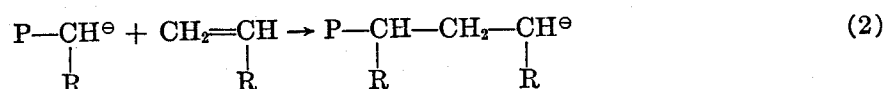
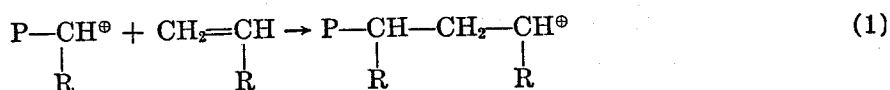


COORDINATE POLYMERIZATION

This article describes the main properties of coordinate polymerization and reports briefly on the catalysts that act through an ionic coordinate mechanism and the different types of stereoregularity present in the polymers obtained by these catalysts. It only describes the addition polymerization of monomers that leads to the formation of polymers having, exclusively, carbon atoms in the main chain, although some polar monomers, such as aldehydes and cyclic ethers have also been polymerized in a stereospecific manner by an ionic coordinate mechanism (see ALDEHYDE POLYMERS; EPOXIDE POLYMERS). For a more extensive discussion, see STEREOREGULAR-LINEAR POLYMERS.

Addition polymerization processes are usually grouped according to the reaction mechanism in the following manner: (a) radical processes, in which the end group of the growing polymeric chain is a free radical (the process is generally initiated by substances or energy sources capable of yielding or producing free radicals (see FREE-RADICAL POLYMERIZATION)), (b) ionic processes, in which the bond between the terminal atom of the growing chain and the catalyst is of an ionic type or is strongly polarized. These processes are cationic (qv) when the growing chain presents a positive charge, though partial, whereas they are anionic (qv) when this charge is negative.

In general, the propagation reaction in an ionic polymerization has long been considered as a simple addition of the polarized monomer unit at the end of the chain exhibiting the positive or the negative charge (eqs. 1 and 2).



For the sake of simplicity, this scheme fails to include in the growth reaction the counterion associated with the end of the chain by electrostatic attraction or by means of a polarized covalent bond since the type of association depends on the nature of the ionic pair components and on the solvent (eg, in an anionic polymerization).



Only since 1955, after the discovery of new catalysts leading to the formation of polymers with an exceptional regularity of structure, was it found that in many ionic polymerizations the counterion controls the propagation reaction by *coordinating* and by *orienting* the monomer before its insertion in the bond between the counterion and the growing chain. These are the reasons why these particular polymerizations have been defined as *ionic coordinate* (or ionic coordinated) (1). The term *coordination polymerization* has also been used, but it introduces a needless confusion with coordination polymers (qv), which are derived by entirely different methods.

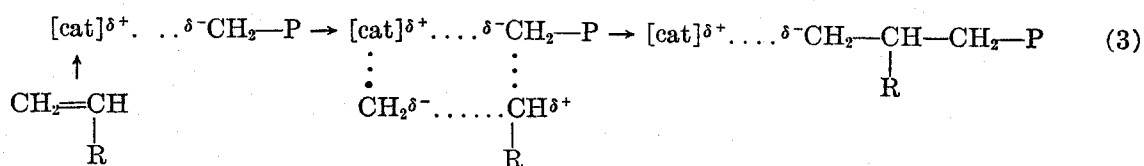
In practice, a sharp distinction between merely ionic and coordinate ionic processes hardly can be drawn: in fact many processes usually described as merely ionic also involve a precomplexation of the monomer with the catalyst. However, several cases exist in which the presence in the catalyst of metals having a particular tendency to coordinate with the unsaturated monomers can influence considerably the rate of

reaction or can act, in a selective or elective manner, in inducing a particular type of polymerization or the formation of polymers having a particular chemical or steric structure. In general, the *ionic coordinate catalysts* are electron-deficient complexes which contain a metal that has a marked tendency to form complexes and to coordinate the monomer molecules, and, sometimes, the unsaturated groups present in the last monomeric unit of the growing polymeric chain.

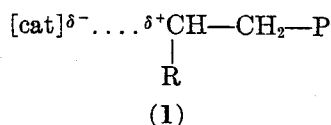
The metals most frequently found as components of the catalysts acting through an ionic coordinated mechanism are some light elements of the first, second, and third group of the periodic system (eg, Li, Be, Mg, Al) present as organometallic compounds, and several transition metals (eg, Ti, V, Cr, Mo, Rh, Ru, Co, Ni) present in a valence state lower than the maximum, thus corresponding to a higher electropositivity.

