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CHAPTER 7

ELASTOMERS BY COORDINATED ANIONIC MECHANISM

A. Diene Elastomers

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I. HOMOPOLYMERS OF BUTADIENE, ISOPRENE, AND PIPERYLENE

A. Introduction

Diolefins have represented and still represent the most widely used raw materials for the production of synthetic rubber. Methods for the polymerization of diolefins have been known for a long time. However, no method of polymerization known before 1954 (when stereospecific polymerization was discovered) allowed one to obtain polymers with a high regularity of structure from the most common diolefins.

With Na or K catalysts it was possible to obtain polymers consisting predominantly of 1,2 units, in some cases above 95% (1–3). However, no crystallinity has been detected in these polymers by x-ray examination, evidently because of the lack of steric regularity, that is lack of order in the configurations of the tertiary carbon atoms of each chain.

It is now known that, among the alkali metals, lithium and its derivatives can yield diolefin polymers with a certain degree of regularity (cf. Chapter 6). Thus, polymers which are 90–92% *cis*-1,4 can be obtained from isoprene (4–6), and polymers having a *trans*-1,4 isotactic structure can be obtained from 1,3-pentadiene (7). Such stereospecific properties of the lithium catalysts were recognized, however, only after the discovery of the coordination catalysts. Thus, it may be said that no polymer with a regular structure was synthesized by alkali metal catalysts before 1954.

Structurally very irregular polymers were obtained by cationic initiators, due to the formation of crosslinks and to cyclization (8,9). These products are completely amorphous by x-rays.

Polymers having a certain structural regularity were obtained by radical initiators, but only from some diolefins. By these initiators, it is possible to obtain butadiene polymers containing up to 80% *trans*-1,4 units (10). The most regular of these polymers exhibit, at low temperatures and under stretching, low crystallinity due to the presence of *trans*-1,4 sequences in the chain (11).

Polymers containing up to 90% *trans*-1,4 units can be obtained from isoprene with the help of radical initiators. However, they appear completely amorphous by x-rays, probably because of lack of a regular head-to-tail arrangement (12).

Only from particular diolefins is it possible to obtain, by radical initiators, polymers having a certain regularity of structure. Thus, from chloroprene, polymers consisting of about 95% *trans*-1,4 units were obtained, which showed good crystallinity at room temperature (13). Polymers of this type can be obtained only by operating at about −40°, while far more irregular polymers are obtained at room temperature (14).

The Alfin catalysts (15,16) (cf. Chapter 6, p. 575) certainly represent progress with respect to the previous catalysts as to the ability to yield regular polymers of diolefins. In fact, unstretched polybutadienes obtained by these catalysts show a certain amount of crystallinity even at room temperature due to the presence of *trans*-1,4 sequences in the chain (17,18). However, the polymers of isoprene obtained by these catalysts are completely amorphous (17).

The discovery of stereospecific catalysts based on transition metals completely changed the situation in the field of diolefin polymers. With these catalysts polymers have been obtained with 98–100% units of the same type (1,2; *trans*-1,4 or *cis*-1,4) in a regular head-to-tail arrangement, representing a far higher structural regularity than the synthetic polymers previously known. Moreover macromolecules with a high degree of steric regularity have been obtained from monomers yielding units that contain asymmetric carbon atoms. The results obtained during twelve years of activity in this field are not only of great scientific interest, but also of great practical importance, especially in the field of synthetic elastomers.

This chapter deals with the homopolymerization, by anionic coordination catalysts, of the three simplest diolefins, i.e., butadiene, isoprene, and 1,3-pentadiene. These are the most important diolefins from the industrial point of view.

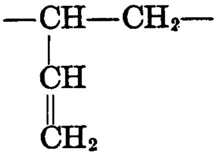
This chapter presents a general outline of the polymerization of these monomers and the topics of interest from the elastomeric point of view will be emphasized.

B. Isomerism in Diolefin Polymers

Before considering the results obtained in the stereospecific polymerization of butadiene, isoprene, and pentadiene, we think it useful to describe the phenomena of isomerism that can occur in the polymerization of diolefins. A comparison between the theoretically foreseeable possibilities and the results actually obtained will show the progress that stereospecific polymerization has made in the field of conjugated diolefins.

Isomerism in conjugated diolefin polymers is a considerably more complex phenomenon than that encountered in vinyl polymers. Butadiene can polymerize to yield 1,4 or 1,2 units. The 1,4 units, $-CH_2-CH=CH-CH_2-$, contain an internal double bond, which represents a site of geometric isomerism, since it can be of the *cis* or the *trans* type. It is therefore possible to foresee two types of regular polybutadienes with 1,4 arrangement, i.e., *trans*-1,4 and *cis*-1,4 polybutadienes.

The 1,2 units,



$$\begin{array}{l} -\mathrm{CH}-\mathrm{CH_2}- \\ \;\;| \\ \;\mathrm{CH} \\ \;\;\| \\ \;\mathrm{CH_2} \end{array}$$

on the other hand, contain a site of steric isomerism, i.e., the tertiary carbon atom, which can assume two opposite configurations. 1,2 Polybutadienes, therefore, show the same type of isomerism as vinyl polymers. Hence two types of regular 1,2 polybutadienes are possible, one of the isotactic, the other of the syndiotactic type. Also, atactic-1,2 polybutadiene can exist, in which there is a statistical distribution of the two configurations of the tertiary carbon atoms of each chain.*

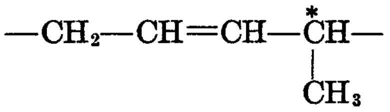
In the case of isoprene, two types of regular *cis*-1,4 and *trans*-1,4 polymers can be foreseen. When only one unsaturated group is involved in the polymerization, different polymers are obtained depending on whether the polymerization involves the vinyl (3,4 units) or the vinylidenic group (1,2 units). Both 1,2 and 3,4 polyisoprenes exhibit vinyl type isomerism; therefore two types of regular 3,4 stereoisomers (iso and syndio), two types of regular 1,2 stereoisomers (iso and syndio), as well as atactic 1,2 and 3,4 polyisoprenes can be foreseen. To summarize, six types of regular simple isomers of polyisoprene are possible: i.e., two 1,4 polyisoprenes, two 3,4 polyisoprenes, and two 1,2 polyisoprenes.

Isomerism becomes more complex in the case of pentadiene polymers. Every unit derived from this monomer, whatever its structure, shows two

---

* More complex phenomena of isomerism, such as those deriving from a regular alternation of units of different type (e.g., *trans*-1,4 and *cis*-1,4 units) or, in the case of 1,2 polymers, from a regular head-to-head, tail-to-tail structure will be neglected here. Polymers of this type, although possible, do not seem easily obtainable by simple homopolymerization by the catalysts known so far.

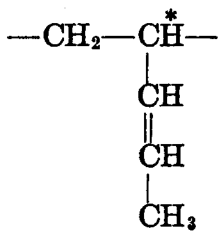
sites of isomerism. The 1,4 units show a site of geometric isomerism at the double bond and a site of steric isomerism at the asymmetric carbon atom:



$$-CH_2-CH=CH-\underset{\displaystyle CH_3}{\underset{|}{\overset{*}{C}H}}-$$

Consequently, while polybutadiene or polyisoprene can each have only one stereoisomer with *trans*-1,4 or *cis*-1,4 structure, in the case of pentadiene, due to the presence of an asymmetric carbon atom in each 1,4 unit, two different *trans*-1,4 or *cis*-1,4 stereoregular polymers are possible, namely the isotactic and syndiotactic isomers. Stereoregular polymers of this type, in which there are two sites of isomerism per monomer unit, have been called ditactic. Obviously, there can be 1,4 polypentadienes having regularity only with respect to one type of isomerism, e.g., all-*trans*-1,4 or all-*cis*-1,4 polymers, in which there is no order as to the configurations of the asymmetric carbon atoms of each chain.

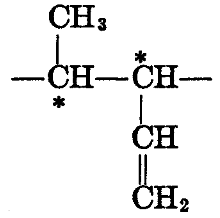
Polymerization involving only the vinyl group gives rise to 1,2 units,



$$-CH_2-\overset{*}{C}H(-CH=CH-CH_3)-$$

which contain a site of steric isomerism at the tertiary carbon atom and a site of geometric isomerism at the double bond of the side group. Four types of stereoregular 1,2 polypentadiene are therefore possible, two types of isotactic polymers, which differ in that they contain all-*cis* or all-*trans* double bonds in the side groups, and analogously, two types of syndiotactic polymers.

Polymerization involving only the internal double bond of pentadiene gives rise to 3,4 units,



$$-\underset{*}{\overset{\displaystyle CH_3}{\overset{|}{C}H}}-\overset{*}{C}H(-CH=CH_2)-$$

which contain two sites of steric isomerism. Three types of stereoregular 3,4 polypentadienes are possible: (*1*) disyndiotactic polymers, in every chain of which the configuration of each tertiary carbon atom of a monomer unit is opposite to that of the corresponding carbon atom of the preceding or following unit; (*2*) *erythro*-diisotactic polymers; (*3*) *threo*-diisotactic polymers. The latter (*2* and *3*) differ with regard to the relative configuration of the adjacent tertiary carbon atoms.

Isomerism becomes far more complex with polymers of 1,4 substituted butadienes. This case is beyond the scope of this chapter, and will not be discussed here. A more detailed discussion of the configurational possibilities shown by vinyl and diolefin polymers can be found in recent publications (19–22).

C. Polymerization Catalysts

1. General Considerations

The first coordination catalysts, based on transition metals, used for the polymerization of conjugated diolefins (principally butadiene and isoprene) were obtained by reacting $TiCl_4$ or $TiCl_3$ and an alkyl aluminum compound (trialkyl aluminum, dialkylaluminum halide, lithium aluminum tetraalkyls).

Subsequently, a vast number of compounds of transition metals from groups IV–VIII of the periodic table have been used in combination with alkylaluminum compounds for the preparation of catalysts for the polymerization of conjugated diolefins. These compounds include halides, alcoholates, acetylacetonates, complexes with CO, amines, isonitriles, nitriles, etc. A large number of catalysts can be prepared from the combination of one of the various aluminum alkyl derivatives with each of these transition metal compounds. This number increases if one considers that instead of aluminum alkyls, other organometallic compounds can be used, e.g., aluminum hydrides or alkyl derivatives of Be, Zn, Mg, Cd, etc.

Only a few catalysts, however, are of practical importance in the preparation of diolefin polymers, if one takes into account their activity and stereospecificity. These are the catalysts obtained from an aluminum trialkyl or an alkylaluminum halide and a compound of the following metals: Ti, V, Cr, Mo, Co, Ni. Catalysts from other transition metals are of less interest. The transition metal compounds mostly used are halides (particularly chlorides and iodides), complexes of the chlorides with a Lewis base, alcoholates, and acetylacetonates.

Some of the transition metal catalysts are heterogeneous, e.g., those obtained from AlR_3 or AlR_2Cl* and either $TiCl_4$, $TiCl_3$, VCl_3, $VOCl_3$, or VCl_4. Others are homogeneous, e.g., those from AlR_3 and either $Ti(OR)_4$, $VO(OR)_3$, $V(acac)_3$, $Cr(acac)_3$, or $Co(acac)_2$, and also those obtained from AlR_2Cl and a compound of Co (e.g., $CoCl_2{\cdot}2py$; $Co(acac)_2$) or V (e.g., $V(acac)_3$; $VCl_3{\cdot}3THF$).

The reactions between aluminum alkyls and transition metal compounds have been studied extensively but the nature of the reaction products has not been always clarified. These reactions proceed through several stages. One of these appears to be the alkylation of the transition metal compound, with formation of a transition metal–carbon bond. This bond is often (but not always) unstable under the reaction conditions and breaks homolytically with formation of a free alkyl radical. As a consequence, gas evolution is observed in most of the reactions between an aluminum alkyl and a transition metal compound. The cleavage of the transition metal–carbon bond also causes a decrease in the formal valence of the transition metal, which, in most of the cases, is stabilized in the lower valence state through complexation with the aluminum compound.

The following part of this section deals with a detailed examination of the catalyst systems most important for the polymerization of diolefins to elastomeric products. These are the catalysts based on either Ti halides or Co compounds.

