattice in which metal atom layers alternate with chlorine atom layers. The fact that one plane of metal and two of chlorine follow one another along the axis in the crystals explains the easy cleavage of the crystals,

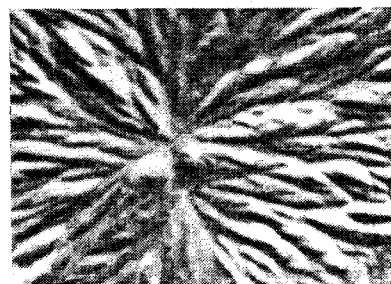


FIG. 7.—Electronmicrograph of part of a Spherulite of polybutene



FIG. 8.—Isotactic polystyrene aggregates

which takes place during polymerization as a result of the mechanical strains induced by the growing chains. These catalysts, after an initial settlement period, are characterized by a very regular type of kinetics. The catalytic activity remains constant for hundreds of hours provided that the polymer produced does not prevent the diffusion of the monomer on the surface of the catalyst.¹⁴

In some laboratory tests employing small quantities of catalyst in the presence of considerable quantities of solvents, thousands of grams of polymers were obtained for each gram of solid catalyst and polymerization ended only when the reaction vessel was completely filled by the polymer.

Figs. 9-12 show some curves of polymerization rate. The reaction rate is proportional to the partial pressure of the monomer, to the weight (and therefore to the surface of the solid catalyst) and it is independent of the concentration of metal-alkyl compound over a large concentration interval. The crystallinity of the polymer, its molecular weight, and therefore also the stereospecificity of the catalyst, are practically independent of the quantity of polymer produced if one excludes a brief initial period in which the molecular weight increases. The activation heat is about 12-15,000 Kcal.

The kinetics of polymerization using another type of freshly prepared TiCl_3 is given in Fig. 13. In

this case, during the settlement period the activity is higher.

The study of this and other catalysts obtained by changing the transition metal compounds and the organo-metallic compounds leads us to attribute to the polymerization an anionic mechanism based on the introduction of a molecule of a monomer through the polarized bond between a metal atom and the growing chain.

This conclusion was reached after a series of experiments which have shown us that:

1. The molecules of the polymer produced at first, contain a terminal group which was bound initially to the organo-metallic component of the catalyst.¹⁰
2. Using aluminium triphenyl as a catalyst, a phenyl end group is bound to a tertiary carbon atom of some polymer chain.
3. Using catalysts prepared from titanium dicyclopentadienyldiethyl and aluminium triphenyl in ethylene polymerization, we have observed the presence of phenyl groups in the polymer, whilst they are absent when the polymer is obtained from titanium dicyclopentadienyldiphenyl and aluminium triethyl. Therefore, we think that in the last cases mentioned the growing chain is bound to the aluminium and not to the transition metal.¹⁵
4. The unsaturated end groups are almost always merely vinylidene groups.¹⁰