With the former elements, the coordination with the monomer involves overlap of the π electrons of the double bond with vacant *sp* hybrid orbitals of the metal; in the case of the transition elements, complexation occurs through their *d* orbitals. In the polymerization of vinyl monomers, eg, in the case of monomers containing atoms with unbonded electron pairs, such as oxygen and nitrogen, the coordination can involve such electron pairs in addition to the π electrons of the double bond. Thus, the resulting coordination complexes are more stable than those obtained if the coordination involves only the electrons of the vinyl double bond.

As in ionic polymerizations, two different cases can be distinguished in ionic coordinate polymerization: the terminal carbon atom of the growing chain can exhibit a partial negative charge δ^- (anionic coordinate) or a partial positive charge δ^+ (cationic coordinate). These two cases will be dealt with separately, although the polymerization mechanisms show some analogies. In both cases, the growth reaction occurs in two steps; first, coordination of the monomer to the counterion of the catalyst; second, insertion of the polarized double bond of the monomer in the polarized bond between the counterion and the end group of the growing chain. In the case of coordinate anionic polymerization of olefins, the polymerization reaction takes place according to equation 3, where $[\text{cat}]^{\delta^+}$ may be a catalyst complex or a metal ion.



In coordinate cationic catalysis, the mechanism differs exclusively from the above in the opposite dislocation of the partial charges and in the location of the positive charge on the more highly substituted carbon atom (1).



The great importance, both theoretical and practical, of coordinated catalysis is due to the fact that the nature of the coordinating metal present in the catalyst can impose a particular orientation to the adsorbed monomer; thus, in many cases, the same monomer can yield polymers with different steric structures to which different chemical and physical properties correspond. In many cases, the exceptional steric

regularity in addition to the chemical regularity of the polymer chain can result in the crystallizability of the polymer.

The two cases relating to anionic coordinate and cationic coordinate polymerizations will be examined separately.

Coordinate Anionic Polymerization

An essential condition for an anionic coordinate polymerization of a vinyl monomer is, as already pointed out, that the monomer be complexed by a metal atom of the catalytic system before its insertion in a metal-carbon bond, the carbon atom of this bond having a partial negative charge. The most commonly used catalysts in anionic coordinate polymerization contain organometallic compounds of lithium, beryllium, magnesium, and aluminum, which exhibit some peculiar properties. Firstly, these metals show a high electron-withdrawing power, and consequently have the ability to coordinate with the monomer double bond. This property is demonstrated especially by those metals that, having a small ionic radius, determine the formation of a very intense electric field (see Table 1). In fact, among the elements of the first

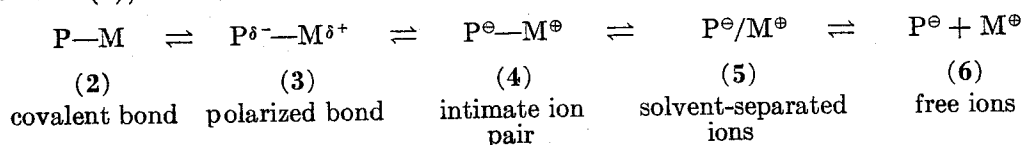
Table 1. Properties of Some Metals of Groups 1-3

Metal	Electronegativity (according to Pauling)	Atomic radius, ^a Å	Ionic radius, ^a Å
Li	1	1.33	0.68
Na	0.9	1.57	0.97
K	0.8	2.03	1.33
Rb	0.8	2.16	1.47
Cs	0.7	2.35	1.67
Be	1.5	0.90	0.35
Mg	1.2	1.36	0.66
Zn	1.5	1.31	0.74
B	2	0.88	0.23
Al	1.5	1.26	0.51

^a See Ref. 2.

group of the periodic system, only the organometallic compounds of lithium show a considerable tendency to give stereospecific catalysts. This tendency decreases for the elements of the same group with increase of the atomic radius. Secondly, a further requisite of anionic coordinate polymerization is the presence of a covalent bond, at least partially polarized, between the metal of the catalyst and the end carbon atom of the polymer chain.

Since the anionic coordinate polymerization in the presence of the organometallic compounds mentioned above can be considered as the formation reaction of a high-molecular-weight organometallic compound, in analogy with the stepwise growth of the alkylaluminum compounds in the reaction with ethylene (see ALUMINUM COMPOUNDS), the ionization of the bond between the metal and the polymer can be represented as the ionic dissociation of the metal-carbon bond in the organometallic compounds (3), as follows:



The degree of ionization of the bond not only depends on the electropositivity of the metal, but also on the resonance stabilization of the anion and on the degree of solvation of the cation.

Anionic coordinate polymerization will probably occur only when the bond between the metal and the polymer chain is of type (3). Sterically regular structures of polymers are generally obtained when free ions are not present, but when there is a certain degree of polarization, as in (3). Therefore, when the metal is very electropositive or the polymerization is carried out in the presence of solvents with high solvating power, such as ethers or amines, it can be assumed that the growing polymer anion is essentially a free ion, (6), and that the positive counterion exerts only a very slight influence on the regularity of the growth reaction.

