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Stereospecific Polymerizations

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Most of the research work carried out by my school in these last five years has dealt with the field of stereospecific polymerization and has been documented in more than 160 scientific publications.

For lack of time, I shall only refer here to some of our work in the field of the stereospecific polymerization processes (both anionic and cationic) which we define as "ionic coordinated." Recently we have developed cationic processes for polymerization of monomers which, owing to the presence of atoms containing lone electron pairs, can deactivate some metalloorganic catalysts (for instance, the ones used by Ziegler and by us in the polymerization of olefinic hydrocarbons).

I shall refer particularly to the processes we have been using for some time for the polymerization of butadiene which allow us to obtain four different types of sterically pure polymers in the crystalline state and to determine the lattice structure. In Figure 1 are shown the conformations, as determined by us, which are assumed in the crystals by the chains of the four crystalline polybutadiene stereoisomers. These polymerization processes illustrate well the great number of problems which can be solved with the use of different types of stereospecific catalysts, and the variety of products which can be obtained by varying the steric purity.

With regard to butadiene, I feel obliged to mention that the first and most important syntheses of butadiene rubber by anionic processes were successfully accomplished in Russia: fifty years ago, Lebedev and Ostromislensky were pioneers in the synthesis of butadiene by means of processes which subsequently found important applications also in Italy. The polymerization of butadiene with sodium as catalyst is another early example of polymerization carried out by means of metalloorganic catalysts (the catalyst being formed by reaction of sodium with butadiene). This process (as well as the other processes known before 1954) is neither chemically nor sterically specific.

Stereospecificity in polymerizations carried out by polyaddition appears when, at the very moment of their addition, the single monomeric units assume a chemical and steric regularity of structure.[1–3] This stereospecificity is associated, with few exceptions (in cases of nonhydrocarbon monomers), with the use of complexes which act as catalysts with an ionic coordinated mechanism: i.e., the catalytic complexes show an electrophilic character, being able, under conditions under which they show catalytic

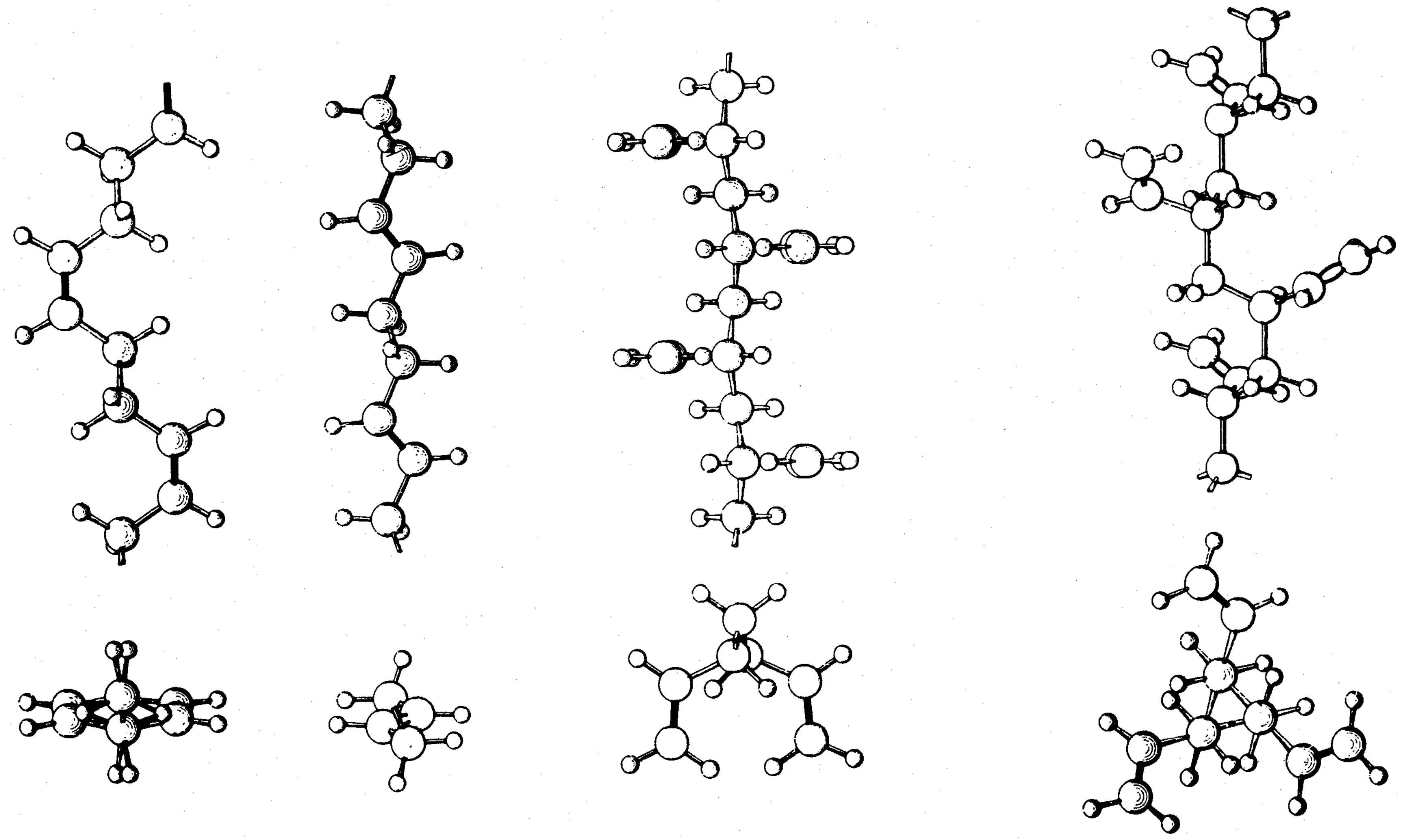


Fig. 1. Chain conformations in the crystals of the four polybutadiene stereoisomers. Left to right: polybutadienes with *trans*-*cis*-1,4 enchainment; with syndiotactic- and isotactic-1,2 enchainment.

activity, to coordinate more or less loosely the nucleophilic groups present in the monomer.

In the case of α-olefins, the catalytic complexes are usually bimetallic; they are characterized by the presence of bridge bonds[4] and act stereospecifically on the surface of a crystalline solid phase.

Stereoregular Polybutadienes

When the monomers to be polymerized contain two groups which can be coordinated to the catalytic complex (for example, by virtue of two double bonds as in conjugated diolefins, or a double bond and one atom with a lone electron pair as in vinyl ethers or in vinylpyridines), both anionic and cationic polymerizations may take place with soluble catalysts. Owing to this behavior the polymerization of diolefins differs from the stereospecific polymerization of α-olefins.

Thus butadiene may give *cis*-1,4 polymers of high purity with some soluble catalysts, such as those which can be obtained from hydrocarbon-soluble complexes of metals of the eighth group formed by the action of dialkylaluminum chloride on different salts of these metals.[5–8]

In many cases, the purity of the catalytic complex and its physical state (homogeneous or heterogeneous phase) influence the steric purity. For instance, soluble complexes between cobalt salts and AlR_2Cl give *cis*-1,4 polymers which are purer than those obtained with the use of complexes acting in heterogeneous phase (Table I). Thus we were able, by operating at low temperature (and at very small concentrations of the transition metal compound), to obtain polymers having a steric purity higher than 99% in *cis* units; these polymers show very interesting elastic properties. Highly *cis*-1,4 polyisoprenes are obtained also with other homogeneous catalysts, for instance, hydrocarbon solutions of lithium alkyls.[18]

TABLE I
Polymerization of Butadiene to Prevailingly *cis*-1,4 Polymers

Catalytic systems	Polymers			M.p., °C.
	cis-1,4, %	*trans*-1,4, %	1,2, %	
AlR_2Cl–$TiCl_3$ (β) (heterogeneous)[a]	55–60	36–41	4	—
AlR_3–TiI_4	93–94	1.5–2	4.5–5	−(8–10)
AlR_2Cl–$CoCl_2$	96–97	2.5	1–1.5	+(0–1)
AlR_2Cl–(cobalt compounds) (homogeneous)	>98	<1	<1	+1
AlR_2Cl–(nickel compounds)[b]	95	3	2	—

[a] Amorphous *cis-trans* copolymers of different compositions.

