

509

509

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From the Stereospecific Polymerization to the Asymmetric Autocatalytic Synthesis of Macromolecules

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Macromolecular chemistry is a relatively young science. Though natural and synthetic macromolecular substances had long been known, it was only between 1920 and 1930 that Hermann Staudinger placed our knowledge of the chemical structure of several macromolecular substances on a scientific basis (1).

In the wake of Staudinger's discoveries and hypotheses, macromolecular chemistry has made considerable progress.

Very many synthetic macromolecular substances were prepared both by polymerization and by polycondensation; methods were found for the regulation of the value and distribution of molecular weights; attempts were made to clarify the relationships existing among structure, chemical regularity, molecular weight, and physical and technological properties of the macromolecular substances. It was far more difficult to obtain synthetic macromolecules having a regular structure from both the chemical and steric point of view.

An early result in this field, which aroused a certain interest in relation to elastomers, was the preparation of a polybutadiene having a very high content of *trans*-1,4 monomeric units, in the presence of heterogeneous catalysts (2).

A wider development of this field was made possible by the recent discovery of stereospecific polymerization. This led to the synthesis of sterically regular polymers as well as to that of new classes of crystalline polymers.

Before referring to the stereospecific polymerizations and to their subsequent developments, I wish to make a short report on the particular conditions that enabled my School to achieve rapidly conclusive results on the genesis and structure of new classes of macromolecules. I also wish to describe the main stages of the synthesis and characterization of the first stereoregular polymers of α -olefins.

The achievement of these results has also been helped by the research I did in 1924 when I was a trainee student under the guidance of Professor Bruni. At that time I began to apply x-ray study of the structures of crystals to the resolution of chemical and structural problems (3).

At first, investigations were mainly directed to the study of low-molecular-weight inorganic substances and of isomorphism phenomena; but, after I had the luck to meet Professor Staudinger in Freiburg in 1932, I was attracted by the study of linear high polymers and tried to determine their lattice structures.

To this end I also employed the electron-diffraction methods which I had learned from Dr. Seemann in Freiburg and which appeared particularly suitable for the examination of thin-oriented films (4).

I applied both x-ray and electron-diffraction methods also to the study of the structure of the heterogeneous catalysts used for certain important organic industrial syntheses, and thus had the possibility of studying in the laboratory the processes for the synthesis of methanol (see 5) and the higher alcohols (see 6), and also of following their industrial development in Italy and abroad.

In view of the experience I had acquired in the field of chemical industry, certain Italian Government and industrial bodies entrusted me in 1938

with the task of instituting research and development studies on the production of synthetic rubber in Italy.

Thus the first industrial production of butadiene-styrene copolymers was realized in Italy at the Ferrara plants, where a purely physical process of fractionated absorption was applied for the first time to the separation of butadiene from 1-butene (7).

At that time I also began to be interested in the possible chemical applications of petroleum derivatives, and particularly in the use of olefins and diolefins as raw materials for chemical syntheses such as oxosynthesis (8) and polymerization (9).

The knowledge acquired in the field of the polymerizations of olefins enabled me to appreciate the singularity of the methods for the dimerization of α -olefins that Karl Ziegler described in a lecture delivered in Frankfurt in 1952 (10); I was struck by the fact that in the presence of organometallic catalysts it was possible to obtain only one dimer from each α -olefin, while I knew that the ordinary, cationic catalysts previously used yielded complex mixtures of isomers with different structures.

At this time I also became acquainted with Ziegler's results on the production of strictly linear ethylene oligomers, obtained in the presence of homogeneous catalysts.

My interest was aroused, and in order to understand better the reaction mechanism (11), concerning which very little was known, I started the kinetic study of such polymerizations. In the meantime Ziegler discovered the process for the low-pressure polymerization of ethylene (12). I then decided to focus attention on the polymerization of monomers other than ethylene; in particular I studied the α -olefins, which were readily available at low cost in the petroleum industry.

At the beginning of 1954 we succeeded in polymerizing propylene, other α -olefins, and styrene; thus we obtained polymers having very different properties from those shown by the previously known polymers obtained from these monomers (13).

I soon observed that the first crude polymers of α -olefins and of styrene, initially obtained in the presence of certain Ziegler catalysts (TiCl_4 + aluminum alkyls), were not homogeneous, but consisted of a mixture of different products, some amorphous and non-crystallizable, others more or less crystalline or crystallizable.

Accordingly, I studied the separation of the different types of polymer by sol-

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vent extraction and the structures of the single separated products.

Even if the more soluble polymers were amorphous and had a molecular weight lower than that of the crystalline, but far less soluble, polymers deriving from the same crude product, I observed that some little-soluble crystalline fractions had a molecular weight only a little higher than that of other amorphous fractions. Therefore, convinced of the well-known saying *natura non facit saltus*, I did not attribute crystallinity to a higher molecular weight, but to a different steric structure of the macromolecules present in the different fractions (14).

In fact all vinyl polymers may be regarded as built from monomeric units containing a tertiary carbon atom. Thus in a polymer of finite length, such a carbon atom can be considered asymmetric, and hence two types of monomeric units may exist, which are enantiomorphous (13, 15).

Since all the polymers of vinyl hydrocarbons previously known, even those recognized as having a head-to-tail chainment like polystyrene, were amorphous, we examined the possibility that the crystallinity we observed was due to a chemically regular (head-to-tail) structure, accompanied by regular succession of steric configurations of

the single monomeric units. Indeed, x-ray analysis permitted us to determine the lattice constants of crystalline polypropylene (16) and polystyrene (17).

The identity period along the chain axis in the fiber spectra was of about 6.5 angstroms and might be attributed to a chain segment containing three monomeric units (18). This led us to exclude the idea that the crystallinity was due to a regular alternation of monomeric units having opposite steric configuration. Thus it could be foreseen, as was in fact later proved by more accurate calculations of the structure factors, that the polymeric chains consisted of regular successions of monomeric units, all having the same steric configuration (14).

In the subsequent study of the butadiene polymers, prepared by us in the presence of organometallic catalysts [for example, catalysts containing chromium (19)] that have 1,2-enchainment, two different types of crystalline polymers were isolated and purified.

The x-ray and electron-diffraction analyses of these products enabled us to establish that the structure of one of them is analogous to the structures of poly- α -olefins (20)—that is, characterized by the repetition of monomeric units having the same configuration. We also established that the other crystalline

product is characterized by a succession of monomeric units, which are chemically equivalent but have alternately opposite steric configuration (21), as confirmed by a thorough x-ray analysis of the structure.

In order to distinguish these different structures I proposed the adoption of terms coined from the ancient Greek, and these are now generally used (22); that is, *isotactic* (14) and *syndiotactic* (21).

Figure 1 shows the first device we used for an easy distinction of the different types of stereoisomery of vinyl polymers; the main chains have been supposed arbitrarily stretched on a plane.

By accurate examination of the structure of isotactic polymers on fiber spectra, we could establish that all crystalline isotactic polymers have a helical structure, analogous to that found by Pauling and Corey (23) for α -keratine (Fig. 2); in fact only the helix allows a regular repetition of the monomeric units containing asymmetric carbon atoms, as was foreseen by Bunn (24).

Soon after the first polymerizations of α -olefins we realized the importance and vastness of the fields that were opened to research, from both the theoretical and the practical points of view.

Our efforts were then directed to three main fields of research:

1) To investigate the structures of the new polymers in order to establish the relationships existing between chemical structure, configuration, and conformation of the macromolecules in the crystalline state.

2) To find the conditions that allowed the synthesis of olefinic polyhydrocarbons having a determined type of steric structure, with high yields and high degree of steric regularity (25), as well as to study the reaction mechanism, and regulation of the molecular weight.

3) To attempt the synthesis, possibly in the presence of nonorganometallic catalysts, of stereoregular polymers corresponding to other classes of monomers having a chemical nature different from that of α -olefins.