Therefore, it may be assumed that, in the anionic polymerization of some vinyl monomers (eg, methyl methacrylate (4,5), acrylic esters (6), 2-vinylpyridine (7), styrene (8), diolefins (9,10), *N,N*-dialkylacrylamides (10), vinyl ketones (11), etc) catalyzed by organometallic compounds, the variations observed in the stereoregularity of the polymers obtained when the metal of the catalyst or the reaction medium is varied are due to the fact that the polymerization mechanism becomes, instead of an anionic coordinated, an essentially anionic one.

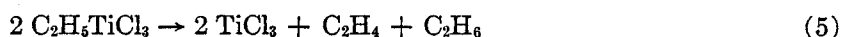
A particular type of anionic coordinate polymerization was carried out by complex catalysts obtained by reaction between organometallic derivatives of metals of the first three groups of the periodic system and transition metal compounds. Professor Ziegler was the first to prepare these catalysts and to use them in 1953 for the low-pressure polymerization of ethylene (12). Such a discovery immediately had worldwide impact and spurred a considerable amount of research in industrial and university laboratories on different monomers. See also ZIEGLER-NATTA CATALYSTS.

Olefins. The interest aroused by Ziegler's discovery was due not only to the greater safety presented by the low-pressure process for the polymerization of ethylene as compared with the high-pressure method (which was the only previously known process used for commercial production of polyethylene), but, above all, to the better properties of the resultant polymer. In fact, the crystallinity, density, melting point, and mechanical properties of Ziegler's polyethylene are higher than those of the same polymer obtained by high-pressure radical processes. These differences are due to a higher chain linearity resulting from the smaller number of branches than in the previously known polymers of ethylene.

The first catalysts, more thoroughly described by Ziegler, were obtained by the reaction of a compound of a transition metal of high valency, soluble in hydrocarbons, (eg, TiCl_4) with an alkylaluminum compound (R_3Al) or an alkylaluminum halide (R_2AlCl). At first, an alkylation reaction occurs by substitution of a group or of an atom (eg, Cl) of the transition metal compound with an alkyl group of the organometallic compound (eq. 4).



Due to the poor stability of the organometallic compounds of the transition metals with high valence, such a reaction usually is followed by a reductive dealkylation of these compounds (eq. 5).



The compound of the transition metal with lower valence can react again with the organometallic compound to give bimetallic electron-deficient complexes, charac-

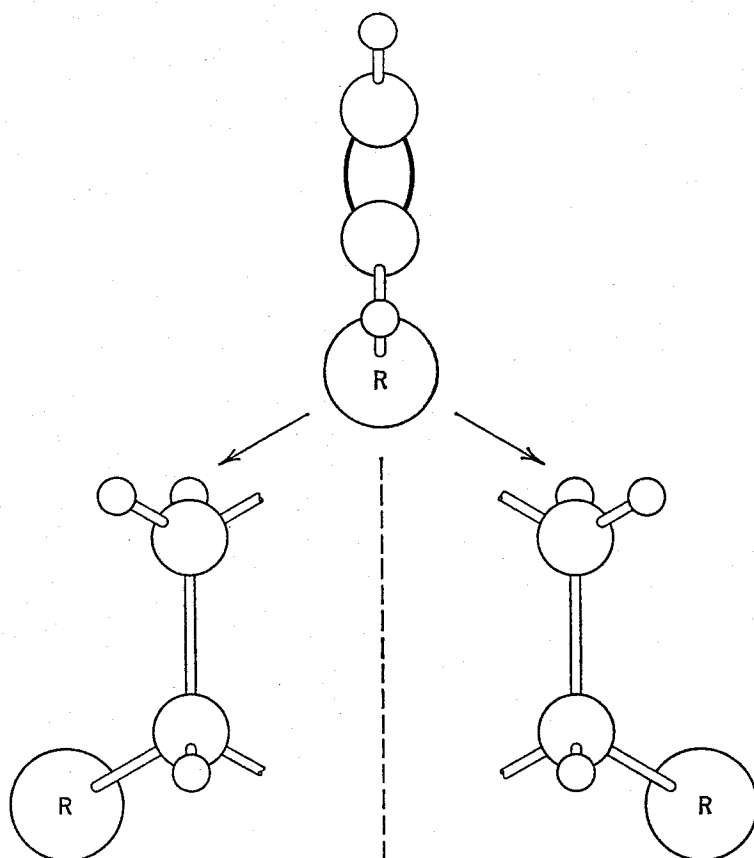


Fig. 1. Enantiomorphous monomeric units derived from a vinyl monomer, $\text{CH}_2=\text{CHR}$.

terized by bridge structures (eg, two chlorine bridges) between the two metals. It is these complexes, which are often of not well-defined composition, that constitute the polymerization catalysts.