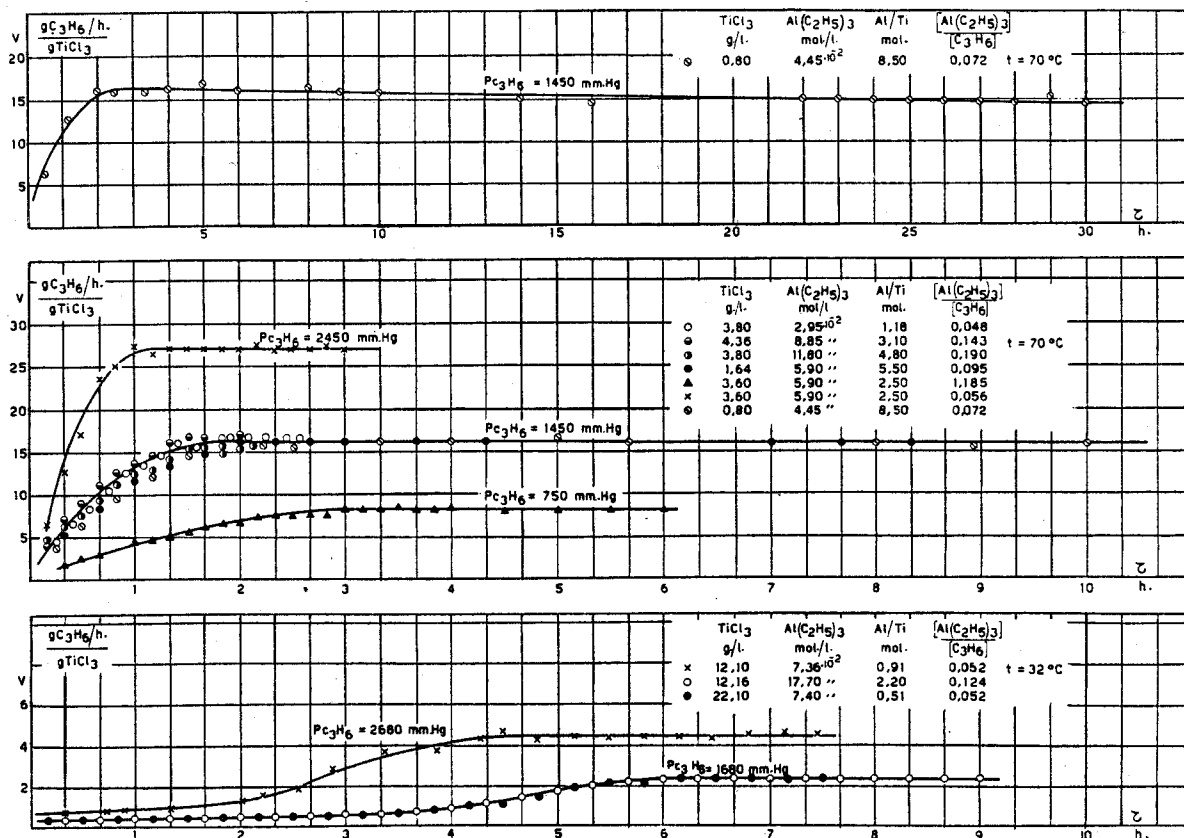


FIG. 9.—Rate of propylene polymerization versus time (in hours) for various monomer pressures and catalyst concentrations

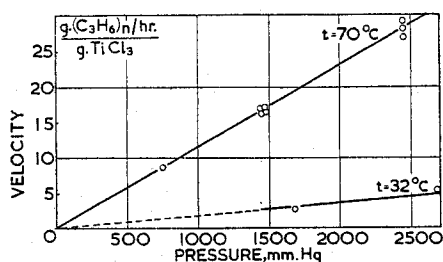


FIG. 10.—Rate of propylene polymerization versus monomer pressure—at two temperatures

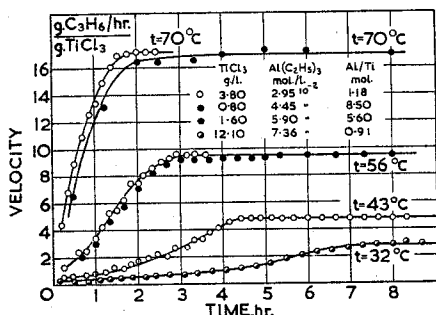


FIG. 11.—Rate of propylene polymerization versus time for various catalyst compositions and temperatures

This is in accord with the hypothesis that the reaction mechanism is of the anionic type. The molecule reacts as if it were polarized in the sense that the CH₂ carbon atom is negative and the CH carbon atom positive, and the said molecule settles between the electropositive aluminium atom belonging to a bimetallic complex and the growing chain in which the terminal CH₂ group, bound to the aluminium, is negatively polarized. The most active catalysts for the polymerization of α -olefins seem all to belong to this type.

One of the most important problems to solve was that of molecular weight control and it has been solved by means of several different methods. Hydrogen pressure reduces the molecular weight and produces saturated polymers.

One process based on the use of hydrogen was elaborated independently and nearly at the same time in America and in Italy—at least, so it would appear from the dates of the patent applications.¹⁶

Temperature has very little influence on the molecular weight at low temperatures, but its effect is greatly increased when over 100°C., at which stereospecificity is also reduced.