2. Catalysts from $TiCl_4$

The use of catalysts from $TiCl_4$ for the polymerization of diolefins (23) dates back to shortly after Ziegler's discovery that the suspension obtained by treating $TiCl_4$ with $AlEt_3$ can polymerize ethylene. Several studies exist on the reaction between AlR_3 or AlR_2Cl and $TiCl_4$ (24–35). In hydrocarbon solvent, the reaction occurs with formation of a precipitate containing Ti in a reduced state, while gas is evolved simultaneously. The composition of the precipitate varies with the $AlR_3/TiCl_4$ ratio as well as with the reaction conditions. The preferred method of preparing the catalyst is gradual introduction of an AlR_3 solution into the $TiCl_4$ solution while stirring. Table I shows the composition of precipitates obtained at 15° from $AlEt_3$ and $TiCl_4$. The solid obtained at a molar ratio $AlR_3/TiCl_4 = 1$ is brown and contains Cl and Ti in a

---

* The following abbreviations will be used in this chapter: AlR_3 = aluminum trialkyl; AlR_2Cl = dialkylaluminum chloride; acac = acetylacetonate group; py = pyridine; $Me(OR)_n$ = metal alkoxide; THF = tetrahydrofuran.

TABLE I

Analyses of the Precipitates Obtained by Reacting $Al(C_2H_5)_3$ with $TiCl_4$ at 15°C (25,27)

$AlEt_3/TiCl_4$ molar ratio	Cl/Ti	Al/Ti	X-ray exam.	Average valence of Ti in the solids
0.5	3.4	0.24	Amorphous	—
1.2	3.08	0.07	Cryst. (β-$TiCl_3$)	3
2.0	2.36	0.33	Amorphous	2.31
2.5	2.15	0.30	Amorphous	—
3.0	2	0.32	Amorphous	2.04
5	1.65	0.31	Amorphous	1.87

molar ratio very close to 3:1, while Al is present in small amounts. The product consists essentially of crystalline $TiCl_3$ which, by x-ray analysis, appears to be identical with that obtained by Böck and Moser by the action of dark discharges on a gaseous mixture of $TiCl_4$ and H_2 (36). The School of Milan designated this crystalline modification β-$TiCl_3$ to distinguish it from the violet modification (called α-$TiCl_3$) which is obtained by the action of H_2 on $TiCl_4$ at high temperatures (37). The differentiation between the two forms is important as they yield catalysts of different stereospecificity. See Sections I-D-1a, b and I-D-2a, b (38).

Upon increasing the $AlR_3/TiCl_4$ ratio, the Cl/Ti ratio in the precipitate decreases, due to alkylation of $TiCl_3$, while the color gradually turns black. The products obtained at a ratio ≥ 2 are amorphous by x-rays. The average valence of Ti in the precipitate is about 3 at an $AlR_3/TiCl_4$ ratio of 1, while it drops even below 2 at higher ratios.

On the other hand, AlR_2Cl does not reduce Ti to a valence below 3 at room temperature, and β-$TiCl_3$ is obtained even at high $AlR_2Cl/TiCl_4$ ratios.

Some data reported in the literature are slightly different from those of Table I; actually some authors report higher and others lower values for the Al content in the precipitates. Despite these disagreements, it is clear that the following reactions take place:

$$AlR_3 + TiCl_4 \rightarrow AlR_2Cl + TiCl_3 + R^{\cdot}$$
$$AlR_3 + TiCl_3 \rightarrow TiCl_2R + AlR_2Cl$$
$$TiCl_2R \rightarrow TiCl_2 + R^{\cdot}$$

Catalysts have recently been proposed for the polymerization of diolefins which, instead of AlR_3, use compounds containing Al—H bonds, such as $AlHCl_2 \cdot O(C_2H_5)_2$, $AlHCl_2 \cdot N(CH_3)_3$, $AlH_2Cl \cdot N(CH_3)_3$, $AlH_3 \cdot N(CH_3)$ (39,40). At low Al/Ti ratios the reaction between these compounds and $TiCl_4$ leads to the formation of β-$TiCl_3$ containing small amounts of Al, while H_2 is evolved. At higher Al/Ti ratios, the precipitate is amorphous by x-rays and the Cl/Ti ratio is lower than 3, while the percentage of Al present increases.

Therefore, the reaction between the above-mentioned Al hydrides and $TiCl_4$ is similar to that with aluminum trialkyls. It is, however, apparent that the former compounds have a higher reducing power than AlR_3; in fact, the reaction between $AlHCl_2 \cdot O(C_2H_5)_2$ and $TiCl_4$ occurs rapidly even at temperatures far below 0°C (39).

3. Titanium Based Catalysts Containing Iodine

It was realized early (41) that the AlR_3–TiI_4 system shows catalytic properties which differ somewhat from those of the AlR_3–$TiCl_4$ system. In fact, the AlR_3–TiI_4 system

1. gives polybutadienes having a higher *cis*-1,4 content than those obtained by the AlR_3–$TiCl_4$ system
2. is active and stereospecific over a wide range of Al/Ti ratios
3. does not polymerize isoprene

The reaction between AlR_3 and TiI_4 in benzene at room temperature, or slightly above, gives insoluble solids that contain reduced Ti (26,42). At sufficiently high Al/Ti ratios (≥ 2.5), practically all the Ti is in the solid phase. This phase also contains I and alkyl groups, while Al is present only in a small percentage. Some disagreement exists among the data published on the composition of the solids. It appears that the reaction of AlR_3 with TiI_4 is analogous to that with $TiCl_4$, except that it is slower. Thus, in the reaction between $Al(i\text{-}C_4H_9)_3$ and $TiCl_4$, at an Al/Ti ratio of 3, the Cl/Ti ratio in the precipitate is less than 2, while in the reaction between $Al(iC_4H_9)_3$ and TiI_4, at the same Al/Ti ratio, the I/Ti ratio in the solids is 2.3–2.4 even after 18 hr at room temperature. According to Saltman (42), also at $Al(i\text{-}C_4H_9)_3/TiI_4$ ratios of about 10, the I/Ti ratio in the solids is higher than 2, while the ratio of isobutyl groups to Ti is 0.5–0.6. This is the main difference between the $TiCl_4$ and TiI_4 systems. The fact that the chemical composition of the precipitate varies slowly with varying AlR_3/TiI_4 ratio, accounts for the fact that the system is active and stereospecific over a wide range of ratios (from 2–3 to about 8–9).

For the synthesis of *cis*-1,4 polybutadienes, the systems AlR_3–$TiCl_2I_2$

(equimolecular mixture of $TiCl_4$ and TiI_4) (26,43–45) and AlR_3–I_2–$TiCl_4$ ($Al/Ti = 5–10$; $I_2/Ti = 1.5$) (43,46,47) were found equivalent to the AlR_3–TiI_4 system. Both $TiCl_4$ and $TiCl_2I_2$ present the advantage of being far more soluble than TiI_4 in hydrocarbon solvents. In the system AlR_3–I_2–$TiCl_4$, iodine reacts readily with AlR_3 (while it does not with $TiCl_4$) to give AlR_2I (42); therefore the system behaves as though it consisted of AlR_3–AlR_2I–$TiCl_4$. The precipitates obtained from the systems based on $TiCl_2I_2$ or $TiCl_4 + I_2$ are practically the same as those from the TiI_4 system. Actually all the Cl passes into the filtrate as AlR_2Cl, while the precipitate contains the entire amount of iodine present in the system. This phenomenon is quite general in systems consisting of Al and Ti compounds and containing Cl and I. Thus, the reaction between $AlEt_2I$ and $TiCl_4$, as well as that between $Al(i\text{-}C_4H_9)_3$ and $TiCl_2I_2$ yield precipitates that practically consist of TiI_3 (26,48).

In a series of catalysts proposed for the *cis*-1,4 polymerization of butadiene, various metal hydrides are used instead of aluminum alkyls as reducing agents. The system $AlHCl_2 \cdot O(C_2H_5)_2$–$TiCl_4$–$AlI_3$ is particularly active and stereospecific (49). As the reducing compounds, $AlH_3 \cdot N(CH_3)_3$, $AlH_2Cl \cdot N(CH_3)_3$, or $AlH_2N(CH_3)_2$ can also be employed (49).

Other systems proposed (49,50) are: $AlHI_2 \cdot O(C_2H_5)_2$–$TiCl_4$;$AlHCl_2 \cdot O(C_2H_5)_2$–$TiI_4$; $LiAlH_4$–$TiCl_2I_2$; $LiAlH_4$–I_2–$TiCl_4$; CaH_2–$AlEt_2I$–$TiCl_4$. The similarity among all the above systems is shown by considering that:

1. they contain a strong reducing agent which is able to decrease the valence of Ti
2. iodine, regardless of the form in which it was initially present, always ends up bonded to Ti

To summarize, in all the iodine-containing systems mentioned above, practically the same solid is formed (TiI_3 and/or TiI_2R, where R = alkyl or H). The Al compounds present are different, but most likely they exert little influence on the stereospecificity.

4. Catalysts from Cobalt Compounds

a. Catalysts from Al Alkylhalides and Cobalt Compounds. These systems are the most stereospecific for the synthesis of *cis*-1,4 polybutadiene. They are used in homogeneous solution (usually in benzene or toluene) at a Co concentration of the order of 1–5 mg per liter of solvent-monomer mixture (51,52). AlR_2Cl, $AlRCl_2$, $Al_2Cl_3R_3$ or the corresponding phenyl derivatives can be used as the Al compound (53–58).

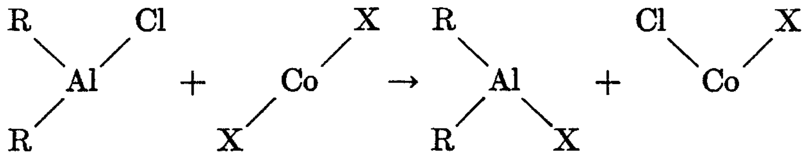
Co-based catalysts exhibit the following characteristics:

1. the Al/Co ratio can be varied within wide limits, from about 20 to more than 1,000 and even above, without varying stereospecificity
2. practically any soluble or insoluble cobalt compound can be used to obtain a stereospecific catalyst. The most commonly used Co compounds are the di- and triacetylacetonates, complexes of $CoCl_2$ with pyridine, ethers, or amines, complexes of Co with various chelates, and salts of organic and inorganic acids.

It can be demonstrated that even with an insoluble Co compound, e.g., a salt of an inorganic acid ($CoCl_2$, $CoSO_4$), a homogeneous catalytic complex is formed as a result of the reaction of the alkyl aluminum with the insoluble Co compound. In fact, if a suspension of insoluble Co compound (e.g., $CoCl_2$) in benzene containing $AlEt_2Cl$ is stirred at room temperature and subsequently filtered, the filtrate shows catalytic activity (51).

The fact that different Co compounds, as reported above, by reaction with $AlEt_2Cl$ (or $AlEtCl_2$, $Al_2Cl_3Et_3$), yield catalysts with equivalent activity and stereospecificity suggests that the catalytic complex is essentially the same in every case. It is actually possible to demonstrate that the first stage of the catalyst-forming reaction is the substitution of the groups bonded to Co by the —Cl of the Al compound (59,60).

The reaction probably occurs according to the scheme:*



(1)

The formation of $CoCl_2$ can be easily demonstrated by performing the reaction in tetrahydrofuran (59). Crystals of $CoCl_2 \cdot THF$ are always isolated from this reaction when the tetrahydrofuran solution is concentrated, regardless of the starting Co compound ($CoSO_4$, Co 2-ethylhexanoate, Co di- or triacetylacetonate, etc.).

It is possible to show the occurrence of reaction 1 in aromatic solvent as well. This can be easily demonstrated by operating at a low Al/Co

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* Reaction 1 is valid not only for Co compounds, but also for other transition metal compounds. Thus the reaction between AlR_2Cl and $Ti(OR)_4$ or $V(acac)_3$ gives β-$TiCl_3$ or VCl_2, respectively.

ratio and at a relatively high concentration of cobalt compound. Under these conditions at room temperature, a blue complex precipitate is formed containing Al, Co, Cl, and the groups initially bonded to the Co. The Co/Cl ratio is close to 1:2 in the precipitate. After separating the precipitate by filtration and treating it with THF, a blue solution is obtained which, after concentrating to a small volume, yields $CoCl_2{\cdot}THF$ crystals (59,61).

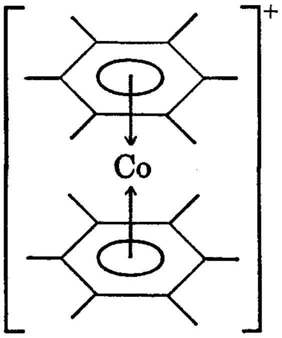
Under the conditions normally used for catalyst preparation (i.e., at 1–5 mg Co per liter of solution and at Al/Co ratios of about 30 or more), the $CoCl_2$ formed according to reaction 1 is rapidly alkylated by $AlEt_2Cl$ to give an unstable species Co(Et)Cl. The latter is transformed into Co^I–Cl by homolytic cleavage of the Co—C bond. The Co compound is stabilized in valency I by complexation with the Al compound.

Alkylation is indicated by gas evolution (mainly ethane*) observed in the reaction between $AlEt_2Cl$ and the cobalt compound.