The first catalysts were described by Ziegler for the low-pressure polymerization of ethylene. After selecting or modifying these catalysts, Natta and his school used them, from 1954 onward, largely for the highly stereospecific polymerization of α -olefins, of diolefins, and of other monomers.

Whereas a crystalline polyethylene can be obtained simply by synthesizing a linear chain with the least possible number of branches, the crystallizability of a polymer obtained from a monomer of the $\text{CH}_2=\text{CHR}$ type requires a high regularity of structure. Very important for this are *chemical regularity*, that is, a regular head-to-tail arrangement with no branches longer than R, and, consequently, the use of processes that do not give rise either to chain transfer or to copolymers between the monomer and its low polymers. A *high regularity of the steric structure* is also necessary. Due to the tetrahedral configuration of the valences of the carbon atom, a monomer of the $\text{CH}_2=\text{CHR}$ type can yield, by the opening of the double bond, one of the two monomer units represented in Figure 1. These units are enantiomorphous, ie, one is the mirror image of the other.

In order to obtain a polymer with a stereoregularity of the *isotactic* type, a regular head-to-tail arrangement of monomer units having all the same steric configuration is necessary. By contrast, a regular succession of monomer units having alternately one or the other of the two enantiomorphous configurations leads to a polymer having stereoregularity of the *syndiotactic* type; on the other hand, a head-to-tail arrangement

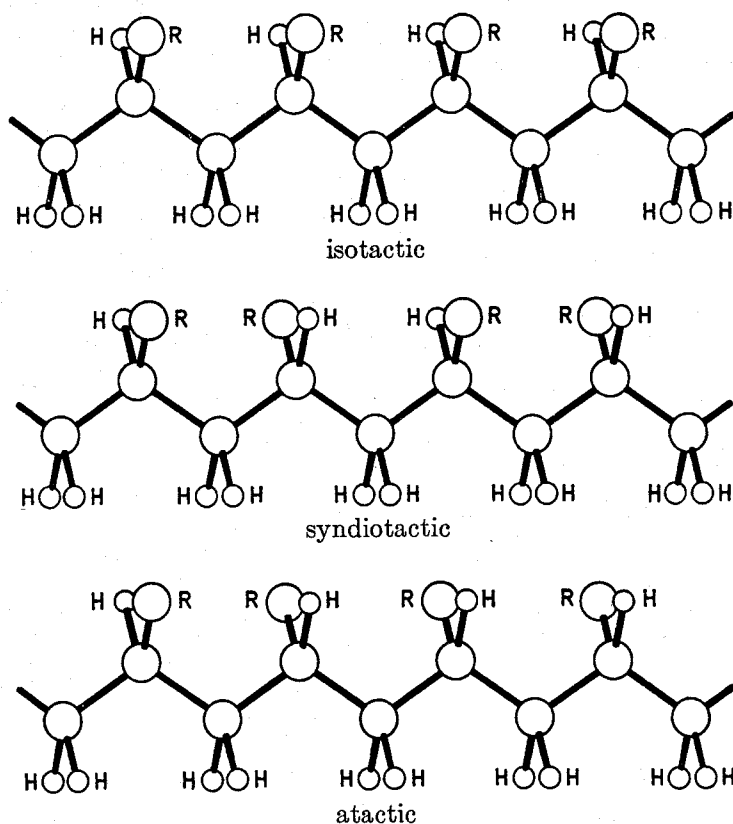
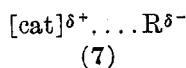


Fig. 2. Chains of different stereoisomers of vinyl polymers (main chain arbitrarily stretched on a plane).

with an unordered succession of monomer units of the two steric configurations leads to the formation of an *atactic* polymer; this polymer is amorphous. Figure 2 shows the chains of these different types of stereoisomeric vinyl polymers, arbitrarily stretched on a plane.

A convenient choice of the catalyst system allows one to obtain either the isotactic, syndiotactic, or atactic polymer of propylene. The catalysts used by Natta and co-workers for the polymerization of propylene to syndiotactic polymer are homogeneous and are stereospecific only at very low temperatures (eg, -70°C); on the other hand, the systems used for the polymerization of α -olefins to isotactic polymers are heterogeneous. Except as noted above for syndiotactic polymers, homogeneous or highly dispersed catalysts generally lead to the formation of atactic polymers (Table 2).