[b] Lower molecular weight material: $[\eta] = 0.6$–0.8 100 cm.^{3}/g.

The polymers containing long segments with very high *cis*-1,4 content (>96%) have, in the vulcanized state, the property of crystallizing under stretching.[9–12] This behavior, which is characteristic of natural rubber also, is emphasized and can be observed at lesser elongations when the *cis*-1,4 content is above 98–99%.

In Table I are indicated also the melting temperatures of other polybutadienes prepared with the use of catalytic systems[13] which, according to our research tests, appeared to be less stereospecific.

The separation of some crystalline complexes, now under study at our Institute, from certain catalytic systems that promote the *cis*-1,4 polymerization is feasible and will allow us to clarify further some characteristics of the stereospecific polymerization of diolefins.

Trans-1,4-polybutadiene with high steric purity is more easily obtained by means of heterogeneous catalysts such as VCl_3 and AlR_3 (Table II); this result probably is related to an adsorption of butadiene on the catalyst, to which both the double bonds are connected in a staggered arrangement.[14–15]

TABLE II

Polymerization of Butadiene to Prevailingly *trans*-1,4 Polymers

Catalytic system (heterogeneous)	Polymer		
	trans-1,4, %	*cis*-1,4, %	1,2, %
AlR_3–VCl_3	99	—	1[a]
AlR_3–$VOCl_3$	97–98	—	2–3[a]
AlR_3–VCl_4	97–98	—	2–3[a]
AlR_3–$TiCl_3$ (α,γ)	80	12	8[b]
AlR_3–$TiCl_3$ (β)	66	29	5[c]

[a] The crude product contains a small amorphous fraction extractable with ethyl ether; the residue is >99% *trans* 1,4.

[b] Separable by extraction with ethyl ether into an amorphous fraction (25–30% of the total, prevailingly 1,4) and a crystalline fraction (insoluble in ether, 95–96% *trans* 1,4).

[c] Separable by extraction with ether into an amorphous fraction (30–35% of the total, prevailingly *cis* 1,4) and a crystalline fraction (90–95% *trans* 1,4).

By use of the same catalyst, *trans*-1,4-polyisoprene with high steric purity (99%) is obtained.[15]

In the presence of certain catalysts in which the transition metal (for instance, chromium or vanadium) is complexed in the starting compounds with several bifunctional molecules (as in the case of acetyl acetonates), a polymerization takes place with formation of 1,2 polymers. Most probably, in the catalytic complexes obtained by reaction with alkylaluminum, the presence of other groups coordinated to the transition metal prevents a further coordination of butadiene to this transition metal with both double bonds, and this favors the 1,2 polymerization.

Generally, by using catalysts of this type we obtained polymers whose steric composition varied both with the molar ratio of AlR_3 to the transition metal compound, and with the aging period. For instance, in the case of catalysts prepared from vanadium triacetyl acetonates, these factors influenced the proportion of crystalline polymer having a syndiotactic structure[16] (Table III).

TABLE III
Polymerization of Butadiene to Prevailingly 1,2 (Syndiotactic and Amorphous) Polymers with Homogeneous Systems Obtained from AlR_3 and Transition Metal Compounds

Catalytic system (homogeneous)	Molar ratio	Polymer	
		Amorphous fraction,[a] %	Syndiotactic fraction,[b] %
AlR_3–$Ti(OR)_4$	Al/Ti ~ 1/10	90	10[c]
AlR_3–$V(Ac\ ac)_3$	Al/V ~ 4 (unaged catalyst)	97–99	1–3
	Al/V ~10 (aged catalyst)	40	60
AlR_3–$MoO_2(OR)_2$	Al/Mo < 6	25	75
AlR_3–$MoO_2(Ac\ ac)_2$	Al/Mo < 6	25–30	70–75

[a] IR: 1,2, 75–80%; *cis*-1,4, 16–22%; *trans*-1,4, 3–7%.
[b] IR: 1,2, 92–96%; *cis*-1,4, 3–6%; *trans*-1,4, 1–2%, m. p., 156°C.
[c] The crude product usually contains a large amount of crosslinked polymer.

A particular case is presented by the catalysts acting in homogeneous phase that were obtained from AlR_3 and chromium compounds (Table IV); according to the Al/Cr ratio and the aging conditions of the experiments, these gave products containing crystalline fractions having syndiotactic or isotactic structure.[14]

TABLE IV
Polymerization of Butadiene to Prevailingly 1,2 (Syndiotactic, Isotactic, and Amorphous) Polymers with Homogeneous Systems Obtained from AlR_3 and Chromium Compounds

Catalytic systems (homogeneous)		Polymers
AlR_3–$Cr(Ac\ ac)_3$	Unaged catalysts, low Al/Cr ratio	Syndiotactic[a] + amorphous 1,2[b]
AlR_3–$Cr(CNC_6H_5)_6$		
AlR_3–$Cr(CO)_nPy_m$ $(m + n = 6)$	Aged catalysts, preferably high Al/Cr ratio	Isotactic[c] + amorphous 1,2[b]
AlR_3–$Cr[DiPy_2]_3$		

[a] IR: 1,2, 90–95%; *cis*-1,4, 4–6%; *trans*-1,4, 1–3%.
[b] IR: 1,2, 70–78%; *cis*-1,4, 20–25%; *trans*-1,4, 5–8%.
[c] IR: 1,2, 97–99%; *cis*-1,4, 1–3%; *trans*-1,4, traces.

In the polymerization of isoprene, the presence of oxygenated compounds, for instance of alkyl ethers, also acts to favor 1,2 enchainment.[18]

Stereospecific Polymerization of Nonhydrocarbon Monomers

The best-known Ziegler-type catalysts (obtained, for instance, from $TiCl_4$ and AlR_3) do not polymerize monomers containing elements with lone electron pairs such as O, N and (nonaromatic) Cl.

These monomers, in fact, react irreversibly with these catalysts, either joining them (vinyl ethers) or destroying them (vinyl or acrylic esters).

It is possible to polymerize these monomers with the use of different catalysts containing metalloorganic bonds, whose reactivity is reduced either by the presence of oxygen atoms and of halides bound to the complex, or by the choice of suitable operating conditions (for instance, very low temperatures).