The formation of a species containing Co(I) is indicated by the following facts:

1. if THF is added to the catalyst solution (preferably if the latter is prepared at a high Co concentration, about 10–20 mg Co/liter) the simultaneous formation of metallic Co and $CoCl_2$ is observed. Evidently the THF destroys the complexation between Co and Al and liberates the species containing Co(I), which disproportionates into metallic Co and $CoCl_2$

2. in the reaction between $AlEt_2Cl$ and $Co(acac)_2$ in benzene solution saturated with hexamethylbenzene† (HMB) it is possible to show the formation of the cation



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* The ethyl radicals formed by cleavage of the Co—C_2H_5 bond should give rise to butane or an equimolar mixture of ethylene and ethane. However, ethane is the major constituent of the gas evolved. The reason for this is not clear. Probably hydrogen is abstracted from the solvent by the ethyl radical, but this point is still to be clarified.

† Since HMB is a solid (mp 166°), it cannot be used alone as a solvent.

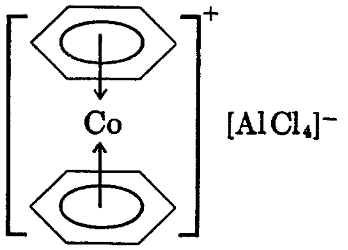
which can be precipitated by anions such as BPh_4^-, BF_4^-, etc. (62). An analogous complex containing benzene coordinated to Co could not be isolated owing to its low stability. It should be pointed out that HMB is a much stronger electron donor than benzene; therefore it coordinates to a metal more strongly than benzene.

The facts described above concerning the reaction between aluminum alkyl halides and Co compounds were confirmed by obtaining a Co (I)-containing crystalline complex that can polymerize butadiene by itself, i.e., without the addition of an aluminum alkyl (59). If equimolecular amounts of $AlPh_2Cl$, $AlPhCl_2$, and $CoCl_2$ are refluxed in benzene for 10–20 min and then filtered while hot, a light yellow solution is obtained. This solution exhibits catalytic activity for the polymerization of butadiene to *cis*-1,4 polymer. Upon cooling this solution, yellow brown crystals of the composition $(AlCl_2Ph)_2 \cdot Co^ICl \cdot 0{\cdot}5C_6H_6$ precipitate. These crystals, when dissolved in benzene, polymerize butadiene.

In conclusion: when an aluminum alkyl (or aryl) chloride and a cobalt compound are reacted in a hydrocarbon solvent, a catalytic complex is formed which contains the species Co^ICl complexed with the Al compound.

b. Catalysts from Al Trihalides and Co Compounds. Co catalysts which are obtained not from Al alkyl chlorides, but from Al trihalides are also known. These catalysts can be prepared, according to some authors, from $AlCl_3$, metallic Al and $CoCl_2$, in benzene (63). By heating the suspension, an oil is formed which appears to be slightly soluble in benzene. The solution of this oil, particularly in the presence of thiophene, exhibits catalytic activity for the *cis*-1,4 polymerization of butadiene.

It has been demonstrated by E. O. Fischer (64) that the complex obtained in this reaction can be formulated as



Therefore it contains monovalent Co just as the complex obtained from $AlEt_2Cl$ and $CoCl_2$. By taking into account that the $[(arene)_2Co]^+$ cation is formed in the reaction between $AlEt_2Cl$ and a Co compound in an aromatic solvent, as stated above, the only difference between the complex obtained from $AlEt_2Cl + CoCl_2$ and $AlCl_3 + Al + CoCl_2 + C_6H_6$, respectively, seems to be that the former contains the anion $AlEt_2Cl_2^-$, and the latter the anion $AlCl_4^-$.

More recently, however, it was shown that the simple complex obtained from $AlCl_3$ and $CoCl_2$ (65) (or other Co compounds such as $Co(acac)_2$ (66)), in the absence of Al, can yield *cis*-1,4 polybutadiene. The complex formed from $AlCl_3$ and $CoCl_2$, which was formulated as $CoCl_2 \cdot 2AlCl_3$, is active, both in benzene and in cyclohexane (65). In complexes of this type the Co present is divalent. Consequently, the existence of Co(I) is not a necessary condition for the formation of a catalyst for the *cis*-1,4 polymerization of butadiene.

During the discussion on the mechanism of polymerization by Co catalysts (Sec. I–F-1), attempts will be made to show that the two types of catalysts, i.e., those containing Co(I) and Co(II), respectively, may belong to the same class.

D. Synthesis of the Polymers

1. Butadiene Polymers

By the use of anionic catalysts based on transition metals it has been possible to obtain from butadiene all four conceivable types of stereoregular polymers, i.e., *trans*-1,4; *cis*-1,4, 1,2 isotactic, and 1,2 syndiotactic.

In addition to these highly regular, and hence highly crystalline or crystallizable, stereoisomers, several other polybutadienes have been obtained with less regular structures. These polymers show only a low degree of crystallinity or are amorphous by x-rays.

Some of the polybutadienes obtained by transition metal catalysts have practical significance. The most important of these is the *cis*-1,4 polybutadiene, which exhibits excellent elastomeric properties.

The preparation of stereoregular polymers of butadiene by coordination catalysts based on transition metals will now be reviewed.

a. *Cis*-1,4 Polybutadiene. The first announcement of the synthesis of a polybutadiene having at least 85% *cis*-1,4 content occurred in a patent of April 1956 (47). A later patent of July 1956 reported the isolation of polybutadienes with high *cis*-1,4 structure obtained by the $AlEt_3$–$TiCl_4$ catalyst system. These high *cis*-1,4 polybutadienes crystallized on stretching at room temperature (67). The structure of crystalline *cis*-1,4 polybutadiene, determined on samples obtained by the $AlEt_3$–$TiCl_4$ system, was published shortly thereafter (68).

New catalyst systems for *cis*-1,4 polybutadiene, based on metals of group VIII, i.e., Co, Ni, Pd, Pt, were discovered later (53–55, 69–72). Among these catalysts, those based on Co seem to be the most important.

In this section we will examine the *cis*-1,4 polymerization of butadiene by the following systems: (1) $AlEt_3$–$TiCl_4$; (2) AlR_3–TiI_4 and related systems; and (3) cobalt catalysts.

Only the systems 2 and 3 are of industrial interest.

(*1*) *Polybutadienes by the* AlR_3–$TiCl_4$ *Systems.* A vast patent literature exists on the polymerization of butadiene by $TiCl_4$-based catalysts (23,41,67,74,80); however, this topic has been examined in but a few papers (27,81,82).

Catalysts prepared by gradual addition of AlR_3 to $TiCl_4$ become active at an Al/Ti ratio of about 0.5. Upon increasing this ratio, the yield of polymer increases rapidly, reaches a maximum at a ratio of about 1, then decreases rapidly (27,82). At an $AlR_3/TiCl_4$ ratio of 3, only a small amount of solid polymer is obtained, together with a large amount of oily products.

The nature of the polybutadienes obtained depends on the $AlR_3/TiCl_4$ ratio (Table II).

1. At an Al/Ti ratio of ~0.5, a powder is obtained which exhibits a much lower than theoretical degree of unsaturation due to cyclization and crosslinking; however, x-ray analysis shows a low degree crystallinity due to *trans*-1,4 sequences. This powder is practically insoluble in benzene and other hydrocarbon solvents.

2. The product obtained at an Al/Ti ratio of about 1 (at this ratio the system is actually $AlR_2Cl + \beta\text{-}TiCl_3$) is an amorphous rubbery polymer consisting of *cis*-1,4 and *trans*-1,4 units, with a very low percentage of 1,2 units (max. 4%). These polymers have the highest *cis*-1,4 content obtainable with this system at different Al/Ti ratios. Their composition was at first reported to be (27): 50–60% *cis*-1,4; 35–45% *trans*-1,4; 2–4% 1,2. These data later proved to be incorrect because of an inaccurate analytical method. The authors of this chapter reexamined the composition of these products by a more precise analytical method (83) and obtained the following values: 75–78% *cis*-1,4; 21–23% *trans*-1,4; 1–2% 1,2. These data are in agreement with those reported by other authors (82). Fractionation of these products is of interest and can be performed by a rapid method as follows: the polymer is dissolved in benzene (in which it is 90–95% soluble) until a solution with a maximum concentration of about 2% is obtained. The benzene solution is

TABLE II

Polymerization of Butadiene by the $Al(C_2H_5)_3$–$TiCl_4$ System in *n*-heptane[a]

	Catalyst[b]				Polymer				
						IR analysis, %			
Run no.	$TiCl_4$ mmoles	Al/Ti molar ratio	Monomer, g	Polymerization Temp., °C	g	*cis*	*trans*	1,2	X-ray examination
1	10	1.1	100	0	35[c]	75	18	2	Amorphous
2	10	1	100	0	34[e]	78	21.5	1.5	Amorphous
3	10	1.3	100	0	38[e]	78	21	1	Amorphous
4	20	2.0	150	13	60[d]	42	51	7	Crystalline[e]
5	20	2.1	150	13	56[d]	46	48	6	Crystalline[e]
6	20	2.3	150	15	63[d]	41	50	9	Crystalline[e]

[a] Solvent 400 ml; polymerization time: 40 min.

[b] Catalyst prepared by introducing slowly a solution of $Al(C_2H_5)_3$ in 50 ml of *n*-heptane into a solution of $TiCl_4$ in 350 ml of *n*-heptane, with stirring (time of addition about 20 min). In runs 1–3 liquid monomer was added about 5 min after the addition of $Al(C_2H_5)_3$ was completed. In runs 4–6 the solid catalyst was washed twice by decantation, then fresh *n*-heptane was added to reach the original volume, then liquid monomer was introduced.

[c] The polymer was fractionated by dissolving in benzene and reprecipitating with MEK. After two dissolutions and reprecipitations, the MEK insoluble fraction analyzed as follows: *cis* 87–89%; *trans* 9–14%; 1,2 $\sim$ 1%.

[d] About 55% of the product is soluble in boiling diethyl ether. IR analysis of the diethyl ether extract, after precipitation with MEK: *cis* 85–86%; *trans* 13–16%; 1,2 $\sim$ 1%. IR analysis of the residue after ether extraction: *trans* 90–95%.

[e] Crystallinity due to *trans*-1,4 polybutadiene.

poured into a large excess of methyl ethyl ketone (MEK), which precipitates about 80% of the dissolved polymer. This product contains 82–83% *cis*-1,4 units and about 1% 1,2 units. After two further dissolutions in benzene and reprecipitations with MEK, a product is obtained containing 87% *cis*-1,4 units and <1% 1,2 units. These results show that the products obtained at an $AlEt_3/TiCl_4$ ratio of ∼1 consist of macromolecules with different *cis*-1,4 contents. Some of them may be even 90% *cis*-1,4. Macromolecules with lower *cis*-1,4 contents are of lower molecular weight and therefore can be removed with MEK. It is of interest that 85–87% *cis*-1,4 polybutadienes isolated by MEK precipitations have final melting temperatures slightly below 0° (about −2°C), that is, only a few degrees below the melting temperature of 99–100% *cis*-1,4 polybutadiene. The reason for this may be that long sequences of exclusively *cis*-1,4 units are present in the polymers prepared with $TiCl_4$.

3. The polymers obtained at an $AlEt_3/TiCl_4$ ratio of 2–2.2 are harder than those obtained at a ratio of 1. According to recent methods of IR analysis (83), they have the following composition: 40–42% *cis*-1,4; 56–58% *trans*-1,4; 3–4% 1,2. X-ray analysis reveals that the polymers have the crystallinity typical for *trans*-1,4 polybutadiene (27). About 35% of the product is extractable with boiling diethyl ether; this fraction is amorphous by x-rays and consists of about 80% *cis*-1,4 units. The residue after the ether extraction is a fibrous mass, which on IR analysis appears to consist of about 90% *trans*-1,4 units.

The ether extractable amorphous fraction can be purified by dissolutions in benzene and reprecipitations with MEK, as mentioned above. By this route, fractions with 91–92% *cis*-1,4 content were isolated, having melting temperatures between 0 and −1°C. These fractions contain about 2% 1,2 units.