It must be assumed that the catalytic complexes obtained by reaction between the transition metal compounds and the organometallic derivatives of metals of the first, second, and third group of the periodic system contain metal-carbon bonds in which the monomer units are inserted. These complexes can be represented by (7)



where R is the alkyl group which is initially present in the organometallic compound and which, after completion of the polymerization, is found in the polymer as an end group (16). The metal-carbon bond is polarized in such a manner that the partial negative charge is located on the carbon atom. It is likely that in all the catalyst systems reported in Table 2, even in those yielding atactic polymers, the

monomer molecule, before being inserted in the $[\text{cat}]^{\delta+} \dots \text{R}^{\delta-}$ bond, is *coordinated* by the ion of the transition metal present. In the catalysts containing TiCl_3 , such a coordination was considered to be an overlap of the π electrons of the olefin with the vacant orbital $d_{x^2 - y^2}$ of titanium and a simultaneous transfer of electrons from the d_{xy} orbital of titanium into the vacant antibonding orbital of the olefin (17).

It should be noted that the coordination of the olefin to the transition metal does not always determine by itself the stereospecific growth of the polymer chain. In order to obtain an isotactic polymer, the presence of other steric order limitations is required, when the monomer approaches the bond between catalyst and polymer. These conditions come true when the polymerization takes place in the presence of crystalline salts of transition metals having a layer lattice (eg, the violet modifications of TiCl_3). In this case, the coordination of the olefin to transition metal atoms, in particular to

Table 2. Stereoisomerism in the Polymerization of Propylene by Ziegler-Natta Catalysts

Transition metal compound ^a	Organometallic compound	Physical state of catalyst system	Type of stereoisomerism of polymer	Ref.
crystalline compounds having valence lower than maximum with a layer lattice of ions, eg, TiCl_3 , TiCl_2 , VCl_3 , CrCl_3	organometallic compounds of Be, Al	heterogeneous	predominantly isotactic	13
hydrocarbon-soluble compounds with higher valence, eg, TiCl_4 , VCl_4 , VOCl_3	organometallic compounds of Be, Al	partially heterogeneous	both atactic and isotactic	14
$\text{VO}(\text{OR})_3$	dialkylaluminum halides	homogeneous at low temperature	atactic	
$\text{VCl}_4 \cdot \text{An}$, $\text{V}(\text{AcAc})_3$ -30°C -78°C	dialkylaluminum halides	homogeneous at low temperature	atactic syndiotactic	15

^a An = anisole; AcAc = acetylacetonate.

the surface atoms arranged on the crystal edges and on other discontinuities or irregularities of the outer faces, can take place exclusively according to particular steric configurations. Thus, the configuration of the monomer molecule is *controlled* at the moment of its insertion in the bond between the growing chain and the catalyst complex containing the coordinating transition metal.

The stereoregularity in poly- α -olefins is important because the crystalline polymers have a high melting temperature and such mechanical properties that they can be advantageously used in plastics, textile fibers, and films (18). Since the production of these stereoregular polymers is possible only by anionic coordinate catalysis, the commercial importance of this type of polymerization is readily apparent. See also ETHYLENE POLYMERS; PROPYLENE POLYMERS.

Dienes. The versatility and selectivity of the catalysts acting through an ionic coordinate mechanism are even more evident in the polymerization of conjugated dienes.