Magnesium metalloorganic compounds act as catalysts in the stereospecific polymerizations of various nonhydrocarbon monomers such as acrylates,[19] methacrylates,[20] and 2-vinylpyridine.[21]

In some instances when an oxygen (or nitrogen) atom is present in the monomer in addition to the vinyl group, both the donor groups of the monomer may be coordinated, even if loosely. Thus it is possible to obtain a stereospecific polymerization even with catalysts which are soluble under the polymerization conditions.[4]

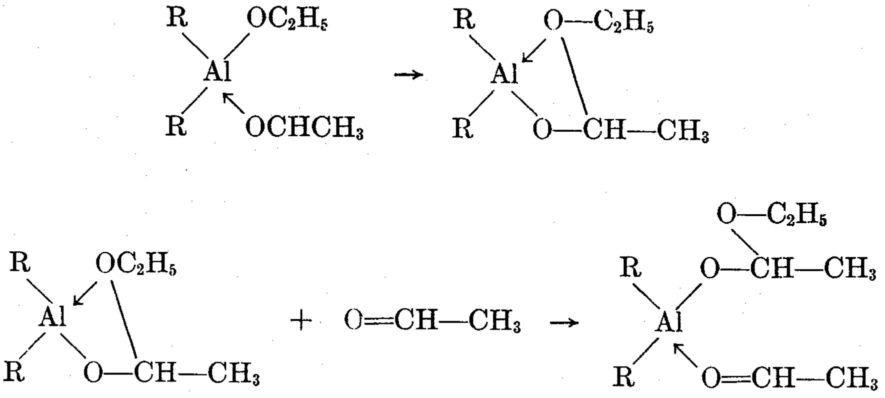
A method which allows one to demonstrate the anionic mechanism is based on the use of catalysts containing labeled carbon.

Metallorganic catalysts obtained from $Al(C_2H_5)_3$, $Be(C_2H_5)_2$, and LiC_2H_5 with labeled ethyl groups, with the addition of transition metal compounds, act by an anionic mechanism. The macromolecular chains formed at the beginning of the polymerization contain a labeled ethyl terminal group (for example, in the polymerizations of α-olefin polymers, vinylxylanes, vinyl derivatives of tin,[22] etc.).

When diethylaluminum alcoholates were used as catalysts in the polymerization of α-olefins by anionic catalysis, the presence of the ethyl group that was originally bound to the metal as the terminal group of the macromolecule was observed. On the other hand, in other polymerization processes the terminal alkyl group was observed to be simply that present in the alkyloxy group.

In the synthesis of isotactic polyaldehydes with $Al(C_2H_5)_2OC_2H_5$ as catalyst, ratioactive polymers are obtained only if the OC_2H_5 group contains labeled carbon atoms. On the other hand, nonradioactive polymers have been obtained with the use of labeled trialkylaluminum as catalyst.[23–25]

These results agree with the following mechanism, which was considered by us[23] in regard to the stereospecific polymerization of acetic aldehyde with catalysts containing alcoholate groups:



The acetaldehyde polymers obtained by us with the use of catalysts of this type are highly crystalline and insoluble in ether, acetone, benzene, etc.[23,25] By an x-ray examination we determined that their structure is isotactic. Their unit cell and chain conformation are shown in Figures 2 and 3.

Aldehydes higher than acetaldehyde (propionic, isobutyric, etc.) give isotactic polymers with a greater variety of stereospecific catalysts.[24,25]

A greater number of nonhydrocarbon monomers polymerize stereospecifically when catalysts acting with a cationic coordinated mechanism are used. Data on some stereoregular polymers obtained with catalysts of this type are shown in the Tables V and VI.

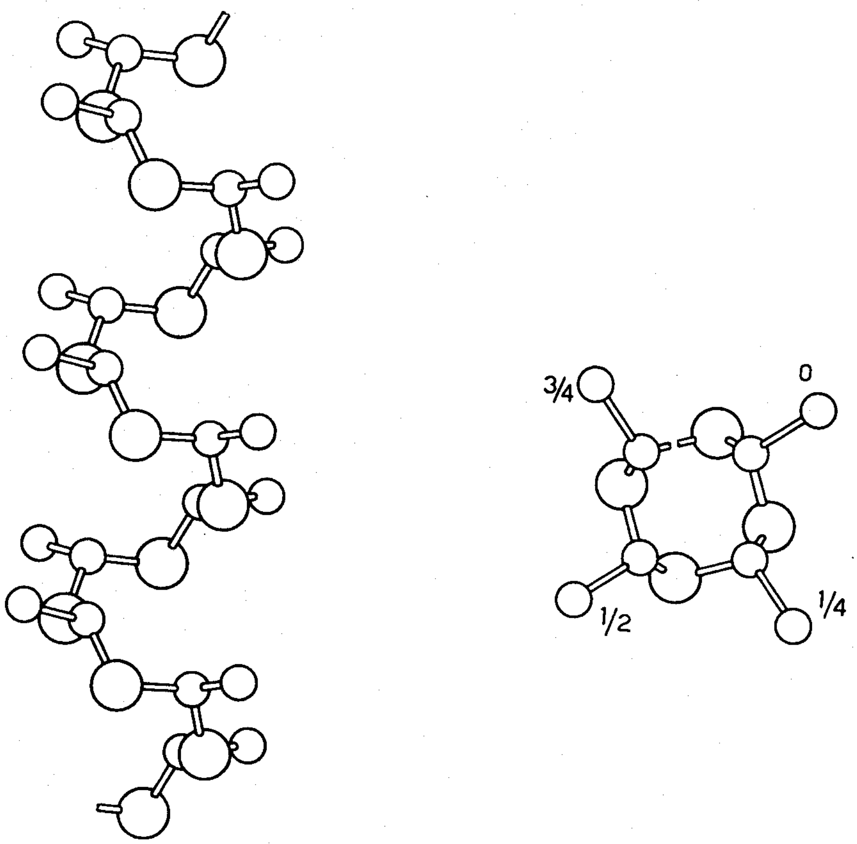


Fig. 2. Side and end views of the isotactic polyacetaldehyde macromolecule.

Vinyl ethers, as well as alkenylalkyl ethers[27] furnish isotactic polymers in the presence of particular cationic catalysts (Tables V and VI).[26] With the *trans* isomer of the monomer as the starting material, alkenyl alkyl ethers give diisotactic crystalline polymers.

Metal atoms with octet incompleteness are present in all the catalysts used in these stereospecific polymerizations. The oxygen atoms in the monomer may therefore be coordinated to the catalyst through bonds of the donor type.

It is interesting to notice that *ortho*-methoxystyrene polymerizes with homogeneous cationic catalysts, such as $AlCl_2C_2H_5$, giving polymers with an ordered structure, in contrast to styrene which gives atactic polymers under