In regard to the composition of the crude polymers Mayer and Lehr's (82) and our data are in agreement. On the other hand, Gaylord et al. (81) reported different data. These authors found maximum activity at an $AlR_3/TiCl_4$ ratio of about 2.8. Furthermore, the product obtained at an $AlR_3/TiCl_4$ ratio of ∼1 was reported to be crystalline *trans*-1,4. This result seems rather strange in view of the fact that, as is shown in Sec. I-D-2a, at this ratio, the AlR_3–$TiCl_4$ system yields a *cis*-1,4 polymer also from isoprene. It seems improbable that the same catalyst system

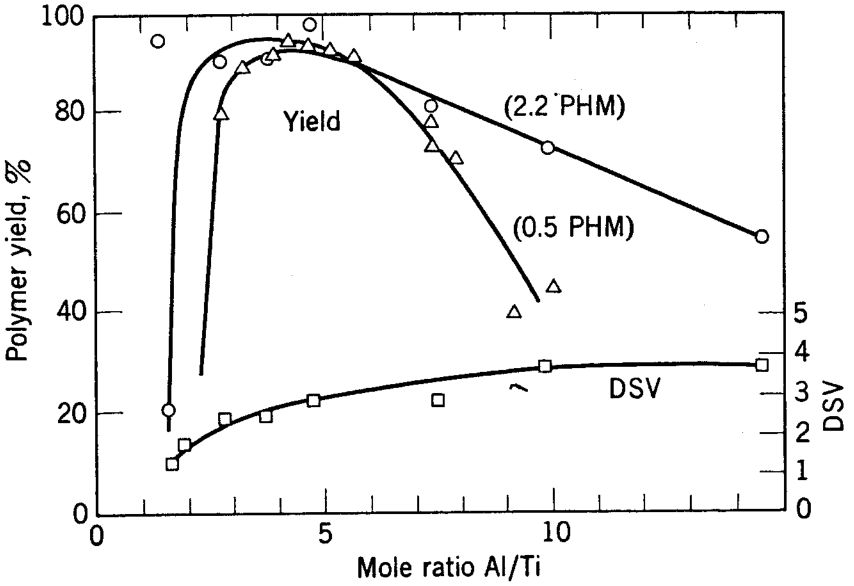


Fig. 1. Yield and dilute solution viscosity of polybutadienes prepared with the Al(i-C_4H_9)$_3$–TiI_4 catalyst. □ and ○ from Ref. 41; △ from Ref. 42. (Phm is catalyst concentration in parts by weight per 100 parts of butadiene.)

(which is actually $AlEt_2Cl$ + β-$TiCl_3$) would yield *trans*-1,4 polymers from butadiene, and *cis*-1,4 polymers from isoprene.

Polybutadienes by Titanium-Based Catalysts Containing Iodine. The characteristics of these catalysts differ from both those prepared from $TiCl_4$ described in the previous paragraph, and those prepared from Co compounds, which will be described later. In addition to several patents (45,47,84,85), various papers have been published on the polymerization of butadiene by catalysts from TiI_4 and analogous systems (42,82,86). Practically identical results are obtained by catalysts prepared from TiI_4, $TiCl_2I_2$, or $TiClI_3$.

The main features of these catalysts are as follows:

1. The catalysts become active at an AlR_3/Ti ratio of about 1 or slightly above. Yields increase rapidly upon increasing the Al/Ti ratio until a maximum is reached, then they decrease very slowly (Fig. 1). The maximum is at a ratio of 1.5–3 according to some authors (82), and around 5 according to others (42).

It should be remembered that in the case of the AlR_3–$TiCl_4$ systems the highest activity is found (24,27) at a Al/Ti ratio of about 1 (corresponding to the formation of β-$TiCl_3$); moreover in the iodine systems the activity vs Al/Ti ratio curves show a narrower peak and the decrease in activity with increasing Al/Ti ratio is much faster than in the $AlR_3/TiCl_4$ systems.

2. The *cis* content of the polymers depends on the concentration of the catalyst, and increases with decreasing concentration. At low catalyst concentrations (of the order of 1–2 mg-atoms of Ti/100 g C_4H_6, in benzene containing 10–15% of C_4H_6 by weight) the *cis* content may reach 94–95%. It does not seem that higher *cis* contents can be reached with TiI_4-based or similar catalysts. It is interesting to compare this behavior with that of the catalysts from $TiCl_4$ (Al/Ti $\sim$1), in which the *cis* content is independent of the catalyst concentration over a wide range.
3. The *cis* content is the highest at Al/Ti ratios corresponding to maximum catalyst activity, then it decreases slightly with increasing Al/Ti ratio, while simultaneously the percentage of 1,2 units increases (about 4% at an Al/Ti ratio of 5, about 10 at an Al/Ti ratio of 10). For polybutadienes obtained with $TiCl_4$, the decrease in the *cis* content with increasing Al/Ti ratio occurs considerably faster.
4. At constant monomer concentration, polymer molecular weight is highly influenced by catalyst concentration: it rapidly decreases with an increase in catalyst concentration. Depending on the conditions, polymers may have molecular weights from a few tens of thousands to about one million.

The various ternary systems exhibit similar characteristics. Catalyst activity as well as the stereospecificity vary with the molar ratio of the catalyst components, and only certain combinations produce good stereospecificity, good activity, and high molecular weights.

In the case of the ternary system $Al(i\text{-}C_4H_9)_3$–I_2–$TiCl_4$, the optimum composition was found to be (42), in mole %: $Al(i\text{-}C_4H_9)_3$, 70–75; I_2, 15–25; $TiCl_4$, 5–12. In the case of the system $AlEt_3$–$AlEt_2I$–$TiCl_4$ the optimum composition is (48) at molar ratios of 4:4:1. Considering that in the former system I_2 reacts with AlR_3 to give AlR_2I (42), it can be seen why these two compositions are equivalent.

There is some literature concerning the polymerizations by metal hydride catalysts (48–50,87). Ternary systems from $TiCl_4 + AlI_3$ and one of the following compounds: $AlHCl_2 \cdot O(C_2H_5)_2$, $AlH_2N(CH_3)_2$, $AlH_2Cl \cdot N(CH_3)_3$, $AlH_3 \cdot N(CH_3)_3$ are particularly stereospecific and active.

The *cis* content of the polymers obtained by these systems is reported to be about 95% (49,87).

It is of interest that the systems $LiAlH_4$–$TiCl_2I_2$ (Al/Ti ≥ 5) or $LiAlH_4$–I_2–$TiCl_4$ (I_2/Ti ~ 0.5; Al/Ti ≥ 8) in benzene, at room temperature or slightly below, yield 93–94% *cis*-1,4 polybutadienes (50). This seems to be in contrast to some patents (41,88), according to which these catalyst systems yield *trans*-1,4 (and not *cis*) polybutadienes or polyisoprenes. This discrepancy is due to the fact that in the patents quoted an ether suspension of $LiAlH_4$ is used and the presence of ether causes the different stereospecificity. This fact will be further discussed in Section I-F, dealing with the polymerization mechanism.

As pointed out earlier, all Ti catalysts containing iodine are equivalent because the final products of the catalyst forming reaction contain all the iodine bonded to Ti. However, this equivalence can be explained only by assuming that halogen exchange among the catalyst components is faster than polymerization initiation, even with catalysts prepared in the presence of monomer (82).

The true nature of the catalyst formation in these systems is not yet clearly understood. The catalyst forming reaction yields a precipitate. Separately, the solid and the liquid phases do not exhibit any catalytic activity (42,82). This may suggest that these catalysts are heterogeneous. Evidently active heterogeneous catalytic species are present in the systems from TiI_4. For instance, the $Al(i\text{-}C_4H_9)_2I$–TiI_3 system which is moderately active and yields 85–90% *cis*-1,4 polymer, seems to be heterogeneous (82).

However, there is also evidence for the presence of active homogeneous complexes. By treating $AlEt_2I$ with $TiCl_3 \cdot \frac{1}{3}AlCl_3$ (obtained by reduction of $TiCl_4$ with Al) for 15 min at 20 to 50°C a clear solution is obtained which, after cooling and filtering, contains from 2 to 4% of the initial Ti. This solution polymerizes butadiene (48) in high yield to a polymer with up to 90% *cis* content. In addition, it has been reported (49) that the $AlHCl_2 \cdot O(C_2H_5)_2$–$AlI_3$–$TiCl_4$ system is apparently soluble when prepared in the presence of monomer.

Most probably, the catalytic species responsible for the formation of high *cis*-1,4 polymer (94–95%), in the case of Ti systems containing iodine, are homogeneous.

Two features of the polymerization support this conclusion:

1. The *cis* content of the polymer increases with decreasing Ti concentration

2. The molecular weight increases greatly with decreasing Ti concentration

These aspects are similar to those observed with the homogeneous Co catalysts, which will be discussed in the next paragraph. In contrast, these aspects differ considerably from those observed when using the heterogeneous $TiCl_4$ catalysts. The homogeneous nature of the polymerization is also indicated by kinetic studies carried out with the $Al(i\text{-}C_4H_9)_3 \cdot O(i\text{-}C_3H_5)_2$–$TiI_4$ system. The termination was found (86) to be a bimolecular process which is conceivable only in a homogeneous system.

Polybutadienes by Co Catalysts. Catalysts from Aluminum Alkyl Halides and Co Compounds. The first catalysts were prepared from heterogeneous Co compounds ($CoCl_2$, CoS, $CoCO_3$, $CoSO_4$, or $Co_3(PO_4)_2$) in combination with $AlEt_2Cl$ (51,54). In conjunction with $CoCl_2$, AlR_3 was also used (69) at a low Al/Co ratio (about 1). It soon became evident that homogeneous catalytic complexes were formed in the reaction between the alkyl aluminum and the Co compound and that AlR_2Cl was the most suitable aluminum compound for the preparation of such catalysts (51,53,55,70–73). In the system AlR_2–$CoCl_2$, Al/Co $\sim$ 1, AlR_2Cl is formed as a result of the alkylation of $CoCl_2$ by AlR_3. The only practically used Co compounds are the soluble ones.

That the Co catalysts obtained from AlR_2Cl and a Co compound are actually homogeneous is indicated by the absence of a Tyndall effect (51,89,90).

Polymerization of butadiene by the AlR_2Cl–Co compound system in benzene, yields polymers with as high as 99% or even higher *cis*-1,4 content and with molecular weights varying from about 10,000 to more than one million, depending on the experimental conditions. Co catalysts are highly stereospecific only for the polymerization of butadiene. From isoprene, they yield only about 65% *cis*-1,4 units, the remaining being predominantly 3,4 (61). From 1,3-pentadiene they give predominantly (80–90%) *cis*-1,4 polymers. This subject will be discussed later (this Section, 3b).

Since the issue of the first patents, various papers have been published on the polymerization of butadiene by Co catalysts (51,52,60, 91–94). Unfortunately, the data reported are often in disagreement. The amount of catalyst used in these polymerizations is very low (1–5 mg of Co per liter of solvent–monomer mixture) and its efficiency is influenced by electron donors, H_2O and Lewis acids. Substances of this type may be present in the solvent or in the monomer in amounts of the order of magnitude of the catalyst, and may, at least partially, be responsible for the discrepancies among the results reported by the various authors.

While the first patents and papers refer to catalyst systems obtained only from $AlEt_2Cl$ and a Co compound in an anhydrous medium, subsequent papers claim that the presence of an activator is also required. Gippin examined this particular aspect (52,92). He found that the system $AlEt_2Cl$–$CoCl_2 \cdot py$ (Al/Co from 100 to 200; $CoCl_2 \cdot py$ from 0.2 to 0.02 mmoles per 100 g of monomer), in benzene at about 6°C, does not yield solid polymer in 24 hr in the absence of an activator. When H_2O or O_2 was added (in amounts from 5 to 50 moles on $AlEt_2Cl$) rapid polymerization ensued and practically quantitative yields of nearly 98% *cis*-1,4 high molecular weight polybutadiene was obtained. According to Gippin, besides H_2O and O_2 other substances can also act as activators, i.e., $AlCl_3$, organic hydroperoxides, halogens, some alcohols (e.g., *t*-butyl alcohol), some organic halides (e.g., 2-chloro-ethanol, allyl chloride, isochlorobutanes), and also metallic Al. All these compounds (except metallic Al) are used in amounts corresponding to 2–10 mmoles per 20 mmoles of $AlEt_2Cl$.

It is difficult to establish whether or not the presence of an activator is absolutely necessary to obtain high molecular weight *cis*-1,4 polybutadiene with the $AlEt_2Cl$–Co compound catalyst system. This is mainly due to the fact that, unless extreme precautions are taken, trace amounts of many substances which may act as activators may be present in the solvent, in the monomer or in the reagents used to prepare the catalyst. These include H_2O, $AlEtCl_2$ (which may be present in $AlEt_2Cl$), and $AlEt(OEt)Cl$, which constitutes the major impurity of $AlEt_2Cl$.