Molecular weight increases and stereospecificity decreases the higher the polarizability of the metal-alkyl link. The ability to give organo-metallic complexes of the type described is dependent on the presence of metal cations of small diameter. Catalysts acting with anionic mechanism and containing large diameter metals, for example alkali metals with atomic weight greater than that of lithium, characterized by atomic radius exceeding 1 Å., are not able to give stereospecific catalysts. Organo-metallic compounds of lithium, beryllium, aluminium, whose

metallic ions have a very small radius (less than 0.8 Å.) are best used for preparation of catalysts acting stereospecifically with anionic mechanism.

It is interesting to note that the only catalysts having a certain stereospecificity in vinyl ether polymerization and acting with cationic mechanism, are, according to Schildnecht, boron fluoride compounds, and these also contain small diameter atoms. We have been able to demonstrate that crystalline polymers obtained with these catalysts have isotactic structure.¹⁷

The processes controlling the molecular weight of polymers are of different types:

1. Dissociation into hydride ion and olefin with formation of vinylidene terminal groups.

2. A chain termination process of first order in regard to the concentration of the monomer, which may be considered to be like a chain transfer with monomer. This is the cause of propyl terminal groups in prolonged polymerization of propylene.

3. Chain exchange between dissolved organo-metallic compounds and catalytic complexes.

The first process predominates only at high temperatures.

The above mentioned mechanism does not explain the stereospecificity of catalysts. Catalysts acting in the above way can produce crystalline or amorphous polymers. The cause of the stereospecificity is not to be attributed to the chemical mechanism of polymerization, but to the monomer molecule orientation during polymerization.

One of our first observations in 1954 was that the catalysts obtained from crystalline compounds of transition metals, insoluble in the solvent used, produce crystalline polymers, while dispersed catalysts, not revealing crystallinity under X-rays, produce generally amorphous polymers.¹³ The concept of crystallinity

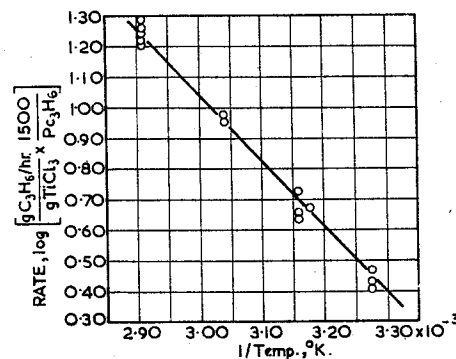


FIG. 12.—Arrhenius plot for propylene polymerization

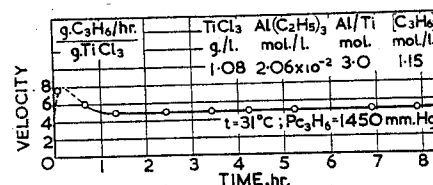


FIG. 13.—Rate of propylene polymerization versus time curve for catalyst showing high initial activity

must here be extended to the limit of X-ray or infrared sensitivity. X-ray examination in general allows perception of crystal dimensions of over 50 Å. Hexagonal titanium trichloride in crystals having a layer lattice and dimensions microscopically visible (from 1 to 10 microns) produces highly crystalline polymers. Titanium trichloride obtained by reducing one molecule of titanium tetrachloride with one molecule of aluminium triethyl is crystalline to X-rays, but not under the microscope and generally shows a different crystal structure. It is less stereoselective giving only 60% of insoluble polymers in boiling heptane.

The catalyst obtained by reducing titanium tetrachloride with a greater quantity of triethyl aluminium reveals lesser crystallinity under X-rays than the trichloride previously described. It is also less stereospecific, giving only 35 to 40% of polymers insoluble in boiling heptane.

Catalysts obtained from chloro-alkoxides are not crystalline, neither are they stereospecific in general.

Atactic polymers and block polymers

The new polymerization processes have allowed us to produce, using stereospecific catalysts, not only linear crystalline α -olefin polymers having congruent steric structure, but also, using non-stereospecific catalysts, amorphous polymers. These have also a linear main chain without long branching and can be obtained with very high molecular weights.