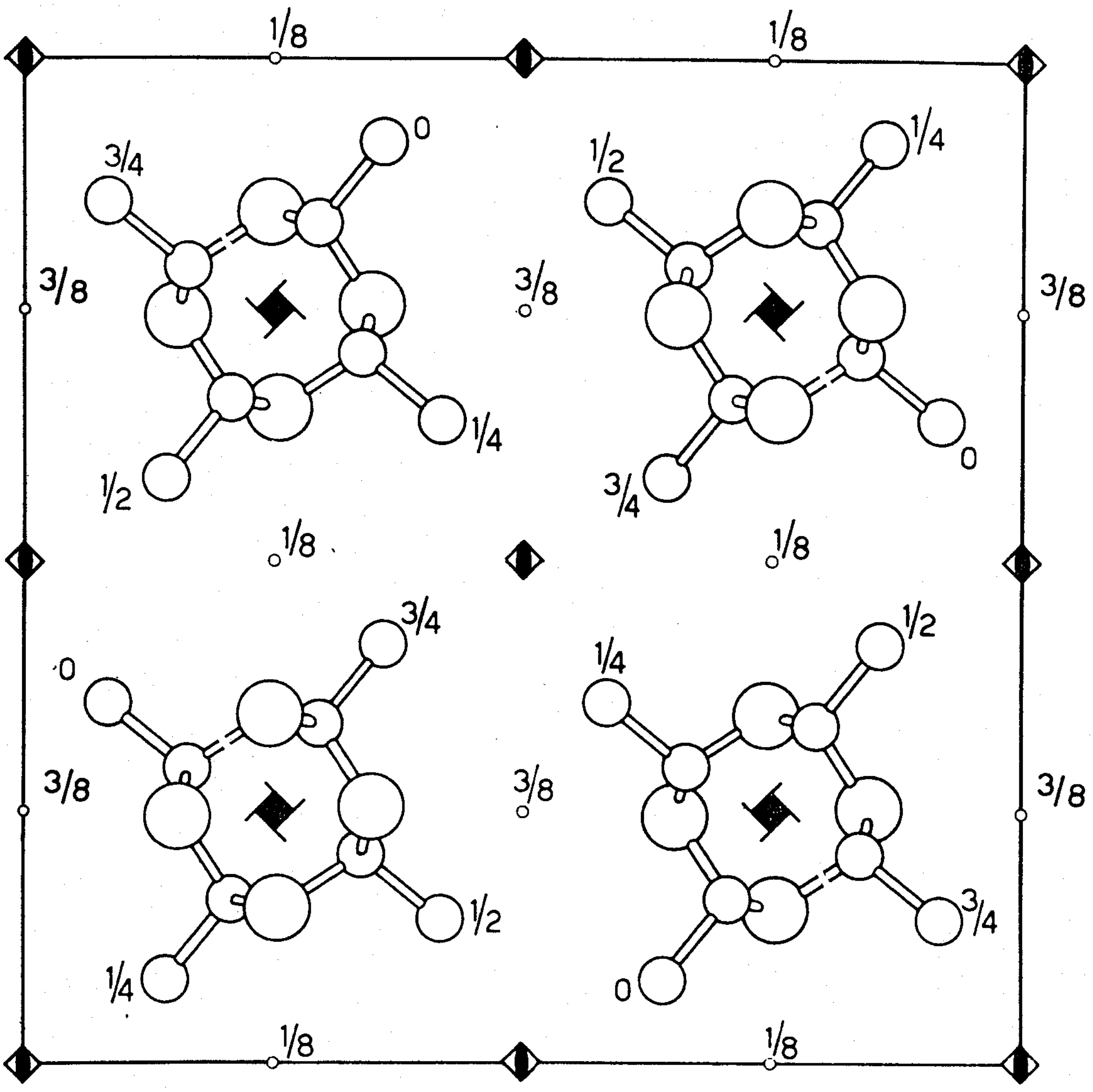


Fig. 3. Crystal structure of isotactic polyacetaldehyde.

the same conditions.[28] Stereospecificity may be ascribed to the fact that the *ortho* isomer contains the ethereal oxygen at a position not too far distant from the vinyl group; therefore, two different groups—the vinyl group

TABLE V

Stereospecific Polymerization of Some Alkylvinyl Ethers at −78°C. in Homogeneous Phase, in the Presence of Different Aluminum Compounds

Monomer	Catalyst	Polymer Properties
Isopropyl vinyl ether	$Al(C_2H_5)_2Cl$	Insoluble in boiling methyl alcohol; soluble in boiling acetone; highly crystalline under x-rays in the oriented state; [η] in toluene at 30°C. = 3–3.5
Isobutyl vinyl ether	$Al(C_2H_5)_2Cl$ or $Al(C_2H_5)Cl_2$	Crystalline under x-rays; substantially insoluble in boiling acetone; [η] in toluene at 30°C. = 3–4
Neopentyl vinyl ether	$Al(C_2H_5)Cl_2$ or $Al(C_2H_5)_2Cl$	Crystalline under x-rays; insoluble in boiling acetone; [η] in tetralin at 135°C. = 0.3–1

TABLE VI
Polymerization of Alkenyl Ethers in Toluene in the Presence of $Al(C_2H_5)_2Cl$
Polymerization Temperature: 78°C.

Polymer	Steric purity of monomer, %	X-ray examination	$[\eta]$ at 30°C. in toluene, 100 cm.^{3}/g.	Solubility
Poly(*cis*-methylpropenyl ether)	90	Amorphous	0.44	Insoluble in methanol; soluble in toluene
Poly(*trans*-methylpropenyl ether)	96	Crystalline	0.42	Insoluble in methanol; partly soluble in acetone; soluble in toluene
Poly(*cis*-isobutylpropenyl ether)	97	Amorphous	0.49	Insoluble in methanol; soluble in toluene
Poly(*trans*-isobutylpropenyl ether)	95	Crystalline	0.92	Insoluble in methanol and acetone; partly soluble in methyl ethyl ketone; soluble in toluene

with its π electrons and the ethereal oxygen group with the lone electron pair—may both be coordinated to the catalytic complex, thus determining the configuration of the monomeric unit. The poly-*ortho*-methoxystyrene thus obtained is not crystalline, but it possesses an ordered isotactic structure. In fact, catalytic hydrogenation of this polymer at temperatures lower than 200°C. yields crystalline poly(-2-methoxy) vinylcyclohexane. Other examples of isotactic non-crystalline polymers have been described in previous papers of ours.[12,29]

Nonmetalloorganic Catalysts

A great number of cationic stereospecific catalyses may be initiated with nonmetalloorganic complexes. The etherates of boron fluoride and of aluminum bromide, when employed at low temperatures (−100 to −40°C.) in many polymerizations, e.g., of aldehydes higher than acetaldehyde, appeared to be very stereospecific.[24,25]

The polymers thus obtained from a great number of aldehydes (propionic, *n*-butyric, isobutyric, valeric, etc.) appeared to be highly crystalline and isotactic.[24]

The lattice constants of some of these polymers are shown in Table VII. Nonmetalloorganic catalysts have been used by Price[30] for the stereospecific polymerization of propyleneoxide. Schildknecht, using boron trifluoride etherate, obtained crystalline polymers of vinyl ethers[31] which we found to be isotactic.[32]

Nonmetalloorganic anionic initiators, constituted of metal amides of very electropositive metals of groups I, II, and III of the periodic system, have been used by us to initiate stereospecific polymerizations. Some of

TABLE VII
Comparison Between the Lattice Constants of Some Isotactic Polyaldehydes

Polyaldehyde	*a*, A.	*c*, A.	Space group
Polyacetaldehyde	14.60	4.79	$I4_1/a$
Polypropionaldehyde	17.52	4.78	$I4_1/a$
Poly-*n*-butyraldehyde	20.01	4.78	$I4_1/a$

them, beryllium or aluminum amides in particular, in the presence of $TiCl_3$ polymerize ethylene and α-olefins, even though their activity is lower than that displayed by the most active polymerization catalysts prepared from metalloorganic compounds (see Table VIII).[33]

TABLE VIII
Ethylene and Propylene Polymerizations with Catalysts Obtained from Aluminum or Beryllium Amides

Monomer	Catalyst starting materials	Temp., °C.	Initial pressure, atm.	Characteristics of polymer obtained
Ethylene	$Al[N(C_6H_5)_2]_3 + TiCl_3$	118	50	Crystallinity 80%; m.p. 132–134°C; $[\eta] > 6$[a]
Ethylene	$Be[N(C_6H_5)_2]_2 + TiCl_3$	90	55	Crystallinity 86%; $[\eta] > 6$
Propylene	$Al[N(C_6H_5)_2]_3 + TiCl_3$	130	35	52% nonextractable by boiling heptane; m.p. 173°C; $[\eta] = 3.2$

[a] $[\eta]$ was measured in tetraline at 135°C.