Although the results obtained by the various authors in the polymerization of butadiene with Co catalysts often cannot be compared, some fundamental characteristics of this type of polymerization are now well established:

1. Conversion varies with time as shown in Fig. 2. Practically complete conversions can be obtained provided the viscosity of the solution does not become prohibitive.
2. The rate of polymerization depends on the aromatic solvent used and decreases in the order: benzene > toluene > xylene > mesitylene. In toluene, the rate is 3 to 4 times as slow as in benzene (61). The addition of hexamethylbenzene to the catalyst solution in aromatic solvent inhibits polymerization (62).
3. The Al/Co ratio does not influence stereospecificity above a mini-

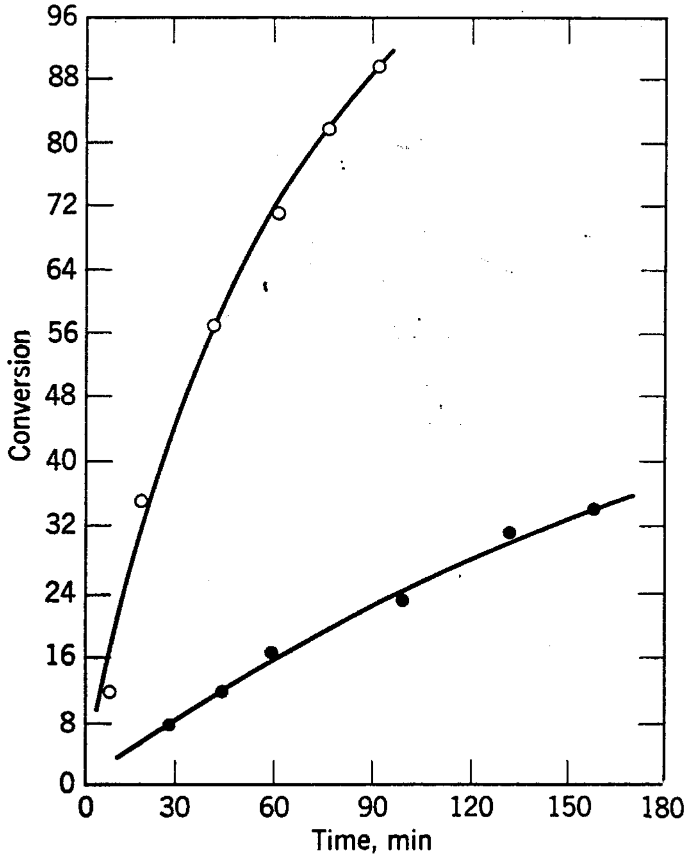


Fig. 2. Conversion vs. time curves for *cis*-1,4 polybutadiene with $AlEt_2Cl$–Co(acac)$_2$ catalyst. Solvent (sodium-dried) 250 ml (⊙ benzene; ● toluene); $AlEt_2Cl$ 2.5 ml; Co 0.5 mg; catalyst aged for 30 min at 0°C; monomer: ⊙ 10 g, ● 15 g; polymerization temperature 0°C.

mum value depending on the catalyst concentration (about 30–40 for Co concentration of 5–10 mg/liter of monomer–solvent mixture).

4. For a given set of experimental conditions, the average molecular weight of the polymers initially increases rapidly with increasing conversion; then the increase gradually becomes less rapid and, in some cases, after a certain conversion is reached, the molecular weight no longer increases and may even decrease. The behavior of the molecular weight vs amount of polymer curves depends on the nature of the solvent and on monomer concentration (Fig. 3).
5. The molecular weight increases with increasing monomer concentration (Table III and Fig. 3), while it decreases with increasing Co concentration. Zgormick et al. reported (95) that the molecular weight is approximately proportional to the inverse of [Co], at least up to $5\text{–}6 \times 10^{-4}$ moles/liter. Molecular weight, on the other hand, does not seem to be influenced by the concentration of $AlEt_2Cl$. This seems to indicate that transfer between growing

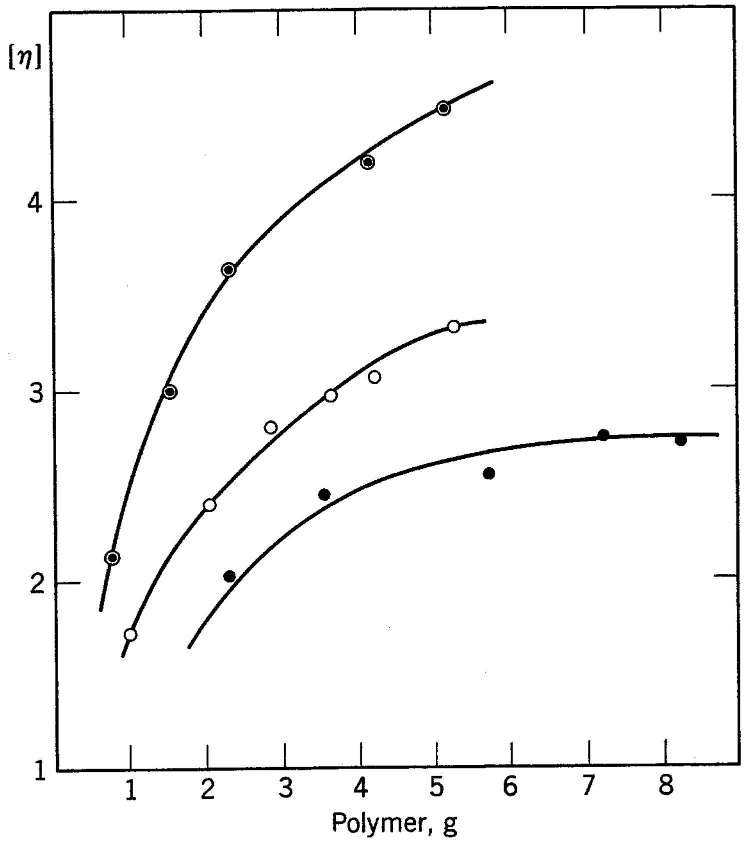


Fig. 3. Intrinsic viscosities vs. polymer curves for *cis*-1,4 polybutadiene obtained by the $AlEt_2Cl$–Co(acac)$_2$ catalyst. Solvent (sodium-dried) 250 ml (⊙, ● benzene: ○ toluene). Monomer: ⊙, ○ 20 g; ● 10 g. Other conditions as under Fig. 2.

TABLE III

Effect of Monomer Concentration on the Molecular Weight of Polybutadienes Obtained by the $Al(C_2H_5)_2Cl$–Co(acac)$_2$ System in Benzene[a] (61)

Concentration of C_4H_6 g/liter charge	Polymerization time, min	Polymer g	Polymer [η], dl g^{-1}
19.3	240	25.4	1.44
28.6	210	24.4	1.61
87	20	9.3	5.27

[a] Experimental conditions: benzene 250 ml; monomer (total amount added): 25 g; Co(acac)$_2$: 3.8 × 10^{-6} moles; polymerization temperature +4°C; catalysts aged for 15 min before monomer addition. The monomer concentration was kept as constant as possible by the continuous addition of fresh butadiene. Monomer consumption per unit time, under the conditions used, was known from previously determined kinetic data.

chains and $AlEt_2Cl$ is rather limited if occurring at all. On the other hand, Fig. 3 indicates that chain termination occurs. This seems to be mainly due to transfer with monomer.

6. The temperature of polymerization can be varied over a wide range, from low temperatures up to about +30°C, without influencing stereospecificity. Above about +30°C, the *cis*-1,4 content decreases, while the 1,2 content increases. The *cis* content of polymers obtained at +50°C are below 90%, and their intrinsic viscosity is less than one-half of that obtained at +5°C (51,52).
7. Monomer concentrations up to about 40 wt% do not influence the *cis* content of the polymers. At higher monomer concentrations small amounts of gel are formed and the *cis*-1,4 content decreases (52).

Various methods have been developed for regulating polymer molecular weight. This is of practical importance, since polymers of too high molecular weight are difficult to process. Hydrogen can be used as a regulator (96), as in the case of the polymerization of α-olefins. In addition to H_2, also ethylene, α-olefins, allenes (96), or some unsaturated compounds containing internal double bonds, such as cyclooctadiene (97) can be used as chain transfer agents. Data showing the influence of these agents on the molecular weight are reported in Tables IV–VI.

TABLE IV

Effect of H_2 on the Molecular Weight of *cis*-1,4 Polybutadiene Obtained by the $Al(C_2H_5)_2Cl$–$CoCl_2 \cdot py$ System in Benzene[a] (96)

			Polymer[b]	
p_{H_2}, atm	Polymerization time, min	Conversion, %	$[\eta]$, dl g^{-1}	mol wt[c]
0	60	99	5.50	742.000
0.39	65	100	4.17	502.000
5	60	98	2.95	316.000
10	65	100	2.65	272.000
20	60	100	1.37	109.700

[a] Experimental conditions: $Al(C_2H_5)_2Cl$, 0.036 moles; $CoCl_2 \cdot py$, 0.0925 mmoles; benzene, 1000 ml; butadiene (Phillips "pure grade"), 100 g; polymerization temp., 15°C.

[b] All the polymers obtained are reported to be at least 97.7% *cis*-1,4.

[c] Calculated from the intrinsic viscosity using the relationship $[\eta] = 3.37 \times 10^{-4} M^{0.715}$ (118).

TABLE V

Effect of Transfer Agents on the Molecular Weight of *cis*-1,4 Polybutadiene Obtained by the $Al(C_2H_5)_2Cl$–$CoCl_2 \cdot py$ System in Benzene[a] (96)

$CoCl_2$ mmoles 10^3	Transfer agent		Polymerization time, min	Conv., %	Polymer[f]	
		mole/100 mole C_4H_6			$[\eta]$, dl g^{-1}	mol, wt[g]
92.5	C_2H_4[b]	0	60	94	5.57	759,000
92.5		0.842	60	96	4.26	519,500
92.5		2.41	65	96	2.72	282,000
92.5		5.08	60	91	1.78	156,700
90.0	C_3H_6[c]	0	60	100	5.70	776,000
90.0		72.2	60	99	3.43	389,000
90.0		137.5	70	99	2.80	292,000
77.0	C_3H_4[d]	0	75	94	6.6	968,000
77.0		0.0225	75	97	4.09	495,000
77.0		0.0930	80	98	2.63	266,000
90.0	C_4H_6[e]	0	60	100	5.95	832,000
90.0		0.090	60	98	3.12	339,000
90.0		0.233	60	96	2.10	200,000

[a] Experimental conditions: $Al(C_2H_5)_2Cl$, 0.036 moles; benzene 1000 ml; butadiene (Phillips "pure grade") 100 g; polymerization temp., 15°C.

[b] Ethylene.

[c] Propylene.

[d] Propa-1,2-diene.

[e] Buta-1,2-diene.

[f] All the polymers are reported to be at least 97% *cis*-1,4.

[g] Calculated from $[\eta]$ using the relationship reported in Ref. 118.

Although the most common solvents are benzene or toluene, the use of aliphatic solvents, such as *n*-hexane, *n*-heptane or cyclohexane is mentioned in the literature (51,52). The *cis* content and the molecular weights of the polymers obtained in these solvents are lower than those obtained in benzene, although high conversions can be obtained.

The kinetics of butadiene polymerization to *cis*-1,4 polymer by Co catalysts in aromatic solvent was studied by several authors (52,60,94,95). It seems established that the polymerization is first order with respect to both monomer and Co. According to some authors, however, this first order dependence with respect to Co holds only for low Co concentrations (94). The activation energy of the polymerization process in toluene is reported to be about 11.86 kcal/mole (60).

Catalysts from $AlCl_3$ or $AlBr_3$ and Co Compounds. The polymerization of butadiene to *cis*-1,4 polymer by catalysts obtained from $CoCl_2$ and

TABLE VI
Effect of Cyclooctadiene on the Molecular Weight of *cis*-1,4 Polybutadiene Obtained by the $Al(C_2H_5)_2Cl$–Co(acac)$_2$ Catalyst System in Benzene (61)

Co(acac)$_2$, mmoles	Al/Co molar ratio	Benzene, ml	C_4H_6, g	COD, g	Polymeriz. time, min	Polymer g	Polymer [η]	Polymer mol wt[a]
5.8×10^{-3}	145	60	26	—	5	2.1	5.3	708,000
5.8×10^{-3}	145	60	26	0.26	10	8	2.07	193,000
5.8×10^{-3}	145	70	19.5	—	10	2.7	4.6	582,000
5.8×10^{-3}	145	70	19.5	0.21	20	9.1	1.81	160,000
5.8×10^{-3}	145	80	13	—	20	3.1	3.76	440,000
5.8×10^{-3}	145	80	13	0.18	40	8.7	2.24	215,000

[a] Determined from [η] using the relationship reported in Ref. 118.

$AlCl_3$ in the absence of aluminum alkyls, was reported by Scott et al. (63), O'Reilly et al. (180), and by Balas et al. (65). The use of catalysts from $AlBr_3$ and Co compounds other than $CoCl_2$ (Co(acac)$_2$, $CoCl_2$·2py, Co(acac)$_3$, Co-octoate, etc.) was also described (66).