Crystalline Structure of High Polymers

Homopolymers. The synthesis of new classes of crystalline macromolecules and the x-ray analysis of their structures led to the formulation of some general rules which determine the structure of linear macromolecules (26). Table 1

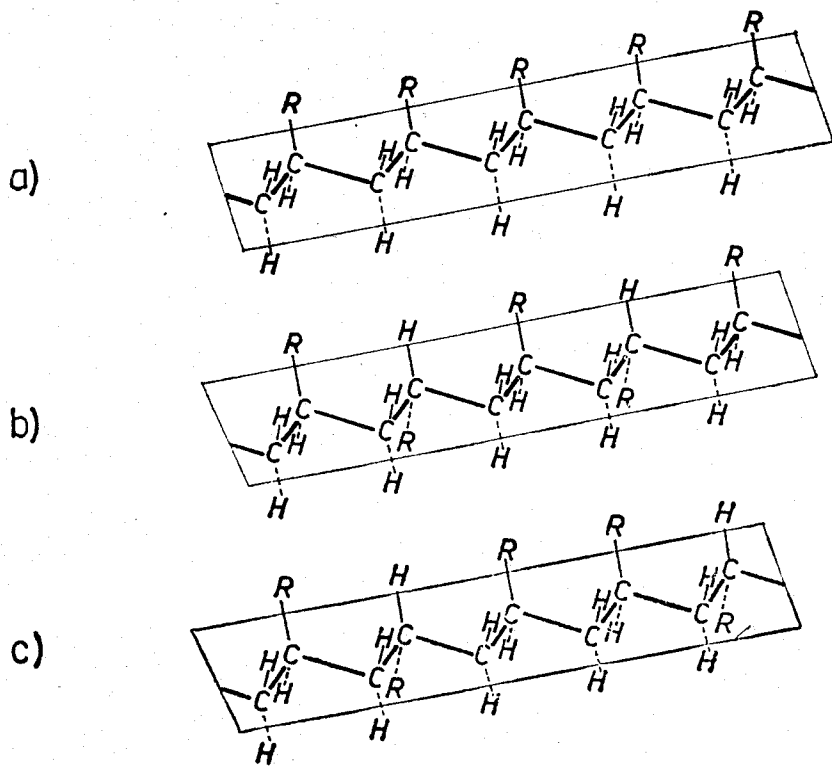


Fig. 1. Models of chains of head-to-tail vinyl polymers supposed arbitrarily stretched on a plane, having, respectively, isotactic (a), syndiotactic (b), and atactic (c) successions of the monomeric units.

summarizes some data concerning the structure of isotactic polymers; the data indicate that fourfold or higher-order helices exist besides the threefold ones already mentioned.

The conformation assumed by the single macromolecules in the lattice always corresponds to the conformation, or to one of the conformations, of the isolated molecule that shows the lowest internal energy content, the intramolecular van der Waals forces being taken into account.

The mode of packing of the polymer chains in a crystalline lattice takes place, as in the case of molecular crystals of low-molecular-weight substances, so as to fill the space in the best possible way.

If the polymer chain assumes a helical conformation in the crystalline state, and if it does not contain asymmetric carbon atoms, it can be expected that either helices of the same sense, or, in equal ratio, helices of opposite sense are represented in the lattice.

Analogous to the case of nonenantiomorphous low-molecular-weight crystalline substances, so also in polymers that do not contain asymmetric carbon atoms, right- and left-handed helices are usually represented in the lattice in equal amount.

On the other hand, in the case of isotactic polymers containing asymmetric carbon atoms, the space group will not contain symmetry elements involving inversion, as, for instance, centers of symmetry or mirror or glide planes.

A racemic mixture of antipode macromolecules can be an exception. Furthermore, it is interesting to note that the chain symmetry is often maintained in the space group to which the unit cell of the polymer belongs.

With regard to the occurrence of enantiomorphous space groups, typical examples are represented by some isotactic poly-1-alkylbutadienes, in the crystalline lattice of which macromolecules with helices of exclusively one sense, right or left, exist for each crystal (27) (Fig. 3). Also in the case of isotactic poly-*t*-butylacrylate, the helices in the lattice seem to be all of the same sense (28).

If the chain symmetry is maintained in the crystal lattice, the possible occurrence of different space groups is considerably restricted.

Where equal amounts of enantiomorphous macromolecules are contained in the lattice, we must distinguish two cases concerning the relative orientation of side groups of enantiomorphous macromolecules facing one another, which

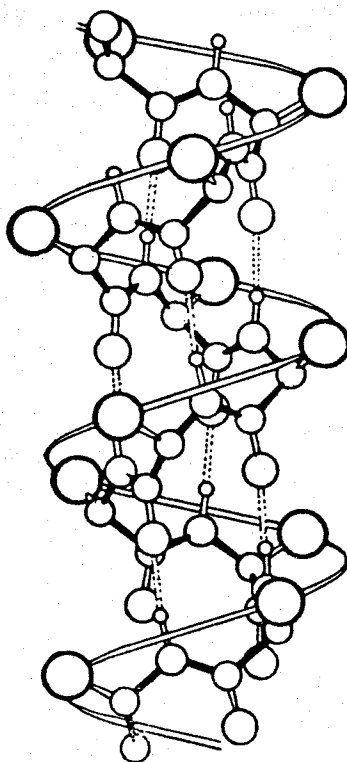


Fig. 2. Model of chain of α -keratine, according to Pauling and Corey.

can be either isoclined or anticlined.

In the first case, possible symmetry operators for the covering of near macromolecules are either a mirror plane or a glide plane, parallel to the chain axis.

It is, however, known that good packing is generally obtained more easily with a glide plane than with a mirror plane, especially in the case of bodies having periodical recesses and prominences, as in the case of spirialized polymer chains.

In the case of a threefold helix, each right-handed helix will be surrounded, because of the existence of the glide plane, by three isoclined left-handed helices, and vice versa; the space group will be $R3c$ (Fig. 4). This lattice is shown, for example, by isotactic polystyrene (29), by polybutene (30), by 1,2-polybutadiene (31), and by poly-*o*-fluorostyrene (32); on the other hand it is not shown by isotactic polypropylene, because it would give rise to an insufficiently compact lattice, if van der Waals contact distances, between carbon atoms of near chains, must be maintained around 4.2 angstroms (3).

In the second case previously considered, in which the relative orientation of the side groups of enantiomorphous macromolecules facing one another is anticlined, the only symmetry operator relating neighboring macromolecules is a symmetry center.

And again, if the helix is threefold, each right-handed helix will be surrounded, by the action of three symmetry centers at 120°C , by three left-handed helices, and vice versa; the macromolecules are oriented so as to minimize the length of the unit cell axes perpendicular to the threefold axis, with the best possible van der Waals distances: the space group, which probably is the one presented, for instance, by polyvinylmethyl ether (33) and by poly-*n*-butylvinyl ether (34), will be $R\bar{3}$ (Fig. 5).

Copolymers. The "random" introduction of different monomeric units in a crystalline polymer by copolymerization generally causes a decrease in crystallinity and melting point when their content is lower than 20 to 25 percent,

Table 1. Roentgenographic data on some typical isotactic polymers with different chain conformations.

Polymer	Helix type *	Chain axis (Å)	Unit cell	Space group
Polypropylene	3_1	6.50	Monoclinic, $a = 6.65 \text{ \AA}$; $b = 20.96 \text{ \AA}$; $\beta = 99^\circ 20'$	$C2/c$
Poly- <i>a</i> -butene †	3_1	6.50	Rhombohedral, $a = 17.70 \text{ \AA}$	$R3c$ or $R\bar{3}c$
Polystyrene	3_1	6.63	Rhombohedral, $a = 21.90 \text{ \AA}$	$R3c$ or $R\bar{3}c$
Poly-5-methylhexene-1	3_1	6.50		
Poly-5-methylheptene-1	3_1	6.40		
Poly-3-phenylpropene-1	3_1	~ 6.40		
Poly-4-phenylbutene	3_1	6.55		
Poly- <i>o</i> -methylstyrene	4_1	8.10	Tetragonal, $a = 19.01 \text{ \AA}$	$I4_{cd}$
Poly- <i>a</i> -vinyl-naphthalene	4_1	8.10	Tetragonal, $a = 21.20 \text{ \AA}$	$I4_{cd}$
Polyvinylcyclohexane	4_1	6.50	Tetragonal, $a = 21.76 \text{ \AA}$	$I4_a$
Poly-3-methylbutene-1	4_1	6.84		
Poly-4-methylpentene-1	7_2	13.85	Tetragonal, $a = 18.60 \text{ \AA}$	$P\bar{4}$
Poly-4-methylhexene-1	7_2	14.00	Tetragonal, $a = 19.64 \text{ \AA}$	
Poly- <i>m</i> -methylstyrene	11_2	21.74	Tetragonal, $a = 19.81 \text{ \AA}$	

* It is to be understood that, besides the right-handed X_n helix, the left-handed X_{n-n} helix also exists.
† Modification 1.