Perfectly linear aliphatic olefin polymers, having a molecular weight of some hundreds of thousands, were hitherto unknown except for vinylidene monomers. In fact, all the processes previously employed were unsuitable for the production of linear α -olefin polymers. Because of frequent chain transfers accompanying polymerization, these processes produced polymers having, in general, a low molecular weight or else long branched chains.

The comparison between the properties of amorphous α -olefin polymers in the aliphatic series, having a linear structure, which we call atactic, and those of crystalline isotactic polymers emphasizes the enormous influence that stereoisomeric phenomena exercise on the physical properties of macromolecular substances. The visco-elastic properties are more influenced than the others by the regular or irregular steric structure of the chains. So much so, that low molecular weight isotactic polymers, composed for example of some dozens of monomer units, are already high melting-point crystalline solids, whereas atactic polymers with the same molecular weight are still liquid. Their viscosity increases with the increase in molecular weight, and when the latter reaches values of some hundreds of thousands, they present the visco-elastic properties of non-vulcanized rubber. They can still be considered as highly viscous liquids, and can be transformed into true elastomers when cross-linkages prevent viscous flow.

High molecular weight polypropylene, polybutene and polyhexene can be made vulcanizable, for example by sulphochlorination, and then vulcanized using polyvalent bases. They furnish rubbers with

high reversible deformation values. In certain respects, their technical properties seem to be far superior to those of sulphochlorinated polyethylene. So much so, that the production of Hypalon (Du Pont), sulphochlorinated polyethylene, requires the introduction, in a disorderly manner, of considerable quantities of chlorine (25–40%) in order to destroy the original crystallinity and obtain elastomers. If, on the contrary, the starting material is an originally amorphous α -olefin polymer (propylene, *n*-butene etc.) it is not necessary to use great quantities of chlorine. A small quantity of sulphur, less than 1%, plus a small quantity of chlorine necessary for sulphochlorination, will be sufficient to transform the polymer into a vulcanizable material, and the latter into vulcanized products which generally have elastic properties which are superior, and densities which are inferior to those of sulphochlorinated polyethylene (Hypalon).

We have therefore found a category of saturated elastomers¹⁸ which have improved properties, even in respect of elastic hysteresis, over those of the known saturated rubbers obtained from vinylidene olefins (butyl rubber) or from Hypalon.

Besides crystalline isotactic and amorphous atactic polymers there is a range of intermediate products consisting of polymers the chains of which are composed of a succession of isotactic blocks, at the junctions of which inversions of the isotactic order take place.¹⁹

According to the frequency with which inversion of the isotactical order along the chain take place, the polymers show elastomeric properties to a greater or lesser extent.

In practice, low frequency of such inversions in the isotactic chain of very high molecular weight causes only a slight lowering of the melting point

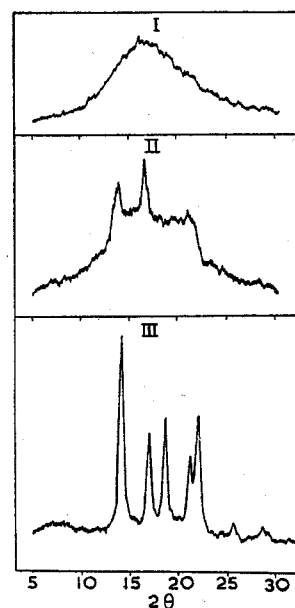


FIG. 14.—Geiger diagram comparing Amorphous (I), Crystalline (II) and a Stereoblock polymer (III)

and a small increase in elastic elongation, but the yield point and ultimate tensile strength are more or less the same. The properties of these polymers are not very different from those of completely isotactic polymers, when they have a sufficiently high molecular weight. In an analogous way, the presence of very small isotactic parts in an atactic chain does not alter appreciably the properties of the atactic polymer. New and interesting characteristics appear only if the isotactic blocks are of sufficient length, giving the stereoblock polymer the property of crystallizing partially. In Fig. 14, Geiger X-ray diagrams of amorphous and crystalline polymers are compared with a stereoblock polymer. In general, block polymers compared with crystalline polymers are characterized by higher solubility and by lower melting point, as can be foreseen theoretically.