TABLE IX
Stereospecific Polymerizations of Vinyl Monomers Containing Strongly Electron-Attracting Groups, with Lithium or Magnesium Amides as Catalysts

Monomer	Catalyst	Temp., °C.	$[\eta]$[a]	Characteristics of polymer obtained
Methyl methacrylate	*N*-carbazyllithium	30	1.60	80–90% insoluble in 2-octanone at 30°C.; highly crystalline (isotactic) under x-rays
	Br $MgN(C_2H_5)_2$	0	3.80	
Isopropyl acrylate	*N*-carbazyllithium	30	1.42	90% insoluble in 2-octanone at 30°C.; highly crystalline under x-rays
	Br $MgN(C_2H_5)_2$	−70	1.30	
2-Vinyl pyridine	Br $MgN(C_2H_5)_2$	40	0.40	95% insoluble in boiling acetone; crystalline under x-rays; m.p. 200–250°C.

[a] The intrinsic viscosities $[\eta]$ in the case of the polyacrylates and polymethacrylates were determined in $CHCl_3$ at 30°C, and in the case of poly-2-vinylpyridine in dimethylformamide at 30°C.

Some metal amides, in particular the lithium and magnesium amides, promote by themselves (in the absence of transition metals compounds), the stereospecific polymerization of acrylates and methacrylates (Table IX).[34]

Also, vinylpyridines are polymerized by some of these catalysts, and 2-vinylpyridine polymerizes to isotactic macromolecules which are insoluble in boiling acetone and crystalline according to x-ray examination.[20]

It is therefore clear that a great number of stereospecific ionic polymerizations may be initiated by simple catalysts obtained from non-metalloorganic compounds.

Kinetics and Mechanism of Ionic-Coordinated Polymerizations

At the Nottingham Congress in 1958[35] and in several publications[36,37] I dealt with the kinetics of the polymerization and copolymerization of α-olefins. Here, I shall mention only the most important aspects of these stereospecific polymerizations, that is, the processes which may exert an influence on the steric purity.

As I mentioned in previous papers,[35,37] and as I shall describe in more detail at the next Congress on Catalysis in Paris, the factors influencing steric purity are various: one of them is the presence, in one catalytic system, of active centers of differing chemical nature and stereospecificity.

Temperature is another factor; in fact (particularly in the case of cationic catalyses) a lowering of the temperature generally favors an increase in stereospecificity.

In butadiene polymerization, products with high *cis*-1,4 content (>99%) have been obtained in a homogeneous phase, with the use of catalysts containing only one determined catalytic complex (it is less easy to obtain such catalysts in a heterogeneous phase, in which only rarely is there but one type of active center). These homogeneous systems also yield a narrower distribution of molecular weight.

In α-olefin polymerization by heterogeneous systems, even when only one type of active center is considered, e.g., the most stereospecific one, it has been observed that the steric purity depends on a whole set of factors.

The degree of stereospecificity obtained in α-olefin polymerizations by means of heterogeneous catalytic systems, with a given initial transition metal compound, depends on the metalloorganic compound employed. Higher stereospecificity is often accompanied by a lower polymerization rate.

We have examined the causes of decreased steric purity and we have assumed that, during the growth of each chain, an inversion of steric configuration of some of the monomeric units with respect to the adjacent preceding units can take place.[38–40]

We also studied the influence exerted by factors such as temperature, pressure of the monomer, etc., on the frequency of this phenomenon, and found that each process able to cause dissociation of the catalytic complexes, with removal of the polymeric chain (either as an ion or as a metal alkyl) and subsequent reassociation to an active center, can cause an inversion of configuration.

The steric purity depends on the ratio of the rate of the processes causing an inversion of configuration to the rate of the polyaddition process.[39,40] Other conditions being equal, a lowering of the polymerization rate (obtained, for instance, by very markedly decreasing the monomer pressure) causes an increase in the percentage of configuration inversions, referred to the polymerized monomer molecules. We ascribe this phenomenon to the existence of dissociation and reassociation of the catalytic complexes, at a rate which is independent of the polymerization rate.

Characteristics of Ionic-Coordinated Polymerization

In the previous sections we have described examples of stereospecific polymerizations with metallorganic catalysts and monomers of different types; some of the monomers had been known previously to respond, in nonstereospecific polymerizations, better to cationic than to anionic catalyses.

We ascribed an anionic coordinated mechanism to the stereospecific polymerizations of α-olefins, which were the first polymerizations we performed using metallorganic catalysts. Other authors,[41] however, had ascribed a radical mechanism to such polymerizations.

In previous communications[2,42,43] I referred to a series of experimental data which cannot be construed as supporting chain initiation, propagation, and termination through free radicals, particularly in view of the fact that some stereospecific catalysts showed constant activity over a considerable period during the experiment.

Even now, some authors are inclined toward a radical mechanism according to which radicals should be formed which would remain bound on certain parts of the solid catalyst surface.[44] Such a mechanism would not be a free-radical mechanism of the type we consider in the usual radical polymerizations, in which the free radical of the growing chain migrates far from the starting point. One would conclude from this interpretation that a radical type catalyst should differ from an anionic catalyst in that the dissociation of the carbon-metal bond would be homolytic rather than heterolytic.

In opposition to this hypothesis, however, is the behavior of alkyls of less electropositive metals such as lead, tin, and mercury, which dissociate in a homolytic way and do not give (even in the presence of transition metal compounds) good catalysts for α-olefin polymerizations.

Therefore, we prefer to attribute an anionic coordinated mechanism to the α-olefin polymerizations catalyzed by complexes of very electropositive transition metals and alkyls of Al, Be, Li, etc. To the arguments supporting this thesis that are given in previous papers of ours,[2,42,43] we can now add the following, which cannot be explained easily by a free-radical mechanism:

(*1*) The long mean life of the growing macromolecules.[35]

(*2*) The constant number of active centers we observed in certain catalysts, even when the polymerization was interrupted for lack of monomer and started again after a certain time had elapsed.[45]

(*3*) The possibility of producing block copolymers by alternately feeding different monomers, even with periodic interruptions of the polymerization.[46]

(*4*) The observed change (which was sometimes remarkable) in the reactivity ratios of two different monomers in copolymerization when the type of the catalyst was varied[47–50], and the near constancy of the product of these ratios at a value of one.

(*5*) The polar effect of substituents in series of vinyl- aromatic monomers, which is opposite to that known in radical polymerizations.[51]

(*6*) The high percentage of macromolecules to which aluminum is bound when a catalytic system containing aluminumalkyls is used.[52]

(*7*) The possibility of obtaining, depending on the conditions, either isotactic, or syndiotactic polybutadienes with the use of a soluble transition metal–metal alkyl complex as described previously.[16,17]

(*8*) The fairly low heat of activation of the polyaddition reaction, in some cases (for instance, with catalysts prepared from vanadium halides) as low as 2,000 cal.[53]

The stereospecific catalysts we used are formed generally of complexes containing at least one central metal atom of small radius to which a terminal carbon atom of the growing chain is directly bound. If the terminal carbon atom of the growing polymeric chain is bound directly to a very electropositive metal of the catalytic complex, it may assume (at least in the activated state) a negative charge; in this case the polymerization mechanism will be of the anionic type. If, however, the carbon atom is bound to a highly electronegative metalloid in the catalytic complex, it assumes (at least in the activated state) an electropositive character, and thus a cationic polymerization takes place.