Scott's catalyst consists of a complex obtained from $CoCl_2$ and $AlCl_3$, having the formula $Co(AlCl_4)_2$. Solutions obtained by dissolving this complex in benzene polymerize butadiene. The addition of thiophene to the system (thiophene/$AlCl_3$ from 1 to about 5) before polymerization initiation, seems a necessary condition to obtain high conversions of a polymer with a *cis*-1,4 content of about 94–95%. In the absence of thiophene, tacky low polymers containing phenyl groups and having a *cis*-1,4 content of only 48–56% are obtained. However, in a subsequent paper, Balas and co-workers report that dilute solutions of the $AlCl_3$–$CoCl_2$ complex in benzene or even in cyclohexane (Al/Co molar ratio from 2.4 to about 12.5) can yield, even without addition of thiophene, polymers with high *cis*-1,4 content (~95%) and high molecular weight ([η] up to about 6.8).

In analogy with the catalysts obtained from aluminum alkyl halides and Co compounds, the catalysts obtained from $AlCl_3$ and $CoCl_2$ are highly stereospecific only for the polymerization of butadiene, and are far less stereospecific for the polymerization of isoprene.

b. *Trans*-1,4 Polybutadiene. The synthesis of a highly crystalline *trans*-1,4 butadiene polymer was first announced in a patent of March 1955 (98). The catalyst used was the heterogeneous $AlEt_3$–$\alpha TiCl_3$ system. Polymers of the same type were later obtained with hetero-

TABLE VII
Polymerization of Butadiene by Catalysts from $Al(C_2H_5)_3$ or $Al(C_2H_5)_2Cl$ and Vanadium Chlorides[a] (103,104)

				Polymer				
					IR analysis			
V halide, mmoles	Aluminum compound, mmoles	Poly-meriz. temp., °C	Poly-meriz. time, hr	g	*cis*, %	*trans*, %	1,2, %	Diethyl ether extract,[c] %
VCl_3 3.18	6.36	25	19	26.8	—	99	1	1.8
3.18	31.8	25	15	23.7	—	99	1	1.8
$VOCl_3$[b] 3.4	3.74	15	6	6.2	1	96	3	9.8
3.4	6.8	15	8	18.5	1	94	5	15.6
3.4	17	15	7	12.4	1	95	4	15.5
VCl_4[b] 3.4	5.1	15	3	15	1	97	2	7.5
2.1	4.2	15	2	9.2	1	95	4	12.9
2.1	6.3	15	2	14.5	1	95	4	11.6
2.1	10.5	15	3	14	1	95	4	12

[a] Experimental conditions: solvent (*n*-heptane) 100 ml; monomer (Phillips 99%) 50 g.

[b] Catalyst prepared by introducing slowly a solution of $AlEt_3$ in *n*-heptane into a solution of VCl_4 or $VOCl_3$ in the same solvent, with stirring.

[c] Amorphous by x-ray examination. The residue after diethyl ether extraction contains 98–99% *trans*-1,4 units and has a final melting temperature of about 145°C.

geneous catalysts from $TiCl_4$ (23,27,88), TiI_4 (47), VCl_4 (76), $VOCl_3$ (99), and VCl_3 (99). More recently, 99–100% *trans*-1,4 polybutadienes were also obtained with homogeneous systems prepared from compounds of V (100) or of metals of the VIIIth group (61,102).

(*1*) *Heterogeneous Catalysts.* The most stereospecific system for the synthesis of *trans*-1,4 polybutadiene (and of *trans*-1,4 polydiolefins in general) is probably that from aluminum trialkyl and VCl_3 (103). This catalyst system yields products (Table VII) which, even in the crude state, consist of 98–99% *trans*-1,4 units. The amorphous fraction (extractable with diethyl ether) is of the order of about 2% in polymerizations carried out at room temperature or below. The residue after the ether extraction consists of 99–100% *trans*-1,4 units; vinyl groups are hardly detectable while *cis*-1,4 units seem to be completely absent.

The catalysts from VCl_4 or $VOCl_3$, combined with either AlR_3 (Al/V = 1.5–3) or AlR_2Cl (Al/V = about 5–10) are also highly stereospecific (104). The products obtained by these catalysts contain a larger amorphous fraction (up to about 10%) than the products from VCl_3 catalysts

(Table VII). However, if only the heterogeneous phase of the catalyst is used, after filtration and resuspension in fresh *n*-heptane, polymers are obtained that contain a lower amount of amorphous fraction and that differ only slightly from the products obtained by VCl_3-based catalysts. The catalysts obtained from VCl_4 or $VOCl_3$ give much higher polymerization rate than those obtained from VCl_3.

The catalysts from Ti halides are less stereospecific than those from V for the synthesis of *trans*-1,4 polybutadiene or *trans*-1,4 polydiolefins in general. The system AlR_3–$TiCl_4$, Al/Ti about 0.5, yields *trans*-1,4 polymers of low crystallinity, (23,27). Moreover, the degree of unsaturation is considerably lower than the theoretical one, due to cyclization or crosslinking. The same system, at an Al/Ti ratio of about 2, gives a mixture of amorphous (predominantly *cis*-1,4) and crystalline (predominantly *trans*-1,4) products. The *trans*-1,4 content of the latter, which can be isolated by removing the amorphous fraction with diethyl ether, is 90–95%.

Catalysts obtained from violet $TiCl_3$ are more stereospecific than those from $TiCl_4$. However, the polymers obtained with the former catalysts also contain considerable amounts of an ether-extractable amorphous fraction. The amorphous fraction can vary from about 25 to 50%, depending on the type of $TiCl_3$ used and on the polymerization conditions (38). In general, the amorphous fraction increases with increasing polymerization temperature. In runs carried out at room temperature with $TiCl_3$ prepared by reduction of $TiCl_4$ with H_2, at an Al/Ti ratio of about 1–5, polymers are obtained whose IR analysis indicates 70–88% *trans*-1,4, 3–10% *cis*-1,4, and 15–20% 1,2. About 35% of the polymer is soluble in diethyl ether. The residue after the ether extraction contains 90 to 95% *trans*-1,4 units, and shows a fair degree of crystallinity.

According to patents, predominantly *trans*-1,4 polymers of butadiene and of isoprene can also be obtained with the $LiAlH_4$–$TiCl_4$ or $LiAlH_4$–I_2–$TiCl_4$ systems (41,88). These products are probably mixtures of macromolecules with different *trans*-1,4 contents, some of which are able to crystallize. Such catalysts yield *trans*-1,4 polymers only when diethyl ether solutions or suspensions of $LiAlH_4$ are used. In the absence of ether they give predominantly *cis*-1,4 polymers.

(*2*) *Homogeneous Catalysts.* Various homogeneous catalysts are known that can give *trans*-1,4 polymers from butadiene. One of these is the system obtained by the reaction between $AlEt_2Cl$ and a soluble V compound, such as $V(acac)_3$, or complexes of VCl_3 with Lewis bases, e.g., $VCl_3 \cdot 3THF$ (100). A large excess of $AlEt_2Cl$ (Al/V molar ratio of 20–50 or even higher) is usually employed in these systems. They yield poly-

TABLE VIII

Polymerization of Butadiene, Isoprene, and 1,3 Pentadiene by the Homogeneous System $Al(C_2H_5)_2Cl–VCl_3·3THF^a$ (100)

No.	Monomer	g	$VCl_3·3C_4H_8O$, moles	Al/V molar ratio	Temperature, °C	Polymeriz. time, min	Polymer g	Polymer $[\eta]^j$ dl g^{-1}	Polymer IR exam	Polymer X-ray exam
1	Butadiene[b]	15	8×10^{-5}	30	0	30	3.6	1.5^k	99–100% *trans*–1,4	Crystalline
2	Butadiene[b]	15	14×10^{-5}	50	−20	60	6	1.71^k		
3	Butadiene[b]	5	11×10^{-4}	30	0	7	0.1	0.3		
4	Butadiene[b]	15	8×10^{-5c}	30	0	1200	Traces	—		
5	Butadiene[b]	15	8×10^{-5d}	30	0	1200	2.5	—		
6	Pentadiene[e]	12	4×10^{-5}	50	−15	900	2.2	0.3	*trans*-1,4 + 1,2	Amorphous
7	Pentadiene[f]	12	4×10^{-5}	30	−15	900	7	1.87		
8	Pentadiene[g]	10	4×10^{-5}	50	−15	900	6.2	1.		
9	Isoprene[h]	15	8×10^{-5}	30	−15	1440	0.1	—	*trans*-1,4 (95%)	Crystalline
10	Isoprene[i]	20	8×10^{-5}	30	−15	1800	0.4	0.3		

[a] Solvent toluene 100 ml.

[b] Phillips "pure grade" 99%.

[c] Catalyst aged for 3 days at 20°C before introducing the monomer.

[d] Catalyst aged for 3 days at −70°C before introducing the monomer.

[e] Product of Houdry Process Corp., 76% *trans* isomer.

[f] From decomposition of the sulfone; 99% *trans* isomer.

[g] Pure trans isomer, obtained by preparative gas chromatography.

[h] Phillips "polymerization grade" 99%.

[i] ~99.9% pure, obtained by gas chromatography.

[j] Determined in toluene at 30°C.

[k] Determined on the fraction soluble in toluene at 30°C.

butadienes with 99–100% *trans*-1,4 content (Table VIII) which are highly crystalline by x-rays. However, their molecular weight is lower than that of polymers obtained by VCl_3, VCl_4, and $VOCl_3$ catalysts. Polymerizations with catalysts prepared from $AlEt_2Cl$ and V compounds must be carried out at low temperatures, otherwise catalyst activity is rapidly deterioriating.

Crystalline polybutadienes with 97–99% *trans*-1,4 structures were also obtained with Co or Ni catalysts.

As discussed above the $AlEt_2Cl$–Co compound systems in benzene yield *cis*-1,4 polybutadienes. If triethyl- or trimethylamine is added to these systems, *trans*-1,4 polybutadiene is obtained (105). Thus the $AlEt_2Cl$/Co octoate/NEt_3 system, at a molar ratio of 10/1/0 gives 95% *cis*-1,4 polymer; at a ratio of 10/1/7.4 it gives 36% *cis*, 24% *trans*, 40% 1,2 polymer; at a ratio of 10/1/8.4 it gives 95% *trans* and 5% 1,2 polymer.

Polybutadienes with 97–99% *trans*-1,4 structure can also be obtained with the $AlEt_3$–$Co(acac)_2$ or $AlEt_2Cl$–$Co(acac)_2$ systems in THF solvent (61). The reaction between AlR_3 and $Co(acac)_2$ in THF gives rapidly metallic Co. However, if the reaction is carried out in the presence of monomer at 0°C or below, a *trans*-1,4 polymer is formed in low yields.

The synthesis of highly crystalline *trans*-1,4 polybutadiene by π-allyl-Ni-I has recently been reported (102). Some data concerning these polymerizations are shown in Table IX.

c. 1,2 Polybutadienes. (*1*) *1,2 Syndiotactic Polybutadiene.* The synthesis of a crystalline 1,2 syndiotactic polybutadiene was first reported in a patent of 1955 (106). Homogeneous catalysts obtained from $AlEt_3$ and either an acetylacetonate or an alcoholate of Ti, V or Cr (but only under particular conditions that will be specified later) were used. Later, it was observed that many other halogen free compounds of these metals (complexes with CO, isonitriles, nitriles, pyridines, or other Lewis bases) yield, in combination with an aluminum trialkyl, seemingly homogeneous catalysts which give 1,2 syndiotactic polybutadienes. Even some chlorinated compounds (e.g., $MoCl_5$) produce, in combination with AlR_3, catalysts yielding 1,2 syndiotactic polybutadienes (61).