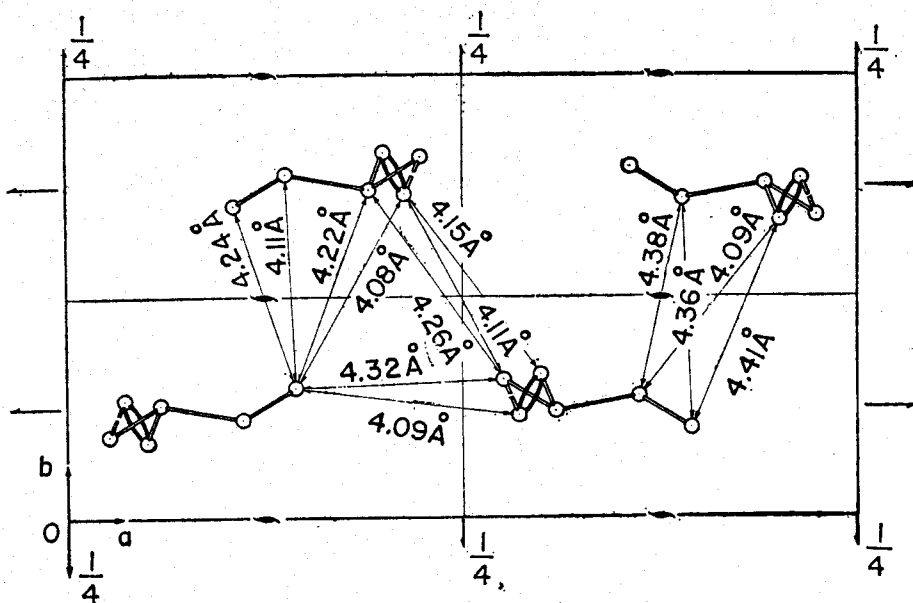


Fig. 3. Model of packing of isotactic *trans*-1,4-poly-1-ethylbutadiene in the crystalline state, projected on the (001) plane. (Space group $P2_12_12_1$.)

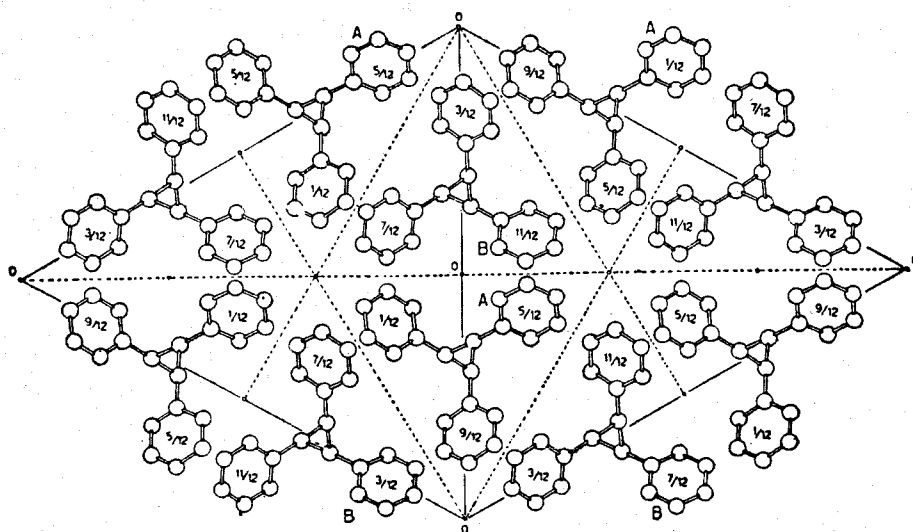


Fig. 4. Model of packing of isotactic polystyrene in the crystalline state, projected on the (001) plane. (Space group $R3c$.)

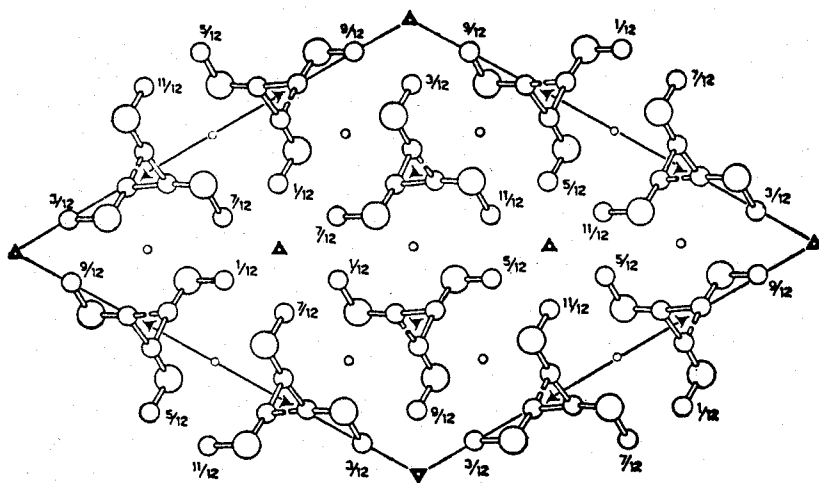


Fig. 5. Model of packing of isotactic polyvinylmethyl ether in the crystalline state, projected on the (001) plane. (Space group $R\bar{3}$.)

but at higher content values the copolymer is generally amorphous.

As we shall remark in the section dealing with the stereoregular polymers of hydrocarbon monomers containing an internal double bond, it is sometimes possible to obtain chemically and sterically regular alternating copolymers of these monomers with ethylene, which are also crystalline. This is the case, for instance, for the alternating ethylene-*cis*-2-butene (35), ethylene-cyclopentene (36), and ethylene-cycloheptene (37) copolymers.

In these cases, reaction conditions were used in which one of the monomers is unable to homopolymerize, but can copolymerize to alternating polymers in the presence of a large excess of the first monomer. Moreover, in the case of other nonhydrocarbon monomers, crystalline alternating copolymers have been obtained (38) from two different monomers that are both very reactive in the presence of stereospecific catalysts [for example, in the copolymerization of dimethylketene with higher aldehydes (39)], when the values of the relative copolymerization rates are much higher than those of homopolymerization. In the cases mentioned above, the repeating structural unit has the structure of a polyester obtained by treating a dimethylketene molecule with one molecule of the carbonyl monomer considered.

Our researches also enabled us to find particular crystalline copolymers, though with a "random" distribution, when the different monomeric units in the polymeric chain showed considerable analogies both in chemical nature and size.

This phenomenon was defined by us as *isomorphism of monomeric units*, even if, in contrast to the isomorphism phenomena of low-molecular-weight substances, the crystals do not consist of physical mixtures of isomorphous molecules, but of macromolecules in which monomeric units of different type can substitute each with the other. In this case, copolymers show physical properties (density, melting temperature, and so on) which vary continuously with the composition, and which are intermediate between those of the pure homopolymers. This phenomenon was observed in the copolymerization of styrene with monofluorostyrenes (40) and also in the copolymerization of butadiene with 1,3-pentadiene to *trans*-1,4 polymer (41).

Crystalline copolymers of a completely different type are obtained by suc-

cessive polymerization of different monomers in the presence of catalysts able to homopolymerize both of them. These are linear copolymers constituted by successive blocks, each consisting of a chemically and sterically regular succession of units of the same type.

In some of these cases x-ray analysis reveals both the crystallinities corresponding to the single homopolymers (42).

Stereospecificities in Polymerization

Processes of Hydrocarbon Monomers

The importance of the stereospecific polymerization—from the standpoint of both theory and practical applications—is due to the fact that in most cases (even if not always) the stereoregularity of linear polymers determines crystallinity. When the glass transition temperature and the melting temperature are very different, the physical and especially the mechanical properties are very different from those of the corresponding stereoirregular polymers. Due to such properties, these materials have very interesting practical applications, either as plastics and textiles when the melting point is high or as elastomers when the melting point does not considerably exceed the temperature of use.

The knowledge acquired in these last 10 years in the field of the stereospecificity of the polymerization processes shows that stereoregular and, in particular, isotactic polymers can be obtained in the presence of suitable catalysts acting through an ionic (both anionic and cationic) coordinated mechanism; however, they cannot generally be obtained by processes characterized by radical mechanism.