Stereospecificity is observed when the particular structure of the complex compels the new monomeric unit to assume a certain orientation, the double bond opening always in the same way: *cis* or *trans.*

In studying the stereospecific polymerization of monomers having an internal double bond, we have found a new, important means of determining the type of opening. It was observed that the *trans* isomer of the 1-methyl-2-isobutoxyethylene polymerizes to crystalline threo-diisotactic polymers, which could take place only by means of a *cis* opening of the double bond according to the general scheme:[27]

$$\begin{tikzcd}
 & \textit{trans}\text{ monomer} \arrow[dl, "\textit{trans}"', "\text{opening}"] \arrow[dr, "\textit{cis}", "\text{opening}"'] & \\
\textit{erythro}\text{ polymer} & & \textit{threo}\text{ polymer} \\
 & \textit{cis}\text{ monomer} \arrow[ul, "\textit{cis}", "\text{opening}"'] \arrow[ur, "\textit{trans}"', "\text{opening}"] &
\end{tikzcd}$$

The *cis* type of opening of the double bond is observed only seldom in organic chemistry, for instance, in the additions of lithiumalkyls to double bonds. In this case, the formation of a cyclic intermediate has been hypothesized (four centers of addition).[54] The formation of cyclic intermediates between the polarized monomer and the catalytic complex was considered by us in previous works.[4,43,55]

The regularity of structure may be ascribed to the steric conformation of the catalytic complex forming the active center, and to the consequent mode of presentation of the monomer unit which, in an intermediate stage, assumes the conformation (among those possible) it will keep as a unit of the isotactic polymer.

Polymers which show different IR spectra in spite of the chemical equivalence of D and H have been obtained by polymerizations of 1-deuteropropene-d_1, with either the *cis* or the *trans* monomer or their mixtures as the starting material.[56] This demonstrates that stereospecific polymerization taking place with an established opening (which is *cis* in the case of alkenyl ethers) determines the configuration not only of the —CHR— group, but also of the —CHD— group.[56]

By following the same reasoning it is possible to deduce that the growth of a syndiotactic chain, on the other hand, requires an alternate presentation and constant opening (or an alternate opening but the constant presentation). The former case seems to be more probable than the latter.

Syndiotactic polymers of α-olefins are less easily obtained and generally are less pure sterically than the corresponding isotactic polymers. Thus, in the fractionation by solvent extraction of polypropylenes containing both isotactic and syndiotactic macromolecules, the latter are usually concentrated in fractions containing also isotactic stereoblock polymer. The macromolecules having syndiotactic structure may be separated from the isotactic molecules by adsorption of the latter on a mass of highly isotactic polymer that is insoluble in solvents which dissolve the stereoblock polymer.[57]

Recently we have found catalytic systems which furnish raw high polymers with only syndiotactic crystallinity—no macromolecules having an isotactic structure are formed.[58]

Differences Between Coordinated Anionic and Cationic Polymerizations

Substantial differences exist between the two types of ionic catalyses, cationic and anionic, and not only with regard to the responsiveness of the monomer to one type or the other.

The polymerization mechanisms differ remarkably, as can be deduced both from the orientation of the monomeric unit with respect to the catalytic complex at the very moment of polymerization and from the structures both of the terminal groups present during propagation and of the groups which are left after termination.

For instance, in the polymerization of α-olefins by the anionic stereospecific mechanism, each monomer molecule during addition is placed with the CH_2 group facing the counterion present in the catalyst; by the cationic mechanism, in contrast, the monomer is oriented with the CHR group facing the counterion.

This is confirmed by the nature of the terminal groups of the macromolecules which, in the case of the anionic polymerization of vinyl monomers (e.g., propylene), at one end are *n*-alkyl groups (for example, *n*-propyls, or other alkyls initially present in the alkyl employed), whereas at the other end they are, at least in part, vinylidenic groups such as $H_2C{=}C(CH_3){-}$. In cationic polymerization, on the other hand, internal double bonds appear, as has also recently been confirmed in the case of polypropylene ($-CH{=}CH{-}CH_3$).[59]

Termination of the macromolecule in the presence of some catalysts (crystalline α-$TiCl_3$ + $Al(C_2H_5)_2Cl$ or $Al(C_2H_5)_3$, for example) does not involve the termination of the reaction chain promoted by an active center of the catalyst. The growth of the macromolecules may be stopped in different ways.[37]

(*1*) By transfer of the polymeric alkyl through an exchange with the metal alkyls present in solution.[60]

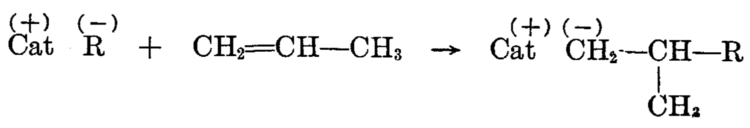
(*2*) By dissociation of the catalytic complex from the polymeric chain through transfer of a hydrogen anion and formation of a metal hydride bond in the catalyst.[28]

(*3*) By chain transfer with the monomer.[61]

These reactions, and the initiation and propagation steps, are as follows: Step (*ii*) and step (*iii*), which may be connected with (*ii*), cause the formation of a terminal vinylidenic group. Step (*i*), which also furnishes a method of regulating the molecular weight, keeps a metal atom bound to the macromolecular chain. In this case, when the crude polymer is purified (e.g., with alcohols and acids), an isopropylic group is formed. Thus both terminal groups of the macromolecules, derived from the polymeric metal alkyls, are saturated.

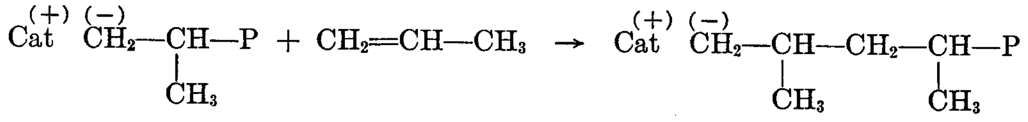
Vinylidene terminal groups can easily be observed in the infrared examination of propylene polymers having viscosity average molecular weights of less than 50,000; however, when polymerization is carried out under hydrogen at high pressure, in order to regulate the molecular weight, the number of these groups, in comparison with the total number of terminal groups, is remarkably reduced. In their place, isopropyl terminal groups appear.[62]

(*1*) Initiation:



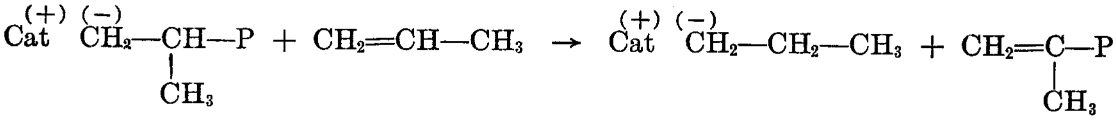
$$\overset{(+)}{\text{Cat}}\ \overset{(-)}{\text{R}} + CH_2{=}CH{-}CH_3 \rightarrow \overset{(+)}{\text{Cat}}\ \overset{(-)}{CH_2}{-}\underset{\substack{|\\ CH_2}}{CH}{-}R$$

(*2*) Propagation:



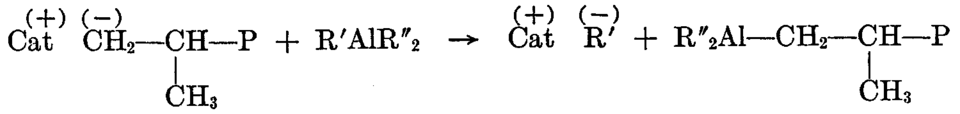
$$\overset{(+)}{\text{Cat}}\ \overset{(-)}{CH_2}{-}\underset{\substack{|\\ CH_3}}{CH}{-}P + CH_2{=}CH{-}CH_3 \rightarrow \overset{(+)}{\text{Cat}}\ \overset{(-)}{CH_2}{-}\underset{\substack{|\\ CH_3}}{CH}{-}CH_2{-}\underset{\substack{|\\ CH_3}}{CH}{-}P$$