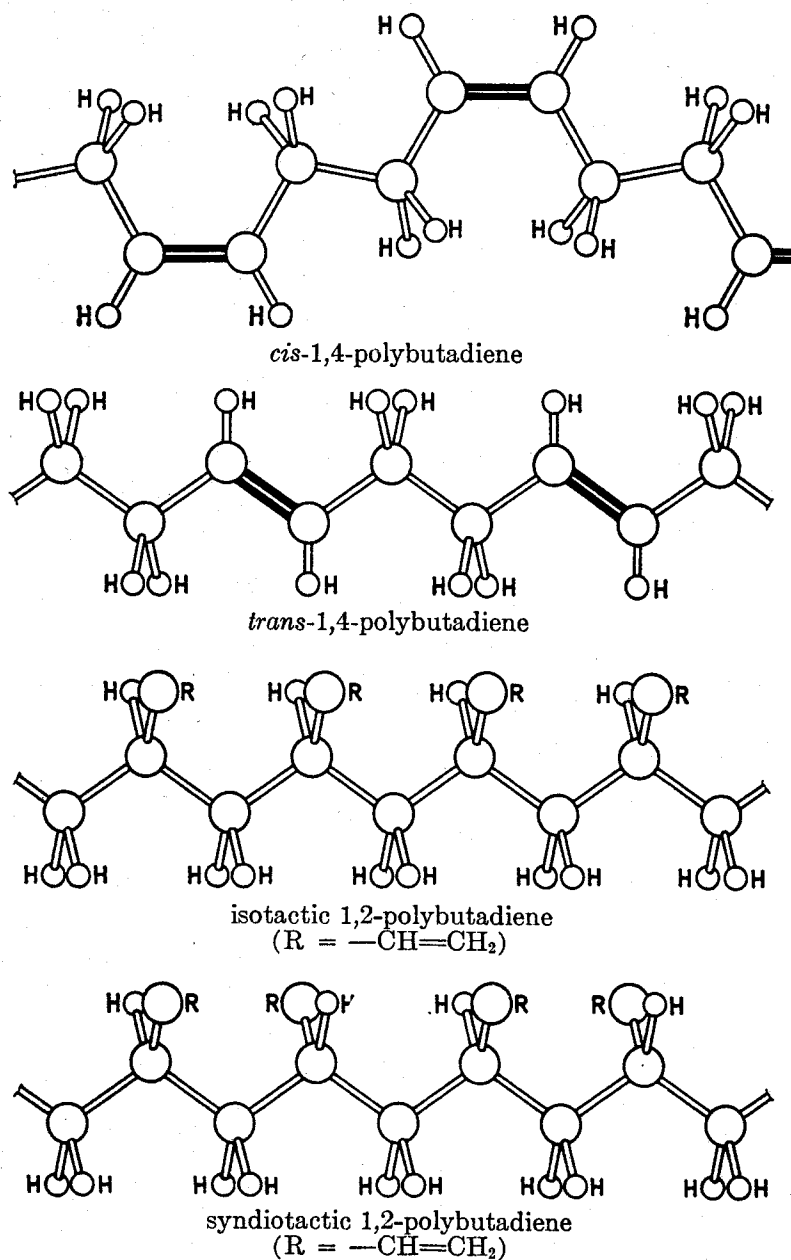


Fig. 3. Chains of the four regular stereoisomers of polybutadiene (main chain arbitrarily stretched on a plane).

Various types of stereoisomerism can be shown to exist in the linear polymers of butadiene. In analogy with what occurs for the vinyl polymers, both isotactic and syndiotactic configurations arise from 1,2 polymerization; on the other hand, if the polymerization occurs by 1,4 addition, the unsaturated linkages present in the polymer chain can assume both the cis and the trans configurations (see Fig. 3). By choosing a suitable combination of organometallic aluminum derivative and transition metal compound, the four stereoisomeric polymers can be obtained with a high degree of purity (see Table 3). The four stereoisomeric polymers of butadiene exhibit different physical properties as shown in Table 4 (see also BUTADIENE POLYMERS).

Three of the six possible stereoregular polymers of isoprene are also obtained by suitable catalytic combinations (Table 5). Two of them have a steric structure that corresponds to the structure of the natural polymers of isoprene, ie, the *cis*-1,4

Table 3. Catalysts for the Preparation of Stereoisomeric Polymers of Butadiene

Catalyst system ^b	Microstructure of the polymers			Reference
	<i>trans</i> -1,4 %	<i>cis</i> -1,4, %	1,2, %	
R ₂ Al or R ₂ AlCl + VOCl ₃ , VCl ₄ , or VCl ₃ (heterogeneous)	97-99	0	1-3	19
R ₂ AlCl + VCl ₃ · 3 THF (homogeneous)	99	0	1	20
R ₂ Al + TiI ₄ (heterogeneous)	1.5-2	93-94	4.5-5	21
R ₂ AlCl + cobalt compounds (homogeneous)	1	98	1	22
R ₂ Al + MoO ₂ (OR) ₂ or MoO ₂ (AcAc) ₃ (homogeneous)	1-2 ^a	3-6	92-96 (syndiotactic)	23
R ₂ Al + Cr(AcAc) ₃ or Cr(CO) ₅ Py high Al/Cr ratio (homogeneous)	^a	0-3	97-99 (isotactic)	24

^a Crystalline fraction.

^b AcAc = acetylacetone; Py = pyridine; THF = tetrahydrofuran.

Table 4. Physical Properties of the Four Stereoregular Polymers of Butadiene

Polymer	Melting temperature, °C	Identity period, Å	Density, g/ml
<i>trans</i> -1,4 (99-100%)	146	4.85 (modification I)	0.97
		4.65 (modification II)	0.93
<i>cis</i> -1,4 (98-99%)	2	8.6	1.01
isotactic-1,2 (99% of 1,2 units)	126	6.5	0.96
syndiotactic-1,2 (99% of 1,2 units)	156	5.14	0.96

Table 5. Catalysts Used for the Preparation of Stereoisomeric Polymers of Isoprene

Catalyst system	Microstructure of the polymer			Reference
	<i>trans</i> -1,4, %	<i>cis</i> -1,4, %	3,4, %	
R ₂ Al + TiCl ₄ (heterogeneous)				
Al:Ti > 1		96	4	25
Al:Ti < 1	95		5	
R ₂ Al + VCl ₃ (heterogeneous)	99-100			19
R ₂ Al + V(AcAc) ₃ or Ti(OR) ₄ (homogeneous)			95	26

structure corresponding to hevea rubber, and the *trans*-1,4 structure to that of gutta percha (see also ISOPRENE POLYMERS).