The catalysts having a higher degree of stereospecificity are characterized by the presence of metal atoms able to coordinate the monomer molecules in a stage immediately preceding that of insertion of the monomeric unit between the end of the growing chain and the catalyst (43–45).

In fact, a stereospecific action is shown either by the catalysts containing metal atoms, the coordinating properties of which are due to their charge and to their small ionic radius (aluminum, beryllium, lithium) (44), or by compounds of the transition metals (46, 47).

Some authors (48) were led to believe that the steric structure of the last monomeric unit, or units, of the growing chain played an important role in

the steric regulation of the polymerization processes. However, the low degree of stereospecificity observed in the radical processes shows that this factor alone cannot exert a determining action. In any case stereoregularity in these last processes is of the syndiotactic type and may be attributed also to thermodynamic factors, according with the strong increase in stereospecificity with decrease in temperature.

The first highly stereoregular isotactic polymers were obtained in the presence of heterogeneous catalysts; however, it soon became clear that the heterogeneity of the catalytic system is an essential factor for the polymerization of aliphatic olefins to isotactic polymers, but not for the polymerization of other types of monomers. In fact it was found that aliphatic aldehydes and certain monomers containing two electron-donor functional groups able to be coordinated (for example, conjugated diolefins, vinyl ethers, alkenyl ethers, acrylic monomers, styrenes that are substituted differently in the benzene ring, vinyl pyridine, and so on) can be polymerized in the stereospecific way also in the presence of soluble catalysts.

It must be borne in mind that, even if the most typical highly stereospecific catalysts for the polymerization of α -olefins contain organometallic compounds, some classes of monomers (for example, vinyl ethers) can be polymerized to isotactic polymers in the presence of cationic catalysts without the presence of organometallic compounds (49).

The stereospecificity of the polymerization processes not only depends on the catalytic system but is a property of each monomer-catalyst system. This is particularly evident in the case of the polymerization of some conjugated homologs of diolefins, in which the variation of the monomer changes both the degree of stereospecificity of the process and, in some cases, the type of stereoregularity of the polymer obtained (50).

Therefore, in order to attain a general view of the present state of the stereospecific polymerization, it is helpful to examine separately the most important results obtained in each class of monomers.

1) α -Olefins

This is the most studied branch of stereospecific polymerization. As already mentioned, isotactic polymers of α -olefins have been obtained so far only

with the use of heterogeneous catalysts.

High stereospecificity is observed only when one employs organometallic catalysts containing a particular crystalline substrate, such as that deriving from the violet α , γ (51), and δ (52) modifications of TiCl_3 , having a layer lattice (42, 53, 54). The use of the β modification of TiCl_3 (55), which does not correspond to layer lattices, or of other heterogeneous catalysts (for example, catalysts containing a substrate formed by metal oxides) which also yield linear polymers of ethylene, leads to the formation of catalysts having little stereospecificity in the polymerization of α -olefins (53, 56).

The study of the catalysts prepared from organometallic compounds containing aromatic groups (56) or labeled carbon enabled us to determine the ionic coordinated mechanism of such polymerization and the number of active centers on the surface of the heterogeneous catalysts (57).

Chemical and kinetic studies led to the conclusion that the stereospecific polymerization of propylene is a polyaddition reaction (stepwise addition), in which each monomeric unit, on its addition, is inserted on the bond between an electropositive metal and the electronegative terminal carbon atom of the growing polymeric chain. This study revealed also that some organometallic catalysts, which contain only titanium as metal atoms, could be stereospecific (58). The first reaction step corresponds to a coordination of the monomer molecule to the transition metal belonging to the active center (43, 45).

The reaction chain generally does not show a kinetic termination (59), the length of the single macromolecules being determined by the rate of the processes of chain transfer either with the monomer (60) or with the alkyls of the organometallic compounds present (61); these transfer processes allow, after the formation of a macromolecule, the start of another macromolecule on the same active center (56, 62).

The single rate constants of the different concurrent processes of chain growth and termination have been determined for some typical catalysts (63). Later on, the study of homogeneous catalysts based on vanadium compounds and on alkyl aluminum monochloride permitted us to synthesize crystalline polypropylenes with a nonisotactic structure. The detailed development of this study led to the preparation of catalysts, obtained by treating

hydrocarbon-soluble vanadium compounds (acetylacetonates or vanadium tetrachloride) with dialkyl aluminum monochloride. These catalysts yield, at

low temperature, more or less crystalline polymers, free, however, from isotactic crystallizable macromolecules (64).

X-ray analysis, applied to the fiber spectra, permitted us to establish that this is a syndiotactic polymer; its lattice structure has an identity period of 7.4 angstroms, corresponding to four monomeric units (65).

The comparison between isotactic and syndiotactic polypropylene structures is shown in Fig. 6.

The same type of homogeneous catalyst, which at low temperature homopolymerizes propylene to syndiotactic polymer, was used at higher temperatures (for example, 0°C) for the production of copolymers having a random distribution of propylene with ethylene (66). These polymers, which are linear, are completely amorphous when the ethylene content decreases below 75 percent.

They have a very flexible chain, due to the frequent $\text{CH}_2\text{--CH}_2$ bonds, while the relatively small number of CH--CH_2 groups is enough to hinder crystallization of the polymethylene chain segments.

These copolymers can be easily vulcanized through the use of peroxides; on the other hand the terpolymers, which contain not only ethylene and

propylene but also small amounts (from 2 to 3 percent, by weight) of monomeric units, originated from the random copolymerizations of suitable diolefins (67) (or of cyclic compounds, such as cyclooctadiene, which can be prepared easily by dimerization of butadiene, following the method proposed by Wilke), can be vulcanized easily by the conventional methods used for the vulcanization of low-unsaturation rubber. They yield elastomers that are very interesting also from the practical point of view, because they can be obtained from low-priced materials and also because of their physical properties and resistance to aging.

2) Ditactic polymers

Polymers of 1-methyl-2-deuteroethylene. The study on the polymerization of differently deuterated propylenes, undertaken by us in order to arrive at more certain and univocal attributions of certain bands to the infrared spectrum of isotactic polypropylene, led us to the discovery of new interesting types of stereoisomerism in polymers of 1-methyl-2-deutero-ethylene, and generally in the case of polymers of 1,2-disubstituted ethylenes (68).

In fact, propylenes deuterated in the methylenic group can lead to monomer units having different steric structure depending on the relative orientation of the CH_2 and D substituents.

Starting from these deuterated monomers showing phenomena of geometric isomerism, two types of polymers were obtained. They exhibited the same x-ray spectra but different infrared spectra (69). This means that such polymers possess the same helix structure as normal isotactic polypropylene, but that the relative orientation of D and CH_2 groups can lead to a new type of stereoisomerism. In general, starting from a monomer of the $\text{CHA}=\text{CHB}$ type, three types of stereoregular isomers can be expected (see Fig. 7).

The type of stereoisomer obtainable by stereoregular polymerization depends on the mode of presentation and type of opening of the double bond of each monomer molecule on entering the growing chain (Fig. 8).

Subsequently, diisotactic polymers were obtained with the aid of cationic catalysts, starting from monomers of the $\text{CHA}=\text{CHB}$ type, wherein A designates an OR group and B, chlorine (70) or an alkyl group (71) (Fig. 7).

Stereoregular homopolymers of hy-

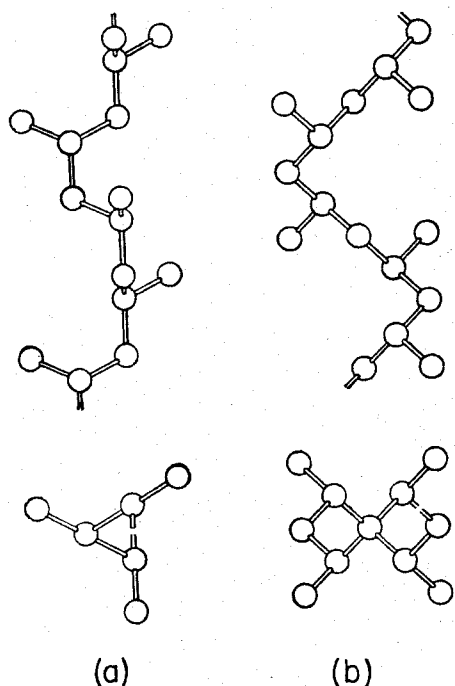


Fig. 6. Comparison between the side and end views of the chain structures of isotactic (a) and syndiotactic (b) polypropylenes (stable modifications) in the crystalline state.