(*3*) Termination by transfer with the monomer:



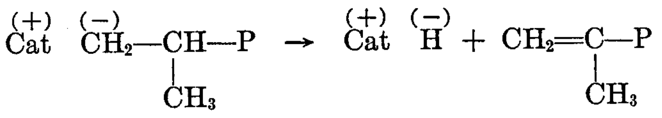
$$\overset{(+)}{\text{Cat}}\ \overset{(-)}{CH_2}{-}\underset{\substack{|\\ CH_3}}{CH}{-}P + CH_2{=}CH{-}CH_3 \rightarrow \overset{(+)}{\text{Cat}}\ \overset{(-)}{CH_2}{-}CH_2{-}CH_3 + CH_2{=}\underset{\substack{|\\ CH_3}}{C}{-}P$$

(*4*) Termination by transfer with the aluminum alkyl compounds present in the solution:



$$\overset{(+)}{\mathrm{Cat}}\ \overset{(-)}{\mathrm{CH_2}}{-}\underset{\mathrm{CH_3}}{\mathrm{CH}}{-}\mathrm{P} + \mathrm{R'AlR''_2} \rightarrow \overset{(+)}{\mathrm{Cat}}\ \overset{(-)}{\mathrm{R'}} + \mathrm{R''_2Al}{-}\mathrm{CH_2}{-}\underset{\mathrm{CH_3}}{\mathrm{CH}}{-}\mathrm{P}$$

(*5*) Termination by hydride dissociation:

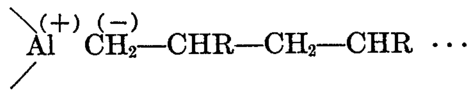


$$\overset{(+)}{\mathrm{Cat}}\ \overset{(-)}{\mathrm{CH_2}}{-}\underset{\mathrm{CH_3}}{\mathrm{CH}}{-}\mathrm{P} \rightarrow \overset{(+)}{\mathrm{Cat}}\ \overset{(-)}{\mathrm{H}} + \mathrm{CH_2}{=}\underset{\mathrm{CH_3}}{\mathrm{C}}{-}\mathrm{P}$$

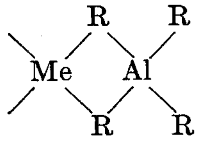
(*6*) Addition of a monomer molecule to the hydride formed in (*5*):

$$\overset{(+)}{\mathrm{Cat}}\ \overset{(-)}{\mathrm{H}} + \mathrm{CH_2}{=}\mathrm{CH}{-}\mathrm{CH_3} \rightarrow \overset{(+)}{\mathrm{Cat}}\ \overset{(-)}{\mathrm{CH_2}}{-}\mathrm{CH_2}{-}\mathrm{CH_3}$$

In the anionic coordinated polymerization of a vinyl monomer, the terminal carbon atom of the growing polymer chain is bound directly to a very electropositive metal atom, of small radius. In the case of an aluminum atom, we obtain

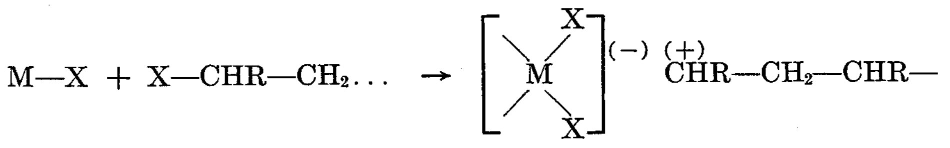


This metal belongs to a complex, usually bimetallic, that is characterized by bridge bonds and in which at least one of the R groups is an alkyl group, of the type



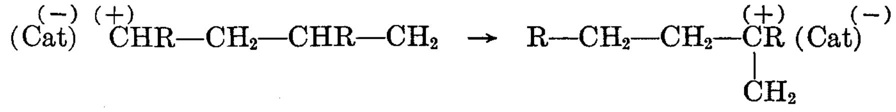
A great number of complexes containing bridge bonds have been isolated by us, in pure state; their catalytic properties have been described in previous papers.[4,63]

In contrast, in the cationic coordinated polymerization of the vinyl monomer, the carbon cation is bound to a metalloid (for instance, —O— or Cl—), and the metalloid, in turn, belongs to a complex of a type such as



Ions of different types coordinated to the central metal atom tend to show equivalent behavior, giving higher symmetry to the complex. This facilitates the dissociation of the X—C bond, which takes place, in particular, when several equal atoms (e.g., of chlorine) are coordinated to the same metal. Therefore, the carbon atom can be associated indifferently to any chlorine ion of the complex, all of them being strictly coordinated because of the high charge and the small diameter of the central metal ion. This, and the large size of the counterion, are some of the factors causing lack of stereospecificity.

Furthermore, since the carbon cation in a hydrocarbon is more stable the more it is substituted, in cationic catalysis the isomerization process of the type



$$\overset{(-)}{(\mathrm{Cat})}\ \overset{(+)}{\mathrm{C}}\mathrm{HR{-}CH_2{-}CHR{-}CH_2} \rightarrow \mathrm{R{-}CH_2{-}CH_2{-}}\underset{\substack{| \\ \mathrm{CH_2}}}{\overset{(+)}{\mathrm{C}}}\mathrm{R}\ (\mathrm{Cat})^{(-)}$$

is thermodynamically favored and consequently causes irregularities in the chemical structure of the chain, particularly when the operating temperature is not very low. This is the reason that the cationic polymerizations of several vinyl monomers yield regular and stereospecific material only when carried out at very low temperatures (−100 to −40°C.), at which proton transfer proceeds relatively slowly.

These irregularities are not observed in anionic coordinated polymerizations, which are still stereospecific even at high temperatures (80–100°C.), but nevertheless, stereospecific polymerization with cationic catalysis represents an important broadening to the existing means of obtaining new classes of stereoregular polymers.

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Synopsis

Recent results of investigations of stereospecific polymerizations are reported. Butadiene polymers very high in *cis*-1,4 content have been obtained through polymerization in the presence of soluble catalysts prepared from compounds of group VIII metals, cobalt in particular, and from dialkylaluminum monohalides. The polymers thus obtained have higher melting temperatures and better elastomeric properties than those of *cis*-1,4 polybutadienes of lower steric purity.

Two types of butadiene polymers having 1,2 enchainment and isotactic or syndiotactic structure may be prepared in the presence of soluble catalytic systems prepared from trialkylaluminum and complexes of chromium or vanadium. A great number of nonhydrocarbon monomers have also been polymerized stereospecifically, in the presence of catalysts acting in homogeneous phase. Metallorganic compounds of magnesium act as stereospecific catalysts for the polymerization of 2-vinylpyridine, with production of crystalline isotactic polymers. Crystalline isotactic polymers of acetaldehyde have been prepared by polymerization at low temperature with the use of metallorganic compounds such as alkylaluminum and alkylzinc as catalysts. Aldehydes higher than acetaldehyde have also been polymerized stereospecifically with catalysts that act usually with a cationic mechanism, such as aluminum bromide. The crystalline structure and the crystalline helical chain conformation of a great number of these polyaldehydes have been determined. A chemical mechanism for this polymerization, which makes clear the stereospecificity of the process even in the presence of soluble catalysts, has been proposed. Stereospecific catalysts have been prepared from compounds of amides with very electropositive metals. In the presence of $TiCl_3$, these catalysts promote the stereospecific polymerization of propylene to isotactic polymer, whereas, as such, they furnish crystalline polymers of acrylates, methacrylates, and 2-vinylpyridine. The nature of the terminal groups of the polymers establishes the fact that the polymerization occurs with an anionic mechanism. The mechanism of the stereospecific polymerization of α-olefins is discussed, and further evidence is given confirming the previously hypothesized anionic coordinated mechanism. The factors determining stereospecificity are also discussed; it is concluded that when a group rich in electrons in addition to the polymerizable double bond is present in the monomer, stereospecific polymerization may take place in the presence of catalysts acting in homogeneous as well as heterogeneous phase. In these cases, stereospecificity must be as-

cribed to the coordination of the monomer to the catalyst, which results in a constant mode of presentation of the monomer to the growing chain, and to a constant type of opening, *cis* or *trans*, of the polymerizable double bond. For the polymerization of propenyl ethers to di-isotactic polymers, we established that this opening is of the *cis* type.