The theories developed by various authors, and in particular by Prof. Flory, on the lowering of the melting point of a copolymer, due to the presence in the chain of chemically different monomer units, can be applied perfectly to the case of linear homopolymers, where structural irregularities are due to different steric configurations of chemically identical monomer units.

The fact that parts of the molecule are constituents of crystalline systems, gives to the oriented materials properties similar to those due to physical vulcanization, for instance, like those produced by the rapid stretching of natural rubber.

These block polymers, when pure (not vulcanized) and after stretching in a given direction, present a reversible elongation in the same direction of the value of 50-100% or more. Furthermore, they present ultimate tensile strengths which are superior to those of the most vulcanized rubbers.

In Fig. 15, curve I represents mechanical properties of a pure isotactic polypropylene, and curve II of an isotactic polymer containing a small number of stereoblocks; curves III and IV show polymers containing only stereoblocks and the last a high molecular weight amorphous polymer. The vulcanizing effect of crystallinity alone, found in block homopolymers, differs from that produced by chemical bonds in that it disappears when the material is heated beyond the melting point of the crystals and reappears when it is cooled and stretched.

Properties of mixtures of stereoisomers

It is possible to obtain widely different types of products from α -olefin polymerization, the properties of which depend on the quality and the quantity of the different stereoisomers present, that is on the percentage of crystallizable isotactic polymers, on the percentage of stereoblock polymers and on the type of blocks, on the percentage of atactic polymers, and on the distribution of the molecular weight of the various stereoisomers.

Hence it is possible to obtain a great variety of products. Those of most practical interest in the plastics field are the ones which are very rich in isotactic polymers and these, in turn, rich in very high molecular-weight blocks, but lacking in completely atactic low molecular-weight molecules.

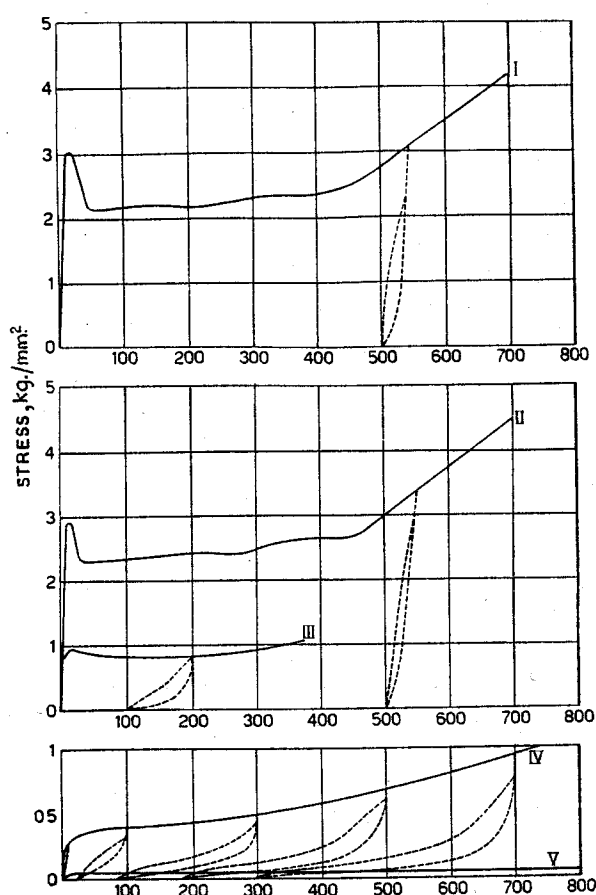


FIG. 15.—Stress-strain curves for Isotactic, Stereoblock and Amorphous polypropylenes (see text for identification of curves)

The simplest methods for the characterization of the different raw products are:

1. Crystallinity determined by means of X-rays or density measurements.
2. Contents of the three types of stereoisomers (isotactic, atactic, stereoblock-polymer) determined by extraction with solvents.
3. Average viscometric molecular weight of the different fractions.

Many physical properties (like density and melting point) vary slightly with the change of the molecular weight above a certain limit (over 50,000), but in the melted state the viscosity varies considerably thus influencing the use of particular processes for extrusion and injection.