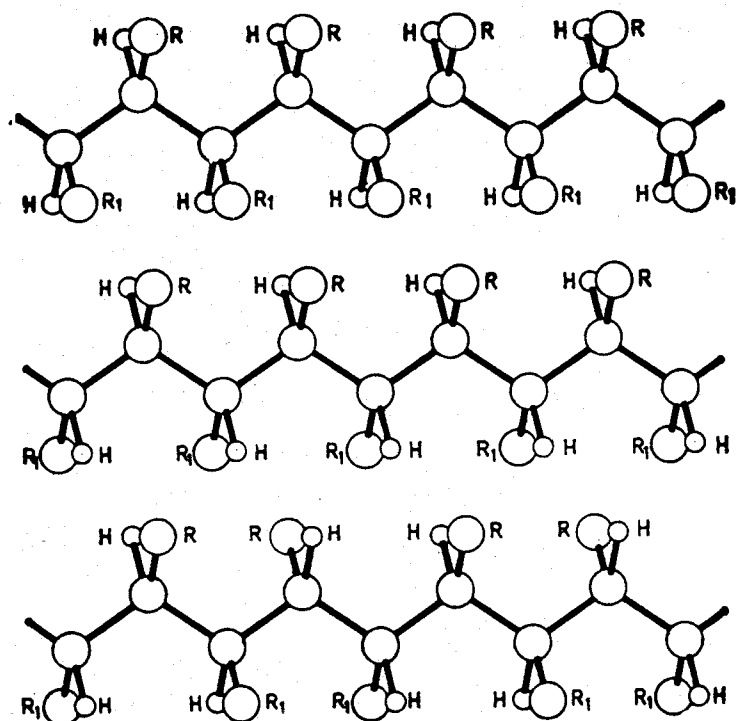


Fig. 7. Models of the chains of head-to-tail ditactic polymers supposed arbitrarily stretched on a plane, having, respectively, threo-diisotactic (a), erythro-diisotactic (b), and disyndiotactic (c) succession of the monomeric units.

drocarbons having an internal double bond. First of all, I wish to report on the results we have obtained in the polymerization of cyclobutene, which is of particular interest as it yields several crystalline polymers having different chemical or steric structure, depending on the catalyst used (72) (Fig. 9).

The different stereoregular polymers we have obtained and a number of their properties are shown in Table 2, from which it may be seen that the polymerization can take place by opening of the double bond to form cyclic monomer units containing two sites of optical type stereoisomerism, so that crystalline polymers are of ditactic type.

In view of the fact that under suitable conditions it is possible to obtain two crystalline polymers containing enchainment rings that show different physical properties, we have ascribed the differences in their properties to the different steric structure and have attributed an erythro-diisotactic structure to one of them and an erythro-disyndiotactic structure to the other (73) (Fig. 10).

In the presence of other catalysts the ring opens to form unsaturated monomer units, which may show isomerism of geometric type. In this case, too, two different products are obtained (depending on the catalyst used), the properties of which correspond to those, respectively, of *cis*-1,4- and *trans*-1,4-polybutadiene (72) (Fig. 9).

Ditactic polymers are also obtained from certain monomers containing internal unsaturation, which are unable to homopolymerize but, as mentioned above, can copolymerize with ethylene, yielding crystalline, alternating copolymers of erythro-diisotactic structure. Among these monomers are *cis*-2-butene (35), cyclopentene (36), and cycloheptene (37); *trans*-2-butene and cyclohexene behave in a different way and do not give crystalline copolymers.

Unlike the ditactic polymers of deuterated propylene, the ditactic polymers obtained by alternate copolymerization can exist in two disyndiotactic forms.

It is to be noted that the copolymerization of *cis*-2-butene is stereospecific only in the presence of heterogeneous catalysts of the type used in polymerizing α -olefins to isotactic polymers, while the copolymerization of cyclopentene and cycloheptene is also stereospecific when homogeneous catalysts are used. We have recently (74) proposed an interpretation of these facts based essentially on steric criteria.

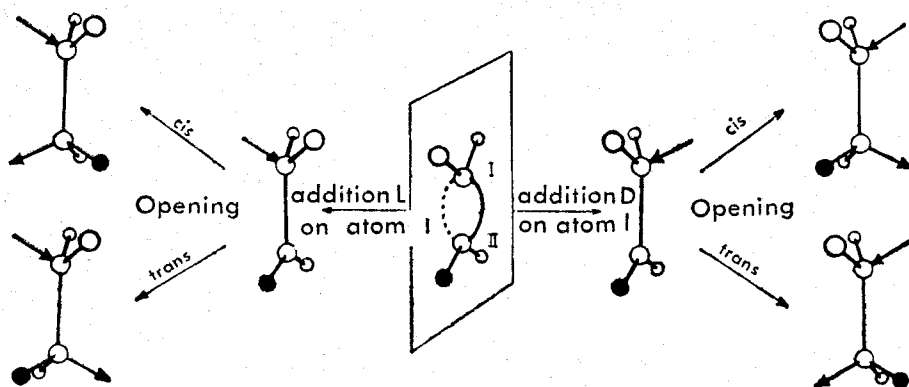
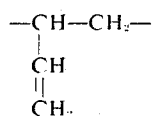


Fig. 8. Scheme of presentation and opening of the double bond of monomeric units when entering the growing chain.

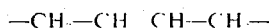
3) Stereoregular polymers of conjugated diolefins

Stereoisomerism phenomena in the field of diolefins, and in particular of conjugated diolefins, are more complex than phenomena occurring in the case of monoolefinic monomers. In fact, besides the stereoisomerism phenomena observed in these last (isomerism due to asymmetric carbon atoms), isomerism phenomena of geometric type may also be present, depending on the *cis*- or *trans*-configuration of the residual double bonds present in the monomeric units.

Butadiene polymers. The simplest conjugated diolefin, 1,3-butadiene, can in fact yield two types of polymers, according to whether the polymerization takes place by opening of the vinyl bond (to form 1,2-enchainment polymers)



or by opening of both conjugated double bonds (to form 1,4-enchainment polymers)



In the first case, the same stereoisomerism phenomena observed in other vinyl polymers (for example, isotactic, syndiotactic, and atactic polymers) can be expected.

In the second case, each monomeric unit still contains a double bond in the 2-3 position, which can assume *cis*- or *trans*- configuration. Thus, four types of stereoregular polymers could be foreseen "a priori" and precisely: *trans*-1,4-, *cis*-1,4-, isotactic-1,2-, and syndiotactic-1,2-polybutadienes. All four of these stereoisomers were prepared at

my Institute with the aid of different stereospecific catalysts (75, 76) with a high degree of steric purity (up to above 98 percent), as shown by infrared analysis (77).

X-ray examination had made it possible for us not only to establish the steric structure of the different polymers but also to determine the conformation of the chains in the crystals and, for three of them, also a detailed

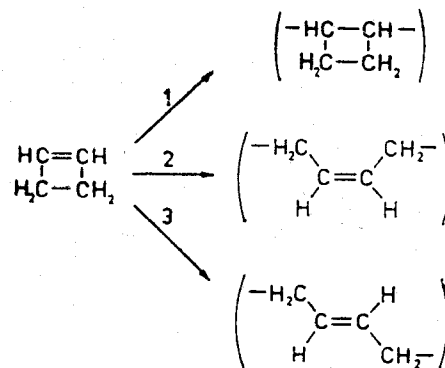


Fig. 9. Types of polymerization of cyclobutene: 1, cyclobutyleneamer; 2, *cis*-1,4-polybutadiene; 3, *trans*-1,4-polybutadiene.

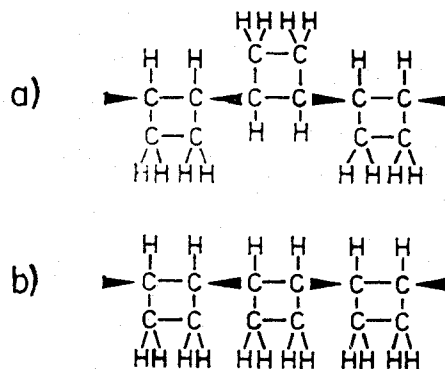


Fig. 10. Schematic drawing of the structures of erythro-diisotactic (a) and erythro-disyndiotactic (b) cyclobutyleneamer.