A detailed study of the polymerization of butadiene by the $AlEt_3$–$V(acac)_3$ system has been published (107). This catalyst combination yields macromolecules with varying degree of stereoregularity. The products can be separated by successive extractions with different solvents into amorphous or slightly crystalline fractions (soluble in boiling

TABLE IX
Polymerization of Butadiene by π-allyl Nickel Iodide (102,61)

					Polymerization product							
					Solid					Oil		
						IR analysis					IR analysis	
No.	Allyl Ni iodide, moles × 10^{-3}	Solvent, type	ml	Butadiene, g	g	*trans*-1,4, %	1,2, %	$\bar{M}_n$	*Tm*	mg	*trans*-1,4, %	1,2, %
1	0.4	Benzene	30	5	2.5	97.6	2.4	4016	125	70	94	6
2	0.25	Dioxane	30	7	1	97.7	2.3	3650	118	30	91	9
3	1	Ethanol	25	3	0.6	97	3.0	1900	95	100	90	10
4	0.45	THF	35	6	3.0	98	2.0	3710	120	30	94	6
5	0.3	Pentane	35	8	0.5	95	5.0	2500	100	80	90	10
6	0.5	Diethylether	30	9	0.5	94.7	5.3	1800	92	60	89.5	10.5

TABLE X

Polymerization of Butadiene by the $Al(C_2H_5)_3$–V(acac)$_3$ Catalyst System[a] (107)

			Polymer				
				IR analysis			Diethyl ether extract,[c] %
Al/V molar ratio	Time of aging of the catalyst, min	Monomer,[b] g	g	*cis,* %	*trans,* %	1,2, %	
3.5	2	30	4.1	12.5	5.5	82	99
4	2	30	13.2	14	5	81	89
6	2	30	10.2	16	4	80	71
6	60	30	10.1	14	6	80	71
6	120	30	10.35	14	5	81	63.5
6	300	30	10.0	13	4	83	60
8	2	30	9.3	10	5	85	64
10	2	30	8.6	12.5	4.5	83	59
10	60	50	8.5	11	3	86	48
10	120	50	7.6	11	4	85	45
10	180	50	7.0	12	5	83	39.4
30	2	30	8.7	11	3	86	59

[a] Experimental conditions: V(acac)$_3$ mmoles, 1.42; solvent (benzene), 80 ml; time and temp. of polymerization: 16 hr at 15°C.

[b] From decomposition of the sulfone: >99.9% pure.

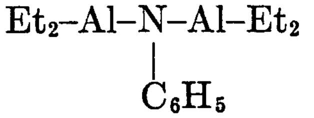
[c] Amorphous or slightly crystalline by x-rays. Residue after ether extraction: crystalline by x-rays; melting temp., 156°C; $[\eta]$ (in toluene at 30°C) 2 dl g^{-1} (determined on the fraction soluble at 30°C); IR analysis: about 95–97% 1,2.

diethyl ether) and highly crystalline fractions (residue after diethyl ether extraction). Both the Al/V ratio and catalyst aging influence stereospecificity (Table X).

The catalyst from $AlEt_3$ and either VO(OR)$_3$ or VO(acac)$_2$ give analogous results to those obtained with the catalysts from V(acac)$_3$ (61).

Catalysts obtained from $AlEt_3$ and Ti(OR)$_4$ are less stereospecific than those obtained from V (108). Furthermore, they tend to give partially crosslinked products especially at high conversions, consequently, they are of little utility for preparative purposes. Among the Ti catalysts good stereospecificity is shown by the system obtained from $Ti[N(C_2H_5)_2]_4$ and $AlH_2N(CH_3)_2$ (109).

Catalysts showing good stereospecificity for the synthesis of 1,2 syndiotactic polybutadiene have been obtained from $AlEt_3$ and various molybdenum compounds i.e., $MoO_2(OR)_2$, MoO_2(acac)$_2$, Mo(acac)$_3$, and $MoCl_5$. The crystalline fraction (residue after diethyl ether extraction) can be as high as 80% (61).

It has been reported recently that 1,2 syndiotactic polybutadiene can be synthetized with catalysts obtained from soluble or insoluble Co compounds ($CoSO_4$, $CoCl_2$, $Co_3(PO_4)_2$, Co-stearate, $CoCl_2{\cdot}2py$, $Co(acac)_2$, etc.). As discussed in Section I-D-1a these Co compounds give, after reaction with AlR_2Cl, catalysts for the *cis*-1,4 polymerization of butadiene. With AlR_3, the same Co compounds give homogeneous catalysts which yield 1,2 syndiotactic polymers (110). In modifications of these catalysts, the reaction product of $AlEt_3$ and H_2O (Al/H_2O ratio = 1:0.5) or of $AlEt_3$ and a primary amine such as aniline (Al/amine ratio = 1:0.5) is used as organoaluminum compound (111). It is believed that in these reactions $Et_2{-}Al{-}O{-}Al{-}Et_2$ and  $Et_2{-}Al{-}\underset{\displaystyle C_6H_5}{\underset{|}{N}}{-}Al{-}Et_2$ are formed, respectively.

The polymers obtained with the above Co systems (either from $AlEt_3$ or from the reaction product of $AlEt_3$ and H_2O or an amine) contain a small amount of amorphous (max. 10%) fraction. The residue after diethyl ether extraction is a highly crystalline white powder containing almost exclusively 1,2 units. Table XI reports data concerning the polymerization of butadiene by the homogeneous systems prepared from $CoCl_2{\cdot}2py$ and either $AlEt_3$ or the reaction product of $AlEt_3$ and H_2O.

The present authors reexamined the polymerization of butadiene by the $AlEt_3{-}Co(acac)_2$ system, but were unable to repeat the results reported in the literature. Probably the formation of 1,2 syndiotactic polybutadiene by the above system requires particular conditions, which do not seem to be completely specified in the literature. It is worth

TABLE XI

Polymerization of Butadiene to Syndiotactic Polymer by Co Catalysts[a]

				Polymer				
Al compound, mmoles	Co compound, mmoles × 10^3	Monomer, g	Polymeriz. time, hr	g	IR anal., 1,2 %	Diethyl ether insoluble fraction, %	Crystallinity, %	Ref.
$Al(C_2H_5)_3$ 33.4	$CoCl_2{\cdot}2py$ 61.5	100	15	31	98	98	76.5	110
$Al(C_2H_5)_3$ 33.4	$Co(acac)_2$ 58	100	15	14	98	90	73.5	110
$(Et_2Al)_2O$ 17.7	$CoCl_2{\cdot}2py$ 77	99	2	45	Not rep.	Not rep.	78	111
$(Et_2Al)_2O$ 21.8	$CoCl_2{\cdot}2py$ 77	100	6.5	70	Not rep.	Not rep.	68.4	111

[a] Solvent (benzene) 1000 ml.

mentioning that the $AlEt_3$–$Co(acac)_2$ system, which according to Susa yields 1,2 syndiotactic polybutadiene, according to other authors yields mainly an oligomer, 4-methyl heptatriene (112,113). Evidently, the experimental conditions which are necessary for the formation of 1,2 stereoregular polymer have not been specified sufficiently.

Finally, 1,2 polybutadienes have also been obtained by the $BrMg(C_6H_5)$–$TiCl_3$ and $MoCl_5$–$Co_2(CO)_8$ systems, respectively (114,115). The latter catalyst gives an amorphous product, while nothing has been reported about the stereoregularity of the polymer obtained by the former system.

(2) 1,2 Isotactic Polybutadiene. The catalysts discussed in the preceding paragraph, prepared from AlR_3 and a Ti, V, Mo, or Co compound, have always yielded, irrespective of the conditions under which the catalyst is prepared, crystalline 1,2 syndiotactic polybutadiene.

The catalysts obtained from AlR_3 and several Cr compounds, i.e., $Cr(acac)_3$, $Cr(CNR)_6$, chromium hexacarbonyl and its derivatives, show different characteristics (116,117). These apparently homogeneous catalysts give either crystalline syndiotactic or isotactic polybutadiene or both depending on the preparation conditions of the catalyst (mainly the Al/Cr ratio and the time of aging).

Table XII shows some data concerning the polymerization of butadiene by Cr catalysts. It is seen that at low Al/Cr ratios, the unaged catalysts give crystalline syndiotactic polybutadiene, or mixtures of predominantly syndiotactic and isotactic polymers.

Upon increasing the Al/Cr ratio, the amount of isotactic polymer increases and becomes predominant at high Al/Cr ratios.

All the homogeneous AlR_3–Cr compound systems are similar with regard to the formation of syndiotactic or isotactic polybutadiene. Differences, however, exist between catalysts obtained from different chromium compounds. Thus, polymer yield and amount of crystalline fraction in the crude polymer varies depending on the particular Cr compound used.

Apparently the reaction between AlR_3 and a Cr compound proceeds stepwise leading to the formation of catalytic complexes having different stereospecificities for the polymerization of butadiene. Evidently first a complex is formed which is stereospecific for the synthesis of syndiotactic polybutadiene. After further reaction with AlR_3 this complex is transformed into a new one which is stereospecific for the synthesis of isotactic polybutadiene. This explanation accounts for the effect of aging of the catalysts on the stereospecificity and also for the effect of the Al/Cr ratio in the unaged catalysts. In fact, at high Al/Cr ratios

TABLE XII
Polymerization of Butadiene by Catalysts from $Al(C_2H_5)_3$ and Cr Compounds[a] (117)

			Polymer		
				Diethyl ether insoluble fraction	
Cr compound, mmoles	Al/Cr molar ratio	Time of aging of catalyst, min	g	%	X-ray examination
$Cr(CNC_6H_5)_6$ 1.49	2	2	0.3	—	syndio
1.49	5	2	14.5	14	syndio (>50%) + iso
1.49	5	240	9.7	32.5	iso
0.745	7.5	2	6.4	15.3	syndio (>50%) + iso
0.745	7.5	120	5.15	25	iso
0.745	15	2	7.2	13.5	iso (>50%) + syndio
0.745	15	120	6.6	24	iso
0.745	15	240	6.8	34	iso
$Cr(acac)_3$ 1.42	3	2	6	15	syndio
1.42	10	2	9.85	2	iso
$Cr(CO)_5py$ 1.84	3	2	5.4	31	syndio + iso
1.84	5	2	5.75	15	iso

[a] Benzene, 80 g; monomer, 30 g; 16 hr at 15°C.

the catalyst forming reaction is so much faster than at low ones that it reaches (the minimum time of aging in the runs of Table XII) an advanced stage even after only 2–3 min, which corresponds to the formation of a catalyst for isotactic polymer.

The reaction between AlR_3 and the Cr compound probably continues also during the polymerization, that is, in the presence of the monomer, although presumably much more slowly. Consequently, it is possible that when mixtures of syndio- and isotactic polymers are obtained, the former is produced mainly during the first part of the polymerization and the latter afterwards.

These data demonstrate the basic difference between the catalysts from Cr compounds and those from Ti, V, Mo, or Co compounds. The latter systems do not yield isotactic polybutadiene even at very high Al/transition metal ratios and after a long aging time.

2. *Isoprene Polymers*

Next to butadiene, isoprene is the monomer which has been studied most thoroughly in polymerizations with coordination catalysts. Two stereoregular polymers of isoprene have been obtained by such catalysts, one with a *trans*-1,4, the other with a *cis*-1,4 structure. These polymers are practically identical with guttapercha and natural rubber, respectively.

Another polymer obtained with these catalysts is a polyisoprene comprised almost completely of 3,4 units. This polymer, however, is amorphous by x-rays, probably due to insufficient order in the configurations of the asymmetric carbon atoms.

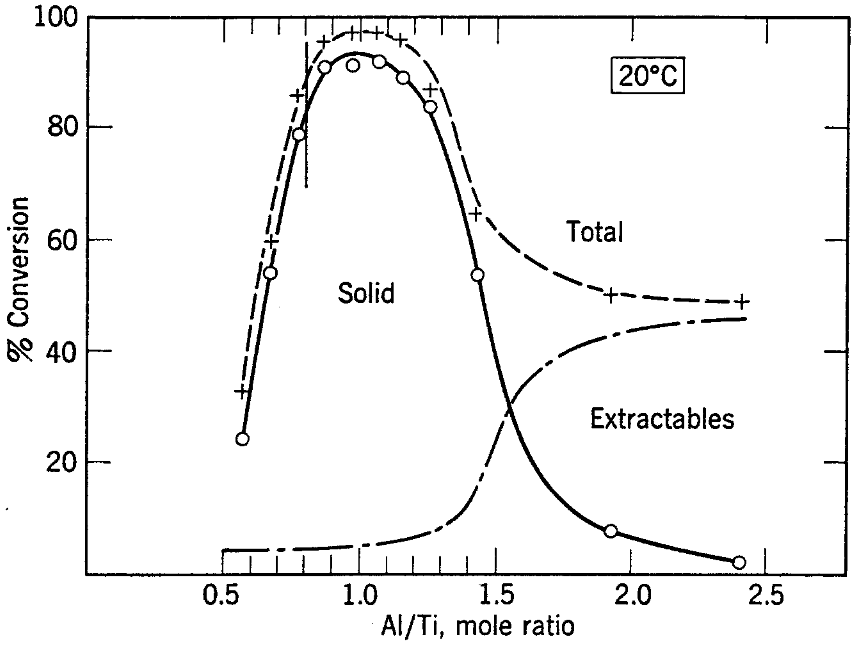


Fig. 4. Isoprene conversion to polymer as a function of the Al/Ti molar ratio. Catalyst preformed by Al to Ti addition at 20°. Polymerizations carried out at 50°C for 22 hr with a 20% solution by weight of isoprene in pentane. Ti, 0.132 mmole per 10 g of isoprene (120).

a. *Cis*-1,4 Polyisoprene. The synthesis of a polyisoprene having a structure practically identical with that of natural rubber, was first reported in a patent of Dec. 1954 (23). The AlR_3–$TiCl_4$ system was used, at an Al/Ti molar ratio of about 1 in a hydrocarbon solvent. As discussed in Sect. I-C-2, it is apparent that the actual catalyst obtained at this ratio consists of β-$TiCl_3$ with $AlEt_2Cl$.