Raw products with high molecular weight (80,000-200,000), good crystallinity (over 60%) and poor in completely atactic parts can be obtained directly by polymerization. These products have good mechanical properties differing slightly from pure steric polymers. The presence of a small quantity of block polymers with very high molecular weights increases the elastic elongation.

We give, in Tables I, II and III, data relating to the raw products obtained by polymerization and it is probable that they will correspond to the products

Table I

<i>Mechanical properties of polypropylene, polybutylene and other plastic films</i>						
	Polypropylene crystallinity: 60—65%	Polybutylene crystallinity: 40—50%	Rotene	Polyethylene Marlex 50 ¹	Fertene	Cellophane
<i>Tensile strength:</i>						
Machine direction p.s.i.	5000—6000	5000—6000	3500	3800	2800	4300—18,000
Transverse „ p.s.i.	4000—5000	4000—5000	3500	3400	2600	—
<i>Elongation:</i>						
Machine direction %	700—750	200—230	800	200	280	15—40
Transverse „ %	730—750	300—320	770	75	235	—
<i>Tear strength²</i>						
Machine direction g./mil	410—490	260—280	330	460	220	51—230
Transverse „ g./mil	360—410	260—280	290	450	190	—

¹ From "Properties of Marlex 50" presented before the division of Petroleum Chemistry—Dallas Meeting, April 8–13, 1956.

² A.S.T.M. D 1004—49 T.

which will be put on the market in the near future by Montecatini's Ferrara plant. We think that, at the beginning, the greatest practical interest will be focussed on the cheaper types of product, on those which, in raw and unfractionated state, already have technically satisfactory characteristics for many practical uses.

Wide applications of the new crystalline polymers are expected in the field of textile fibres. Before the discovery of the new isotactic polymers, it was believed that the presence of macromolecules containing groups capable of association was necessary to prevent viscous flow and to obtain textile fibres with good mechanical properties. The high resistance to traction of nylon is attributed to association forces due to the hydrogen bonds. In other cases, where no such bonds exist, the associative forces between chains are attributed to the presence of polar groups (e.g. Orlon and Terylene). The discovery of isotactic polymers showed us that it is possible to obtain high-tenacity synthetic fibres, corresponding to the best yet known, from polyolefin lacking hydrogen links and without polar groups. It is essential, however, that the polymers have a perfectly linear structure and a very high molecular weight, for example of about 40,000–50,000 for polypropylene, which corresponds to about 1000 monomer units.

It is interesting to observe that polypropylene fibres have tensile strength and elasticity far superior to that of the new best types of linear polythenes. In practice, it is easy to obtain isotactic polypropylene fibres having a breaking point of 5 to 8 g./den. and very high reversible elongation.

Polypropylene fibres have the lowest known density (0.91–0.92). They can be dry-spun without the use of solvents or plasticizers, like nylon. The low melting point (175° for completely isotactic polymers and generally 165–170° for raw polymers) facilitates spinning. Polypropylene fibres have very good electrical and thermal insulating properties, and excellent mechanical characteristics—in particular, outstanding capacity for absorbing elastically high quantities of deformation energy. Furthermore the raw material—propylene—is available in practically unlimited quantities and is very cheap. At present no other monomer can be obtained at a cheaper price (about 3 cents per pound in U.S.A.). Polymerization gives very high yields, especially when the monomer is in a very pure state. The raw product, after the removal of traces of the catalyst, can be woven directly.

In Table IV the main mechanical properties of polypropylene fibres are illustrated, and in Fig. 16 these are compared with other synthetic fibres.

Diolefin stereoisomeric polymers

A field, in which stereospecific polymerization processes present a particular interest, is that of the simple aliphatic diolefin polymers. The most interesting properties of diolefin polymers, from a practical point of view, are their viscoelastic characteristics which are related to the stereoisomeric structure of the chain of the polymer.