Table 2. Stereospecific anionic coordinated polymerization of cyclobutene.

Catalytic system	Prevailing chemical structure of polymer	Stereoregularity of polymer	Properties of crystalline polymers		
			Density	Melting temperature (°C)	Solubility in solvents
$VCl_4 + Al(n-C_6H_{13})_3$	2-Polycyclobutylamer	Presumably erythro-diisotactic	1.06	≈ 200	Insoluble in all the solvents below 150°C
$V(\text{acetylacetonate})_3 + AlCl(C_2H_5)_2$	2-Polycyclobutylamer	Presumably erythro-disyndiotactic	1.035	≈ 150	Soluble in tetralin at 150°C
$TiCl_4 + Al(C_2H_5)_3$	Polybutadiene	Prevailingly <i>cis</i> -1,4			Properties corresponding to those of 1,4-polybutadiene described in the literature
$TiCl_3 + Al(C_2H_5)_3$	Polybutadiene	Prevailingly <i>trans</i> -1,4			

lattice structure (21, 78). Figure 11 shows the conformations of the chains of the various stereoisomers, while in Table 3 a number of physical characteristics of the single polymers are reported.

As mentioned above, stereoregularity in the field of butadiene polymers is not necessarily connected with the use of heterogeneous catalysts, and, in fact, all four regular stereoisomers can be obtained with the aid of homogeneous catalysts.

In the case of *cis*-1,4-polybutadiene, the highest steric purity is obtained by the use of homogeneous catalysts (76). Of the four polybutadiene stereoisomers, the *cis*-1,4 stereoisomer is of particular interest also from a practical viewpoint. Its preparation and properties have been investigated by a large number of workers (79).

Isoprene polymers. The two polyisoprene geometrical isomers were already known in nature: natural rubber (*cis*-1,4 polymer) and gutta-percha and balata (*trans*-1,4 polymers). Both were obtained by synthesis through stereospecific polymerization.

The *cis*-1,4 polymer was obtained in the United States for the first time by Goodrich's workers (80), while the *trans*-1,4 polymer was prepared by us at the beginning of 1955 (81).

The other stereoisomers, having 1,2- or 3,4- enchainment, have not been prepared as yet in such a degree of steric purity as to yield crystalline products. In fact, the only known polymer having 3,4- enchainment, obtained in the presence of the same catalysts yielding syndiotactic 1,2-polybutadiene, is amorphous.

1,3-Pentadiene polymers. Unlike bu-

tadiene polymers, stereoregular polymers of 1,3-pentadiene obtained so far contain at least one asymmetric carbon atom in the monomer unit. Furthermore, for some of them it is possible to expect geometric isomers, due to the presence of internal double bonds which may have *cis*- or *trans*- configuration, so that all the polymers will show two centers of steric isomerism. And in fact polymers having 3,4- enchainment, containing two asymmetric carbon atoms, show two sites of optical isomerism; all the others exhibit one site of optical isomerism and one of geometric isomerism (1,2 and 1,4 units).

On the assumption that only polymers showing stereoregularity in both possible sites (ditactic polymers) will be crystalline, 11 crystalline pentadiene polymers can be expected:

- 1) Polymers having 3,4- enchainment (Fig. 12a):
 - (i) Erythro-diisotactic polymer
 - (ii) Threo-diisotactic polymer
 - (iii) Syndiotactic polymer
- 2) Polymers having 1,2- enchainment (Fig. 12b):
 - (iv, v) Isotactic polymers containing, respectively, one *cis*- or *trans*- double bond in the side chain
 - (vi, vii) Syndiotactic polymers containing, respectively, one *cis*- or *trans*- double bond in the side chain
- 3) Polymers having 1,4- enchainment (Fig. 12c):
 - (viii, ix) *Cis*-1,4- isotactic and syndiotactic polymers, respectively
 - (x, xi) *Trans*-1,4- isotactic and syndiotactic polymers, respectively

Of these stereoisomers the only three so far known were prepared in my Institute: *trans*-1,4-isotactic (82), *cis*-1,4-isotactic (83), and *cis*-1,4-syndiotactic polymer (84). In Table 4 a number of physical properties characteristic of these isomers are reported; Figs. 13 and 14 show the conformation of the chains in the crystals.

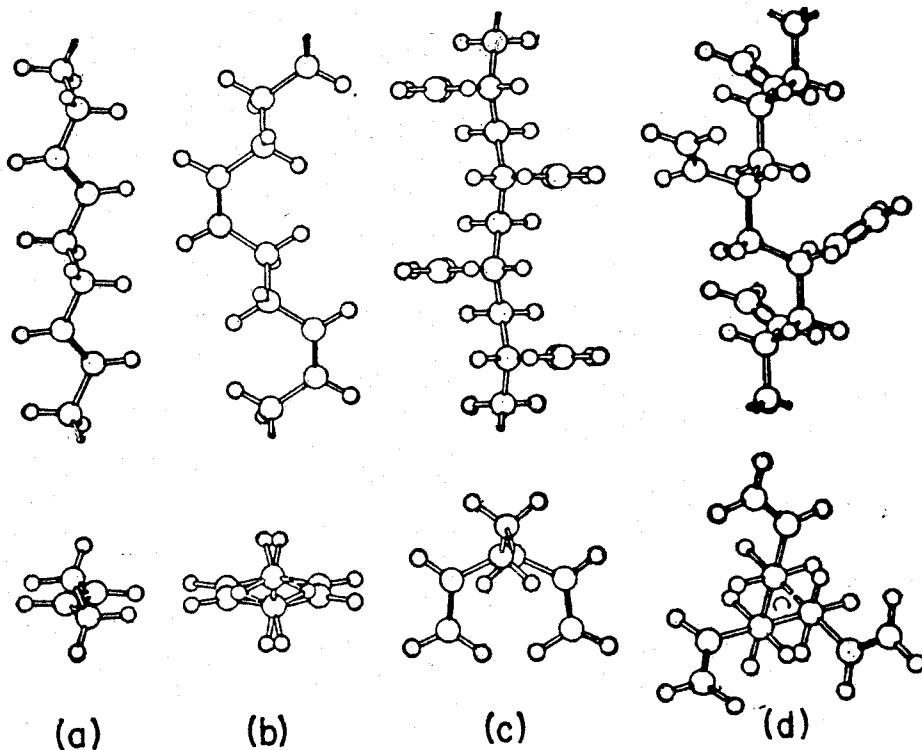


Fig. 11. Side and end views of the chain conformations of the four stereoisomers of polybutadiene: (a) *trans*-1,4; (b) *cis*-1,4; (c) syndiotactic-1,2; (d) isotactic-1,2.

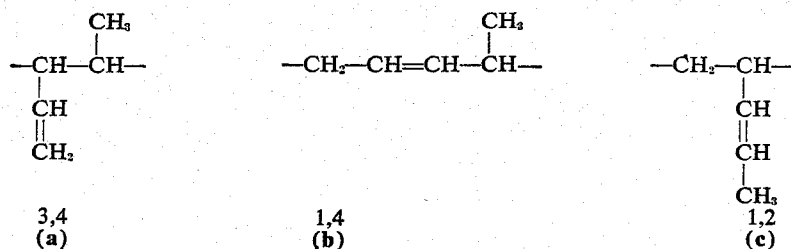


Fig. 12. Structure of 1,3-pentadiene polymers.

As could be expected, the best elastic properties in vulcanized polymers are observed for *cis*-1,4- polymers, owing to their melting point, which is slightly below the melting point of natural rubber.

Stereospecificity in Polymerization of Nonhydrocarbon Monomers

Unlike the polymerization of unsaturated hydrocarbons, and particularly of α -olefins, the polymerization of monomers containing functional groups, in the presence of catalysts based on organometallic compounds, has not been investigated until recently. This is due to the fact that the functional groups

Table 3. Some physical properties of the four stereoregular polymers of butadiene.