In the case of butadienes monosubstituted in the 1 position, CHR=CH—CH=CH₂, or disubstituted in the 1,4 positions, CHR'=CH—CH=CHR'', anionic coordinate polymerization allows the preparation of new classes of polymers having a steric regularity of higher order than that of other polymers previously described, ie, *ditactic* and *tritactic* polymers (27). In fact, the 1,4-polymerization of these monomers yields linear macromolecules which can exhibit more than one center of stereoisomerism. In addition to the *cis* and *trans* isomers of the internal double bonds of the main chain, optical isomerism is also possible because of the presence of asymmetric carbon atoms in the main chain. Thus, for instance, 1,3-pentadiene

can yield *trans*-1,4-isotactic (28) and *cis*-1,4-isotactic (29) or *cis*-1,4-syndiotactic polymers (30).

Although the mechanism of the polymerization of conjugated dienes has not been completely clarified, recent results appear to confirm the hypothesis that the growth of the polymer chain occurs by coordination of the monomer to the transition metal and, at least in some cases, by subsequent insertion of the coordinated monomer in a π -allylic bond between the transition metal and the last polymerized monomeric unit (31). According to this hypothesis, some π allylic compounds of transition metals of the eighth group catalyze the stereospecific polymerization of butadiene and other dienes (32).

This mechanism explains why the stereospecific polymerization of conjugated dienes can in some cases occur in the homogeneous phase. In fact, the formation of a rigid complex between the transition metal, the two double bonds of the diene coordinated to it, and the π allyl group of the last monomer unit of the growing chain restricts considerably the degree of freedom of the monomer at the moment of its insertion in the bond between the catalyst and the polymer chain; thus, a stereospecific polymerization is possible, even in the absence of a solid surface.

Monomer coordination to the catalyst is clearly evidenced by the influence exerted by some π -electron donor solvents (which can compete with the monomer for the catalyst) on the rate of polymerization and on the type of stereoregularity of the resulting polymer. In fact, in the polymerization of butadiene by the catalyst system $\text{CoCl}_2\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, some substituted aromatic hydrocarbons (mesitylene, hexamethylbenzene), if present in high concentrations, can inhibit the polymerization completely, the butadiene being displaced from the catalyst complex by the stronger π -electron donors (33). Moreover, the same catalyst system can yield polymers of 1,3-pentadiene having different types of stereoregularity, depending on whether the reaction is carried out in aromatic or aliphatic solvents (34).

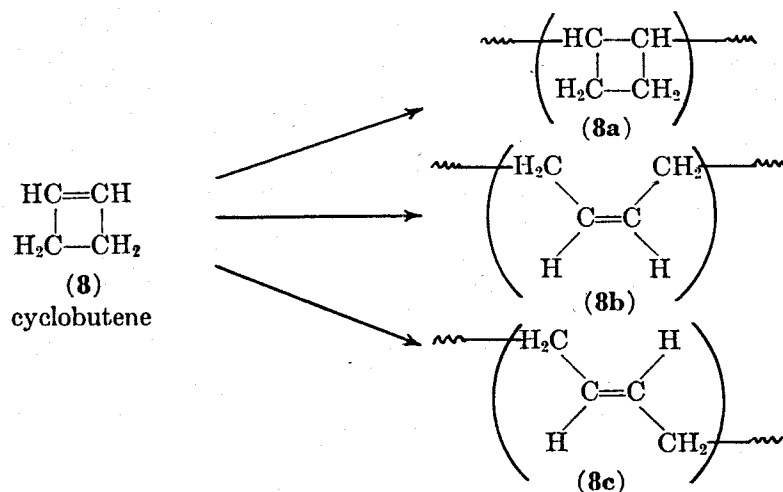
It is interesting to note that the stereospecific polymerization of isoprene to *cis*-1,4 polymer can be also promoted by organometallic compounds of lithium in hydrocarbon solvents (35). As in all anionic coordinate polymerizations catalyzed by organometallic compounds of metals of the first and second group of the periodic system, the presence of solvating or basic solvents, such as ethers and amines, causes a decrease in the stereospecificity of the polymerization, with consequent formation of polyisoprene with a predominantly 3,4 structure.

Other Monomers. The polymerization of monomers with an internal double bond is of particular interest. Aliphatic olefins with an internal double bond do not homopolymerize well owing to steric hindrance. In some cases, some of these monomers (eg, *cis*-2-butene) can be copolymerized with ethylene and, under certain conditions, crystalline alternating stereoregular copolymers are obtained. The stereoregularity of polymers is of the diisotactic type (36).