Résumé

On rapporte certains résultats récents obtenus au cours d'expériences sur la polymérisation stéréospécifique. On a obtenu des polymères de butadiène contenant un pourcentage élevé de *cis*-1,4, lorsqu'on travaille en présence de catalyseurs solubles, préparés avec des composés métalliques du 8ème groupe, (du cobalt en particulier) et de dialcoyles aluminium monohalogénés. Les polymères obtenus par cette méthode ont une température de fusion plus élevée et des propriétés élastomères meilleures que ceux des polybutadiènes cis-1,4 ayant une moins bonne pureté stérique. Des polymères de butadiène cristalables, ayant une mode d'enchaînement 1,2, soit isotactique ou syndiotactique, peuvent être préparés par polymérisation en présence de systèmes catalytiques solubles tels que ceux préparés à partir d'aluminium triacoylé et de complexes du chrome ou du vanadium. On a polymérisé également un grand nombre de monomères non hydrocarbonés de manière stéréospécifique, en employant des catalyseurs réagissant en phase homogène. Des composés organométalliques du magnesium agissent comme catalyseurs stéréospécifiques dans la polymérisation de la 2-vinylpyridine; ils donnent des polymères isotactiques, cristallins. On a préparé par polymérisation de l'aldéhyde acétique à basse température des polymères isotactiques cristallins, à l'aide des composés organométalliques tels que alcoyle aluminium et alcoyle zinc. Les aldéhydes plus élevés que l'aldéhyde acétique ont été également polymérisés stéréospécifiquement avec des catalyseurs qui réagissent ordinairement suivant un mécanisme cationique tel le bromure d'aluminium. On a déterminé la structure cristalline et la conformation en chaine hélicoïdiale dans les cristaux d'un grand nombre de ces polyaldéhydes. On a proposé un mécanisme chimique de cette polymérisation, qui éclaire la stéréospécificité de ce procédé, même en employant des catalyseurs solubles. Des catalyseurs stéréospécifiques ont été préparés à partir des composés métal-amide de métaux très électropositifs. En présence de $TiCl_3$, ils peuvent provoquer la polymérisation stéréospécifique du propylène en polymère isotactique, tandis que, employés en absence de $TiCl_3$, ils donnent des polymères cristallins d'acrylate, méthacrylate et 2-vinylpyridine. La nature des groupes terminaux, présents dans le polymère permet d'établir que le mecanisme de polymérisation est anionique. On discute le mécanisme de polymérisation stéréospécifique que des oléfines. On donne des preuves qui confirment l'hypothese d'un mécanisme anionique à coordination. Les causes provoquant la stéréospécificité sont également discutées: on a tiré la conclusion que la présence dans le monomère d'un autre groupe riche en électrons à côté de la double liaison polymérisable donne lieu à une polymérisation stéréospécifique en présence des catalyseurs agissant en phase homogène. Dans ces cas, la stéréospécificité doit être attribuée à la possibilité de coordination du monomère avec le catalyseur. Ceci provoque une position constante du monomère par rapport à la chaine en croissance et un type constant d'ouverture de la double liaison polymérisable. L'étude de la polymérisation de propényléthers et les polymères di-isotactiques nous ont permis d'établir que cette ouverture est du type *cis*.

Zusammenfassung

Einige neuere Ergebnisse bei der Untersuchung der stereospezifischen Polymerisation werden mitgeteilt. Butadienpolymere mit sehr hohem *cis*-1,4-Gehalt wurden beim Arbeiten in Gegenwart löslicher Katalysatoren aus Metallverbindungen der achten Gruppe, besonders Cobalt, und aus Dialkylaluminiummonohaliden erhalten Die so erhaltenen Polymeren besitzen höhere Schmelztemperaturen und bessere elastische Eigenschaften als cis-1,4-Polybutadiene mit geringerer sterischer Reinheit. Kristallisierbare

Butadienpolymere mit entweder isotaktischer oder syndiotaktischer 1,2-Verkettung können durch Polymerisation in Gegenwart löslicher, aus Trialkylaluminium und Chrom- oder Vanadinkomplexen gebildeten Katalysatoren dargestellt werden. Auch eine grosse Zahl anderer als Kohlenwasserstoffmonomerer wurde mittels in homogener Phase wirksamer Katalysatoren stereospezifisch polymerisiert. Metallorganische Magnesiumverbindungen sind stereospezifische Katalysatoren für die Polymerisation von 2-Vinylpyridin unter Bildung kristalliner, isotaktischer Polymerer. Kristalline, isotaktische Acetaldehydpolymere wurden durch Polymerisation bei tiefer Temperatur mittels metallorganischer Verbindungen, wie Alkylaluminium und Alkylzink hergestellt. Höhere Aldehyde als Acetaldehyd wurden mit Katalysatoren, die gewöhnlich nach einem kationischen Mechanismus wirksam sind, wie Aluminiumbromid, ebenfalls stereospezifisch polymerisiert. Die kristalline Struktur und die Helixkonformation der Kette wurde bei der Kristallen einer grossen Zahl dieser Polyaldehyde bestimmt. Ein chemischer Mechanismus zur Erklärung der Stereospezifität des Prozesses auch bei Anwendung löslicher Katalysatoren wurde angegeben. Stereospezifische Katalysatoren wurden ausgehend von Metall-Amidverbindungen sehr elektropositiver Metalle dargestellt. In Gegenwart von $TiCl_3$ können sie die stereospezifische Polymerisation von Propylen zu isotaktischen Polymeren bewirken, während sie allein kristalline Polymere von Acrylaten, Methacrylaten und 2-Vinylpyridin liefern. Die Natur der in den Polymeren vorhandenen Endgruppen beweist, dass die Polymerisation nach einem anionischen Mechanismus verläuft. Der Mechanismus der stereospezifischen Polymerisation der Alphaolefine wird diskutiert und weitere Beweise für einen anionischen Koordinationsmechanismus werden angeführt. Auch die Ursachen für eine bestimmte Stereospezifität werden diskutiert. Es ergibt sich der Schluss, dass bei Anwesenheit einer zweiten elektronenreichen Gruppe ausser der polymerisationsfähigen Doppelbindung im Monomeren stereospezifische Polymerisation auch in Gegenwart von in homogener Phase wirksamen Katalysatoren stattfinden kann. In diesem Fall muss die Stereospezifität dem Umstand zugeschrieben werden, dass das Monomere an den Katalysator koordinativ gebunden werden kann und dadurch eine konstante Anordnung des Monomeren selbst in bezug auf die wachsende Kette gegeben ist, und dass weiters die polymerisierbare Doppelbindung sich immer in der gleichen Weise öffnet. Die Untersuchung der Polymerisation von Propenyläthern zu Di-isotaktischen Polymeren führte zu der Feststellung, dass diese Öffnung vom *cis*-Typ ist.

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