Polymer (infrared analysis)	Melting point (°C)	Identity period (Å)	Density (g/ml)
<i>Trans</i> -1,4 (99-100%)	146*	4.85 (mod. I)	0.97
		4.65 (mod. II)	.93
<i>Cis</i> -1,4 (98-99%)	2	8.6	1.01
Isotactic-1,2 (99% 1,2 units)	126	6.5	0.96
Syndiotactic-1,2 (99% 1,2 units)	156	5.14	.96

* *Trans*-1,4 polybutadiene exists in two crystalline modifications: one (mod. I) is stable below 75°C, the other (mod. II) is stable between about 75°C and the melting point of the polymer.

Table 4. Some physical properties of the three stereoregular isomers of 1,3-polybutadiene known so far.

Polymer	Infrared analysis	Identity period (Å)	Melting point (°C)	Density (g/ml)
Isotactic <i>trans</i> -1,4	<i>Trans</i> -1,4 (98-99%)	4.85	96	0.98
Isotactic <i>cis</i> -1,4	<i>Cis</i> -1,4 (85%)	8.1	44	.97
Syndiotactic <i>cis</i> -1,4	<i>Cis</i> -1,4 (90%)	8.5	53	1.01

contained in such monomers can react with organometallic catalysts through reactions that are well known in the field of classical organic chemistry, such as Grignard reactions, Michael's reaction, or splitting of an ether bond.

Initially it was feared that these reactions might involve both deactivation of the catalytic agent and total or partial alteration of the said monomers.

In 1956 we demonstrated for the first time in the case of acrylonitrile (85) and its homologs that, by suitably selecting the transition metal compounds and organometallic compounds forming the catalytic complex, it is possible to bring about stereospecific, anionic coordinated polymerization of these monomers while impeding or delaying the above-mentioned side reactions between monomer and catalyst.

Therefore, it has been demonstrated that stereospecific polymerization of nonhydrocarbon monomers can also be carried out with the use of pure organometallic compounds other than those of the Ziegler type, or even with the aid of catalytic compounds that do not contain metal-to-carbon bonds.

The research work on these monomers has taken two separate but parallel paths; that is, on the one hand it was directed to stereospecific cationic coordinated polymerization and, on the other, to stereospecific anionic polymerization (see Tables 5 and 6).

The cationic coordinated polymerizations carried out by us in the presence of catalysts of the type of Lewis acids (based on organometallic compounds or Friedel-Craft catalysts) were chiefly directed to the following classes of monomers: vinyl alkyl ethers (86, 87), alkenyl alkyl ethers (70), alkoxy-styrenes (88), vinylcarbazole (89), and β -chlorovinyl ethers (71).

The polymerization of isobutyl vinyl ethers to crystalline polymers had already been carried out by Schildknecht in 1949 (49). As a result of our further research work it was possible to attribute their crystallinity to an isotactic structure (86).

Stereospecific anionic coordinated polymerization, which is in general carried out in the presence of basic-type catalysts (organometallic or metal amidic compounds, alcoholates) was chiefly investigated in connection with the following classes of monomers: higher homologs of acrylonitrile (90), vinylpyridine (91), sorbates (92), acrylates (93), and aliphatic aldehydes (94).

Unlike the α -olefin polymerization, which requires the presence of a catalyst containing a crystalline substrate in order that it may proceed in a stereospecific isotactic manner, the polymerization of nonhydrocarbon monomers containing functional groups or atoms having free electron pairs (such as, for example, ethereal, carbonylic, or carboxylic oxygen; aminic, amidic, or nitrilic nitrogen) can proceed in a stereospecific way also in the absence of a solid substrate—that is, in a homogeneous phase. Here the stereospecificity—which in this case is also connected with a constant orientation and constant mode of presentation, on polymerizing,

Table 5. Nonhydrocarbon monomers polymerized in a stereospecific way by coordinated cationic catalysis in the homogeneous phase.

Monomer	Type of catalyst	Type of stereospecificity in the polymer
Vinylalkyl ether	Al(C ₂ H ₅)Cl ₂	Isotactic
<i>Trans</i> -alkenyl-alkyl ether	Al(C ₂ H ₅)Cl ₂	Threo-diisotactic
<i>Cis</i> - β -chlorovinylalkyl ether	Al(C ₂ H ₅)Cl ₂	Erythro-diisotactic
<i>Trans</i> - β -chlorovinylalkyl ether	Al(C ₂ H ₅)Cl ₂	Threo-diisotactic
<i>o</i> -Methoxystyrene	Al(C ₂ H ₅)Cl ₂	Isotactic
N-vinylcarbazole	Al(C ₂ H ₅)Cl ₂	
N-vinyldiphenylamine	Al(C ₂ H ₅)Cl ₂	
Benzofuran	AlCl ₃	

Table 6. Nonhydrocarbon monomers polymerized in the stereospecific way by coordinated anionic catalysis in the homogeneous phase.

Monomer	Type of catalyst	Type of stereospecificity in the polymer
Vinylpyridine	Mg(C ₆ H ₅)Br	Isotactic
Acrylonitrile	Cr(Acac) ₃ +Zn(C ₂ H ₅) ₂	Syndiotactic
α -Substituted acrylonitrile	Mg(C ₂ H ₅) ₂	
Sorbates	Butyl-Li	Erythro-diisotactic
Acrylates	Mg amides	Isotactic
Aliphatic aldehydes	Al(C ₂ H ₅) ₃	Isotactic

of the monomer units with respect to the growing chain and to the catalytic agent—is due to the coordination of an electron pair in the monomer with the metal of the catalytic agent by means of a dative bond (47, 95). As the olefinic double bond also is necessarily bound to the active center, such monomers thus appear to be doubly linked to the complex formed by the catalytic agent and the terminal group of the growing chain. A predetermined steric orientation is thus made possible.

Likewise, both the diolefins containing two olefin groups bound to the catalyst complex and certain aromatic α -olefins, wherein the second anchoring point is provided by the aromatic group π -linked to a catalyst containing a highly electropositive atom with a very small radius (lithium) (96), can be polymerized stereospecifically even in the homogeneous phase.

The coordination of the monomer with the catalytic agent, which is the indispensable step preceding any stereospecific polymerization both in the homogeneous and in the heterogeneous phase, has been particularly well exemplified by the stereospecific polymerization of 2-vinylpyridine in the presence of organometallic compounds of magnesium (97).

In fact, the presence of Lewis bases in the polymerization of this monomer exerts a determining influence on its behavior in the polymerizations. Compounds having a higher degree of basicity than vinylpyridine itself (for example, pyridine) form stable coordination compounds with the catalyst, thus impeding the coordination of the monomer; in this way, not only does the catalytic activity appear very much reduced, but also the stereospecificity disappears and the polymer obtained is atactic. Compounds having a lower degree of basicity than the monomer (aliphatic ethers) compete with the monomer only in so far as the association with the catalyst is concerned. Accordingly this does not result in the disappearance of the catalyst reactivity, but

only in its reduction along with the degree of stereospecificity of the reaction.

The asymmetric synthesis of optically active high polymers, starting from monomers showing no centers of optical-type asymmetry, constituted a particular, more advanced case of isotactic stereospecific polymerization.

In fact, whereas in the normal stereospecific polymerization to isotactic polymers a succession of monomer units with a given configuration takes place in each single macromolecule so that enantiomorphous macromolecules in equal amounts are present in crude polymers, in the case of asymmetric synthesis one of the two enantiomorphous isomers of the monomer unit is contained in higher amounts.

Table 7. Asymmetric synthesis of polymers.

Monomer	Catalyst	Structure of polymer	$[\alpha]_D$
Methyl sorbate	(S) Iso-amyl lithium	Erythro-diiso- <i>trans</i> -tactic	- 7.9
Butyl sorbate	Butyl lithium(-) MEE *	Erythro-diiso- <i>trans</i> -tactic	+ 8.4
Benzofuran	$AlCl_3$ (+) PHE †	Not determined	+ 69
<i>Trans</i> -1,3-pentadiene	(+) $Al(iC_2H_5)_3 + VCl_3$	Iso- <i>trans</i> -tactic	- 1.05
<i>Trans</i> -1,3-pentadiene	$Al(C_2H_5)_3$ (-) $Ti(OC_{10}H_{19})_4$ ‡	Iso- <i>cis</i> -tactic	- 22

* MEE, Menthyl ethyl ether; † PHE, β phenyl alanine; ‡ $Ti(OC_{10}H_{19})_4$, titanium tetramentholate.