The anionic coordinate polymerization of cyclic olefins, such as cyclobutene (8), yields, depending on the catalyst used, either polymers with saturated cyclic monomer units by the opening of the monomer double bond (8a), or else unsaturated linear monomer units by the opening of a single bond of the ring. In the latter case, if the cycloolefin is not substituted, the polymers obtained show stereoisomerism of the geometric type only (37) (8b), (8c).

Two polymers (polypentenamers) having respectively *cis* and *trans* structures, can be obtained also from cyclopentene by ring cleavage, depending on the nature of

the transition metal used (38). The elastomeric properties of *trans*-polybutadiene are very analogous to those of natural rubber; moreover, the former polymer, contrary to the latter, has no branches in the main chain, thereby allowing a more regular orientation and crystallization by stretching of the vulcanized products.



Coordinate Cationic Polymerization

Very few examples of coordinate cationic polymerizations leading to the formation of stereoregular polymers exist; moreover, they are almost exclusively limited to the polymerization of monomers containing heteroatoms with unbonded electron pairs, such as oxygen and nitrogen. The most important monomers polymerized by coordinate cationic catalysts are: vinyl ethers (39), alkenyl ethers (40), β -chlorovinyl alkyl ethers (41), α -methylvinyl methyl ethers (42), 1-alkoxybutadiene (43), *o*-methoxystyrene (44), benzofuran (45), and vinyl diphenylamine (46).

The catalysts used in this type of polymerization are either compounds having a low Lewis-acid character, such as some modified Friedel-Crafts catalysts, or complexes obtained by reaction between an organometallic compound and a transition metal salt (Table 6).

Table 6. Catalysis Acting Through a Coordinate Cationic Mechanism

Simple catalysts	Complex catalysts	Reference
	<i>Soluble</i>	
$\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$		39
$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$; $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	$(\text{C}_6\text{H}_5)_2\text{TiCl}_2\text{AlCl}_2$	47
	$(\text{C}_6\text{H}_5)_2\text{TiCl}_2\text{AlCl}(\text{C}_2\text{H}_5)$	47
$\text{BF}_2(n\text{-C}_4\text{H}_9)$		48
	<i>Insoluble</i>	
$\text{TiCl}_2(\text{OCOR})_2$		47
$\text{TiCl}_2(\text{OR})_2$		47
$\text{TiF}_4 + \text{Ti}(\text{OR})_4$		49
$\text{Fe}_2(\text{SO}_4)_3 \cdot 6 \text{H}_2\text{SO}_4 \cdot n \text{H}_2\text{O}$		50
$\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O} + \text{H}_2\text{SO}_4$		51
AlF_3		52
CrO_3		53
TiF_4 , TiF_3 , VF_4		55
	$\text{AlR}_3 + \text{VCl}_3$	54

In cationic coordinate polymerization also, the negative counterion associated with the carbonium ion of the growing chain seems to participate in the growth reaction, coordinating the monomer before its addition to the polymer chain.

In the polymerization of monomers containing heteroatoms, both the monomer and the last monomer unit of the growing chain can coordinate to the metal of the counterion not only by the π electrons of the double bond, but also by the unbonded electron pairs of the heteroatom. Thus a complex forms which exhibits a stability sufficient to allow a close association between the ionic pair and to present the monomer molecule in a constant preferential orientation at the moment of its insertion between the catalyst and the growing chain.

Whereas cationic coordinate polymerizations taking place in the homogeneous phase are stereospecific only if carried out at low temperatures, some heterogeneous catalysts (eg, the $R_3Al-VCl_3$ system in the polymerization of vinyl ethers) allow a stereospecific polymerization at room temperature as well. In this case, it is likely that the coordination centers situated on the surface of the catalyst can form complexes with the ether oxygen of the monomer and of the polymer, even at higher temperatures.

Conclusion

The salient and general characteristics of coordinate ionic polymerizations have been pointed out in this article. Details have been given only for the cases of greater scientific and industrial interest and for the cases in which a coordination of the monomer to the catalyst during the polymerization is more evident.

The more distinctive aspects of these polymerizations will be considered in the article dealing with the polymerization of individual or classes of monomers, and under the headings STEREOREGULAR-LINEAR POLYMERS and ZIEGLER-NATTA CATALYSTS. These articles will describe in much greater detail the preparation and the exceptional properties of those polymers that have acquired or are acquiring great commercial importance. Among these, one may cite the isotactic polymers of propylene and some low-cost synthetic rubbers having high elastic and dynamic properties, such as the amorphous ethylene-propylene copolymers (56) and the stereoregular *cis*-1,4 polymers of butadiene and isoprene; these elastomeric polymers have brought about a complete revolution in the synthetic rubber industry (see also ELASTOMERS, SYNTHETIC).

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