In the natural state there are two polymers of isoprene with a definite steric structure, namely, guttapercha and Hevea rubber. All synthetic poly-

Table II

<i>Physical properties of polypropylene and other thermoplastic materials</i>					
	Polypropylene crystallinity: 60%	low pressure Rotene	Polyethylene low pressure Rotene L	low pressure Marlex ¹	high pressure Fertene 7
Density at 20°C.	0.90–0.91	0.94	0.96–0.97	0.96	0.92
Melting point °F.	330–340	270–278	273–280	275	225–234
Yield strength p.s.i.	5150–5720	3140	4000–4430	3860	1500
Elongation %	100–600	700	650–850	400	400
Stiffness p.s.i.	117,000–143,000	57,000–86,000	100,000–110,000	129,000	24,500
Hardness Brinell p.s.i.	21,500–28,000	10,800	—	—	6800
<i>Vicat, softening point</i>					
(load 5 kg.) °F.	210–234	178–190	201–208	—	—
(load 1 kg.) °F.	—	255–262	271–280	—	197

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mers produced before the year 1953 by diolefin polymerization had disorderly and irregular structures due to the presence of 1:4 linkage with both *cis*- and *trans*-double bond configurations and of 1:2 linkage with the two possible configurations of tertiary carbon atoms. These structural irregularities are the principal cause of the poorer properties of the old synthetic rubber. Practically all types of synthetic rubber obtained from hydrocarbons before 1953 show inferior mechanical properties and, particularly, too high elastic hysteresis.

By the addition of considerable quantities of finely dispersed substances, in particular carbon black, hardness and tensile strength are improved but elastic hysteresis impaired. In the case of pneumatic tyres the old types of synthetic rubber absorb irreversibly a great part of the deformation energy. Because of this they heat excessively during use and therefore they are not suitable for very thick tyres.

The application of stereospecific processes has allowed us to obtain the two butadiene stereoisomeric

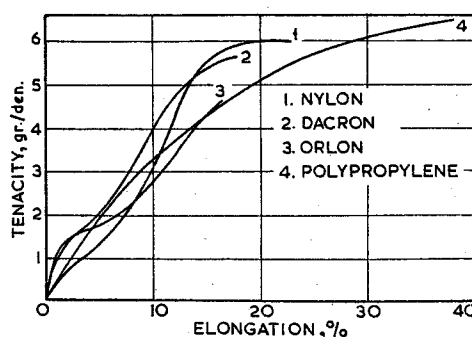


FIG. 16.—Stress-strain curves for synthetic fibres

For a number of the new polymers we have determined the crystal structure and chain configuration. The 1:2 isotactic butadiene polymer has, in the crystalline state, a helicoidal chain structure like other isotactic polymers. It can be regarded practically as a vinyl polymer, as the double bonds left after

Table III

Physical properties of isotactic polymers

	Polypropylene			Polybutylene-1	
	2.66	5.25	1.84	1.12	2.64
Intrinsic viscosity ¹ 10 ² cm. ³ /g.					
Residue from:					
<i>n</i> -heptane extr. %	89	91	100	—	—
ethyl ether „ %	—	—	—	72	91
Yield strength p.s.i.	5150	5400	5700	—	—
Ultimate tensile strength p.s.i.	5500	5850	5700	2150	5200
Elongation at break %	320	670	100	165	320
Stiffness p.s.i.	121,000	117,000	143,000	18,500	24,000
Hardness, Brinell p.s.i. ²	27,000	22,000	28,000	—	—
„ Shore “A”	—	—	—	95	97
Vicat softening point					
(load 1 kg.) °F.	—	—	—	212	265
(load 5 kg.) °F.	210	210	235	—	—

¹ In tetrahydronaphthalene at 135°C.

² D $\frac{1}{2}$ in., 1 min., 70 lbs.

polymers with 1:4 linkage (*cis* and *trans*) and the stereoisomers with 1:2 linkage (isotactic and syndiotactic) in the crystalline state and also the 1:4 and 1:2 amorphous polymers.^{4,5,6} Each crystalline stereoisomer presents a typical crystalline structure and particular physical properties. Amorphous polymers with 1:4 linkage present very slight hysteresis during elastic deformation, less than that of polymers with 1:2 linkage.

Some of the characteristics determined for certain butadiene polymer crystalline stereoisomers are indicated in Table V.