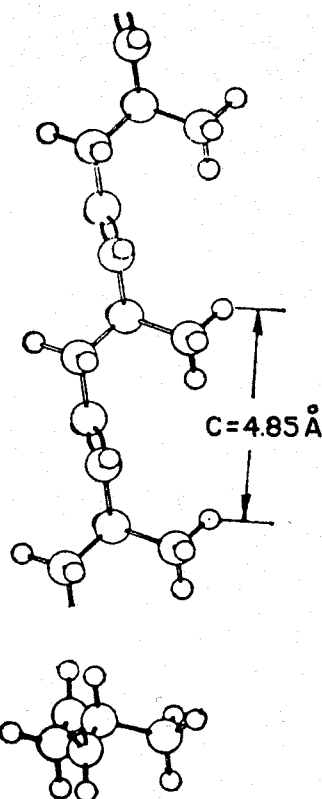


Fig. 13. Side and end views of the macromolecule of isotactic *trans*-poly(1-methylbuta-1,3-diene) (that is, *trans*-1,4-pentadiene) in the crystalline state.

It should be noted that isotactic high polymers of α -olefins or of other simple vinyl monomers cannot show detectable optical activity, since an ideal isotactic polymer of infinite length does not contain asymmetric carbon atoms, and in isotactic polymers having finite length (98) the optical activity, due to a difference in the terminal groups, can be detected only in oligomers and decreases with increase in the molecular weight. This is due to the fact that the asymmetry of each asymmetric carbon atom is to be ascribed not to the chemical difference of contiguous groups linked to the said carbon atom but to a difference in length of the chain segments linked to it (99).

In fact, in the case of poly- α -olefins, optically active polymers were obtained by polymerization only from monomers having an asymmetric carbon atom (100).

On the basis of our investigations it has been possible to obtain optically active polymers from monomers containing no centers of optical asymmetry only when, during the polymerization, monomer units are incorporated so as to develop new asymmetric centers. The asymmetry of the new centers arises from a difference in the chemical constitution of the groups contiguous to the carbon atoms themselves (101-104).

Such a result was obtained by means of stereospecific polymerization processes, operating under conditions that allow asymmetric induction to favor the formation of one of the two enantiomorphous structures of the monomer unit.

The methods that have led us to the asymmetric synthesis of polymers of substituted diolefins and of certain heterocyclic, unsaturated compounds are of two types.

1) The first is the use of normal stereospecific catalysts wherein at least one group bound to the organometallic compound used in the catalyst preparation, which will be the terminal group of the macromolecules, is optically active (101). In this case the asymmetric induction is probably due to the particular configuration of the terminal group of the growing chain bound to the catalyst.

2) A second method is based on the use of conventional stereospecific catalysts prepared without using optically active alkyls, provided they are complexed with optically active Lewis bases, such as β -phenylalanine (102), or with the use of an optically active transition metal compound (104) (Table 7).

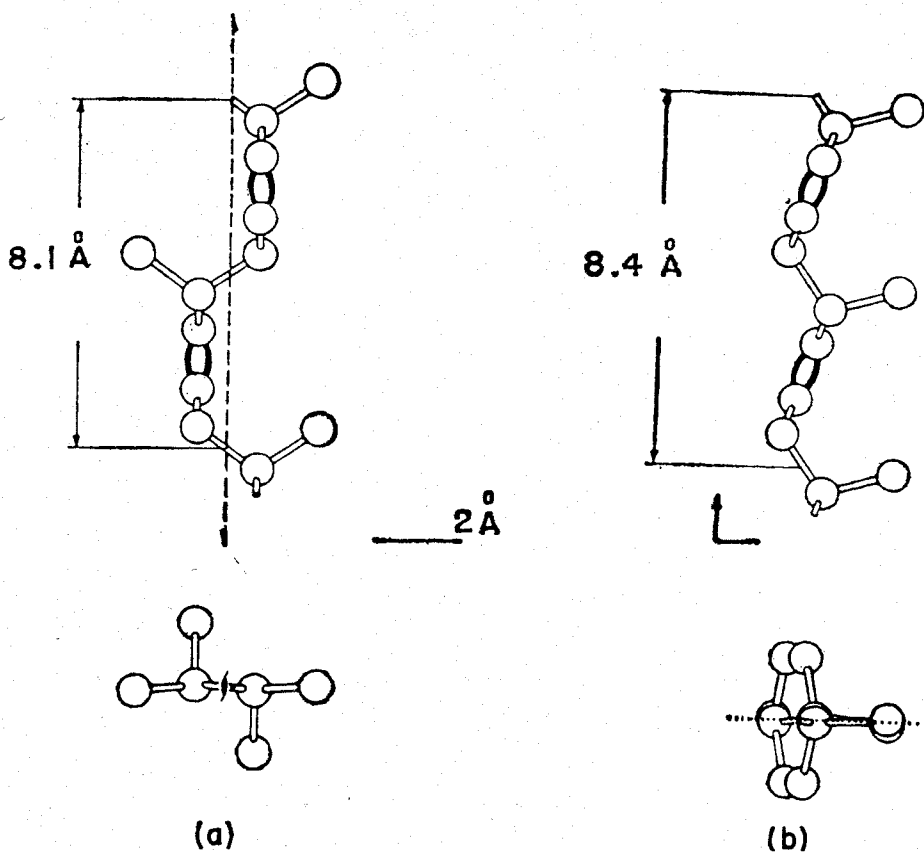


Fig. 14. Side and end views of the macromolecule of isotactic *cis*-1,4-poly(pentadiene) (a) and syndiotactic *cis*-1,4-poly(pentadiene) (b).

In the first case, as the polymerization proceeds, the optical activity decreases, as could be expected in view of the fact that any accidental inversion of configuration exerts an action not confined to one monomer unit only, but tending to extend to subsequent units.

In the second case, on the other hand, the induction is due to the asymmetry of the optically active counterion (105), which maintains its steric structure also in the case where the asymmetric polymerization gives low optical yields.

These results can be extended to the

Table 8. Autocatalytic effect in the asymmetric polymerization of benzofuran in the presence of AlCl_3 -(+)- β -phenylalanine.

Run	Weight *	$[\alpha]$	$\frac{\Delta W[\alpha]}{\Delta W \dagger}$
A	1.48	31.0	
A	2.30	46.7	75
A	2.72	52.7	88
B	1.22	50.2	
B	4.60	76.3	86
C	0.68	51.5	
C	2.30	69.3	77

* Weight (W) in grams of polymer per millimole of phenylalanine. † $\Delta W[\alpha]/\Delta W$. Optical activity of the polymer formed between the two subsequent drawings.

interpretation of stereospecific catalysis of vinyl monomers. They suggest that a higher stereospecificity can be expected when using catalysts, the active centers of which are per se asymmetric, than when symmetric catalysts are used, in which the stereospecificity derives from asymmetric induction brought about by the configuration assumed by the last polymerized unit.

Even before the discovery of the asymmetric synthesis of high polymers, we attributed (106) the stereospecificity of certain heterogeneous catalysts, prepared by reaction of solid titanium halides, to the fact that the active centers contain surface atoms of a transition metal having coordination number 6. In fact it is known that, in such a case, when at least two of the coordinated groups show a different chemical nature with respect to the others, enantiomorphous structures of the surface complexes can exist.

The high stereospecificity of such catalysts is probably due to the fact that the initial complex maintains its asymmetry even when linked to the growing chain.

An interesting aspect of the asymmetric polymerization of benzofuran consists in an autocatalytic effect ob-

served in the first reaction period. In fact it was noticed that the optical activity of the polymers increases as the polymerization proceeds (107) (Table 8).

To clarify this phenomenon further, polymerization runs have been performed in the presence of optically active polybenzofuran previously obtained.

Although the sign of the optical activity always corresponds to that of the β -phenylalanine complexed with the counterion, nevertheless the presence of preformed polymer, obtained in the same polymerization or added to the catalytic system at the beginning of the polymerization, causes an increase in the optical activity of the polymer newly formed.

Such an observation may have an interest that goes beyond the interpretation of stereospecific polymerization; in fact it can suggest suitable patterns characteristic of certain biological processes in which the formation of asymmetric molecules or groups of a given type is connected with the preexistence of optically active macromolecules.

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