Melting point of 1:4-*cis*-polybutadiene is not marked, because it is strongly dependent on the stereoisomeric purity and on the stress.

We have also obtained crystalline polymers from other olefins (isoprene, piperylene, etc.). The lattice structure of 1:4 crystalline isoprene polymer stereoisomers is the same as that of the natural products. The synthesis of the isoprene stereoisomers, which needs very pure monomers, was principally studied in the United States.²⁰ In Europe most of the work was performed in the synthesis of the pure butadiene stereoisomers.

polymerization, are relegated to the side chains. Its principal chain is structurally the same as that of isotactic polybutylene where lateral chains are formed by ethyl groups instead of vinyl groups.

The structure of 1:2 syndiotactic polybutadiene is very different. It is the first synthetic polymer in which monomer units with opposed steric configuration alternate regularly. The principal chain has a nearly planar form and each monomer unit can be brought to cover its neighbour by means of a transla-

Table IV

Mechanical properties of relatively low molecular weight polypropylene fibre: $[\eta]=1$

Standard tenacity (20°C. 65% relative humidity)	6-7 g./den.
Wet tenacity (20°C. in water)	6-7 g./den.
Knot tenacity	5-6 g./den.
Loop tenacity	5-6 g./den.
Elongation at break (20°C. 65% relative humidity)	30-40%
Elongation at break (20°C. in water)	30-40%
Average stiffness	17 g./den.
Average toughness	12 g./den.
Initial modulus	35-45 g./den.
Elastic recovery	100% at 7% elongation
Shrinkage at 100°C.	1-2%

Table V
X-Ray Data on Crystalline Polybutadiene Stereoisomers

Polymer	Space group	Number of monomer per unit cell	Cell dimensions A.		Chain axis c	X-Ray density	X-Ray melting point
			a	b			
1:4 <i>trans</i>	(pseudo)hexagonal	(1)	(4.54 Å.)		4.9 Å.	1.02	148°C.
1:4 <i>cis</i>	C2/c(monoclinic) ($\beta=109^\circ$)	4	4.60	9.50	8.60	1.01	(x)n.d.
1:2 syndiotactic	P6 ₃ m (rhombohedral)	4	10.98	6.60	5.14	0.96	155°C.
1:2 isotactic	R3c (hexagonal)	18	17.3	17.3	6.50	0.96	125°C.

tion on the longitudinal axis of the chain of one half the identity period ($\frac{1}{2}c$) accompanied by specular reflection.

Each monomer unit containing a double bond has a centre of symmetry and is contained in a plane inclined to the axis of the chain.

The structure of *cis*-1:4 polybutadiene is characterized by an identity period containing 2 monomer units. Their arrangement is such that it is possible to pass from one to another by a displacement of $\frac{1}{2}c$ accompanied by specular reflection (as in syndiotactic polymers). The segment of the chain corresponding to the identity period has a symmetric centre, and consequently only one type of chain is present in the system.

A great amount of work has been done in connection with copolymers, which have many interesting possibilities once the difficulty of obtaining homogeneous products has been overcome.

Also for diolefin polymers we can have amorphous copolymers of sterically different units and stereoblock polymers.

Naturally, high melting-point, pure, crystalline diolefin polymers are not, in the pure state and at room temperature, rubbers in the usually understood sense. They become rubber at high temperatures and when their crystallinity is reduced.

Excellent elastic properties can be obtained when the relative mobility of the group of the main chain containing unsaturated links (like those of 1:4 diolefin polymers) is accompanied by low melting temperatures and low melting entropies.

The field of rubbers having very low elastic hysteresis at room temperature is still confined to diolefin polymers but is certainly no longer restricted to natural rubber.

The results obtained by the new discoveries of the stereospecific polymerization processes can lead to further developments. Numerous research chemists are actively working on and perfecting stereospecific processes and extending these to other classes of monomers.

The synthesis of crystalline high melting-point polymers of other vinyl monomers (vinyl chloride, acrylonitrile, vinyl ethers, vinyl esters, etc.) will be the next stage in stereospecific polymerizations. This aim will, perhaps, be more difficult to achieve, but it

certainly will be interesting both from a scientific and a practical point of view.

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