The $AlR_3/TiCl_4$ ratio is the most important variable in this polymerization. Figure 4 shows the effect of the Al/Ti ratio on the conversion at 50°C. At an Al/Ti ratio of 0.2–0.3 the product is a crosslinked powdery substance, which is mostly insoluble in benzene. The microstructure of the polymer resembles products obtained by cationic catalysts. The highest yield is obtained at an Al/Ti ratio of about 1. The polymer obtained under these conditions is mostly (~80%) soluble in benzene and IR analysis reveals that it is 95–96% *cis*-1,4. Molecular weights are ~100,000. At higher Al/Ti ratios, the yield of solid polymer (still 95–96% *cis*-1,4) decreases rapidly and low molecular weight oily products are formed (extractables). At a ratio of 2.5 only oily polymers are formed. Thus the AlR_3–$TiCl_4$ system is highly active and stereospecific for the *cis*-1,4 polymerization of isoprene over only a narrow Al/Ti ratio range. This range corresponds to the formation of β-$TiCl_3$ (24,119–122).

The mode of reaction of $TiCl_4$ with AlR_3 influences the activity of the resulting catalysts.

Due to the industrial importance of *cis*-1,4 polyisoprene as a replacement for natural rubber, considerable work was undertaken to determine the best conditions for catalyst preparation with regard to yield, *cis*-1,4 content, molecular weight, molecular weight distribution, and gel content (122,123).

The catalyst can be prepared either by introducing AlR_3 into the $TiCl_4$ solution or vice-versa, or by simultaneous introduction of the two reagents into the polymerization solvent. Moreover, the formation of the catalyst can be carried out either in the presence (*in situ*) or in the absence ("preformed catalysts") of the monomer.

The diagram of Fig. 4 refers to preformed catalysts, prepared at 20° by introducing a solution of $Al(i\text{-}C_4H_9)_3$ into a $TiCl_4$ solution, and used 5–10 min after preparation.

Although no definitive conclusions can be drawn regarding the best method of catalyst preparation, preformed catalysts obtained by introducing AlR_3 into a $TiCl_4$ solution are generally preferred (122). The catalysts prepared by adding $TiCl_4$ to AlR_3 are less active, and yield higher gel contents. The same drawbacks are shown by catalysts prepared *in situ*, which, in addition, give less reproducible results (122).

The influence of the temperature of preparation on the catalytic properties was investigated. In the case of catalysts prepared by adding AlR_3 to $TiCl_4$, the higher the temperature the lower the activity (122).

Figure 5 shows conversion/time plots for catalysts prepared at −20, +20, and +40°C, and aged for 4 months at room temperature. Even after such a long aging, catalysts prepared at lower temperatures remain more active. Catalysts prepared at +125°C were practically inactive. For catalysts prepared at lower temperatures, the optimum Al/Ti ratio is slightly above 1 and the useful Al/Ti ratio range is rather narrow. With increasing temperature, the optimum Al/Ti ratio gradually decreases, while the Al/Ti range useful for the production of *cis*-1,4 polyisoprene increases. For example, for catalysts prepared at 90°, the optimum Al/Ti ratio is 0.6–0.7.

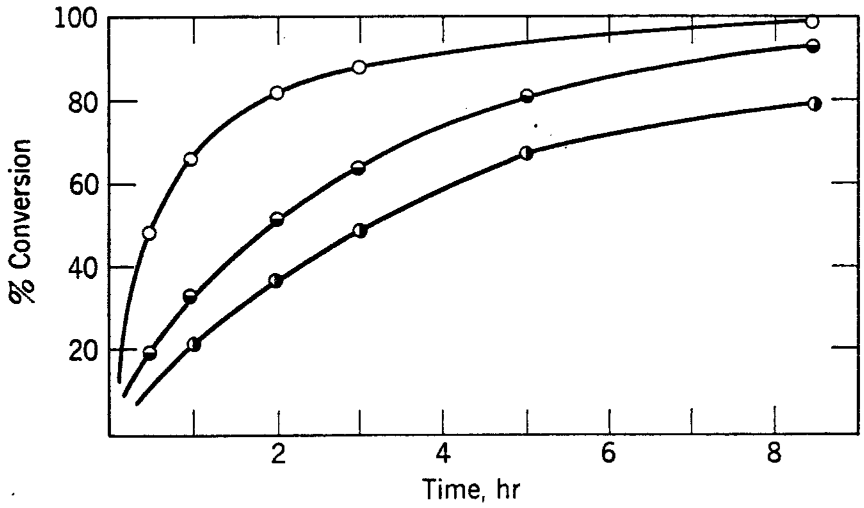


Fig. 5. Effect of catalyst preparation temperature on isoprene conversion to *cis*-1,4 polymer. Catalyst preparation temperature, °C: ○, −20; ◒, 20; ◑, 40. Al/Ti-1.0. Other conditions as under Fig. 4, except for polymerization time.

The above data on the influence of the temperature of catalyst preparation can be interpreted by considering that the optimum Al/Ti ratio corresponds to the formation of β-$TiCl_3$. This ratio is slightly higher than 1 when the reaction between AlR_3 and $TiCl_4$ is carried out at a low temperature, while it is lower than 1 when the reaction is carried out at higher temperatures.

The temperature of catalyst preparation also influences some polymers properties (Table XIII). Other conditions being constant, the catalysts prepared at higher temperatures yield polymers with higher viscosity, while the microstructure of the polymers seems to be practically independent of the temperature of catalyst preparation (122). Moreover, this variable seems to influence the amount of low molecular weight polymers formed. For example, catalysts prepared at +90°C and an Al/Ti ratio of 0.6–0.7, yield products with a high *cis*-1,4 content (96–97%) and no oils. However, as mentioned above, the activity of these catalysts is moderate.

TABLE XIII

Properties of Polymers Obtained with Catalysts Prepared by Adding AlR_3 to $TiCl_4$ at Different Temperatures (122)

Catalyst prep. temp., °C	Al/Ti	Inherent viscosity	Gel, %	*cis*-1,4, %
−20	0.98	1.8	31	96.9
	1.08	2.5	9	
0	0.98	2.8		97.4
40	0.80	2.3	9	95.5
	0.90	2.1	6	96.5
60	0.80	3.1	10	96.4
	0.90	3.0	7	96.9
	1.00	3.0	7	96.9
75	0.81	3.1	9	94.6
90	0.59	5.0	23	96.4
	0.68	5.7	12	95.0

The polymerization temperature influences only slightly the microstructure of the polymers prepared by catalysts at optimum Al/Ti ratio. Polymers with a 95% *cis*-1,4 content, in fact, can be obtained both at +70 and −30°C. Below −30° only low conversions are obtained. At such low temperatures, the polymer does not dissolve and remains attached to the catalyst, thus probably retarding the polymerization.

Molecular weight is practically independent of catalyst concentration, as indicated by the data in Table XIV. This is characteristic of polymerizations by heterogeneous catalysts. Polymerizations by homogeneous catalysts (e.g., catalysts from TiI_4 or Co compounds for *cis*-1,4 polybutadiene) show a noticeable dependence of the molecular weight

TABLE XIV
Effect of Catalyst Concentration on the Molecular Weight of the Polymer (131)

Catalyst conc., mmoles $Al(i\text{-}C_4H_9)_3$ per liter charge	DSV	Gel, %
3.10	2.91	32
5.47	2.87	29
5.97	2.46	19
11.9	2.52	26

on catalyst concentration. In addition the molecular weight is independent of conversion but dependent on the polymerization temperature (Table XV). These results suggest that polymer chain growth is rather rapid and that the molecular weights are determined by transfer with monomer or with aluminum alkyl, but do not depend on the number of catalytic centers.

The influence of the nature of aluminum alkyl on catalyst activity was recently examined by Schoenberg et al. (124). These authors examined the behavior of a series of aluminum trialkyls in preformed catalysts obtained by introducing the aluminum compound into a solution of $TiCl_4$ in heptane. The influence of the Al/Ti ratio was practically the same for all the aluminum alkyls and appeared to be similar to that reported in Fig. 4. At room temperature, the optimum ratio was about 0.9–1, except for $AlMe_3$, which is less active and requires a higher Al/Ti ratio. A slight increase in catalytic activity was observed when the

TABLE XV
Effect of Temperature of Polymerization on the Molecular Weight of Polyisoprene (131)

Temp. of polymerization, °C	DSV
0	3.9
20	3.2
40	2.5
50	2.1

alkyl chain was increased from C_1 to C_8. Higher yields at the optimum Al/Ti ratio were obtained with catalysts from aluminum alkyls containing bulky or branched alkyl groups, i.e., triisohexylaluminum and diisobutylaluminum hydride. The physical properties of the polymers obtained with different aluminum alkyls were similar.

The influence of catalyst aging on the activity was studied by several authors. Schoenberg et al. (124) found that aged catalysts gave higher yields of *cis*-1,4 solid polymer and simultaneously lower amounts of oil. Figure 6 shows results from polymerizations with aluminum trihexyl based catalysts employed 10 min., 1 week and 5 weeks after their preparation. Aged catalysts also give higher intrinsic viscosity polymers.

Adams et al. (121) state that the activity of catalysts from $AlEt_3$ or $Al(i\text{-}C_4H_9)_3$ remains unaltered after 5 days. Different results were reported by Yamazaki et al. (125) who found a rapid decrease in the activity of the $AlEt_3$–$TiCl_4$ system upon aging. It is very difficult to explain these contrasting results concerning the influence of catalyst aging.

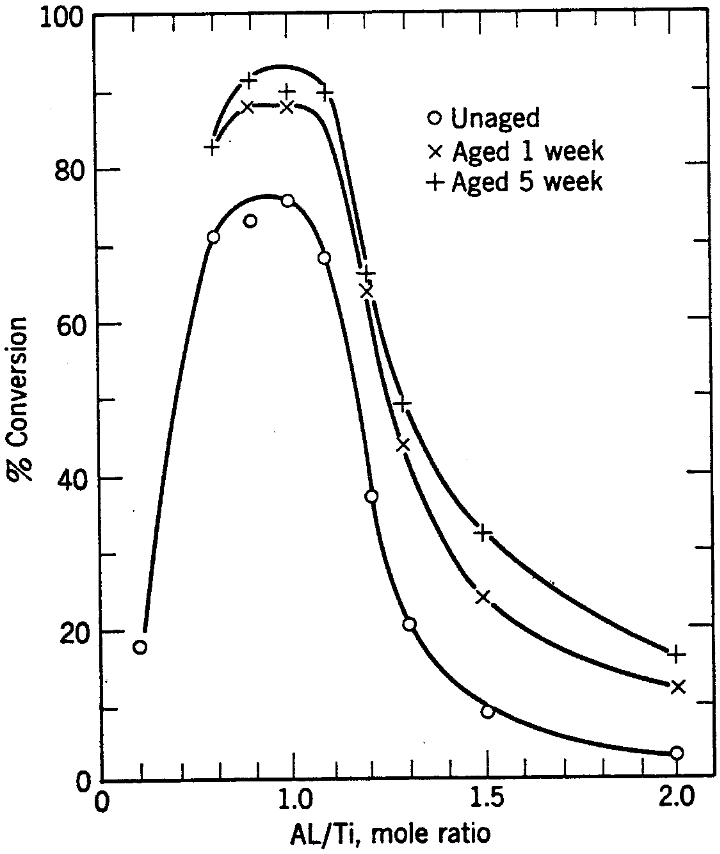


Fig. 6. Isoprene conversion to *cis*-1,4 polymer as a function of the Al/Ti ratio and catalyst aging. Triisohexylaluminum–$TiCl_4$ catalyst system. Experimental conditions as under Fig. 4.

TABLE XVI
Comparison of Catalysts Prepared from AlR_3 Complexed with $(C_6H_5)_2O$ and from Uncomplexed AlR_3 (127)

			% Yield	
Trialkylaluminum	Al/Ti	Polym. time, hr	Complexed Al–alkyl	Noncomplexed Al–alkyl
Ethyl	1.0	2.5	72	25
Propyl	1.0	2.5	88	39
Isobutyl	0.9	2.5	92	61

Good polymerization rates and polymer properties were obtained with catalysts from aluminum trialkyls complexed with a molar amount of ether, i.e., diethyl, dipropyl, diisobutyl, diphenyl ether, and anisole (126,127). Table XVI shows a comparison of the yields obtained, at a given polymerization time, with catalysts complexed with diphenyl ether and with noncomplexed ones (127).

The polymers obtained with aluminum etherates have better physical properties than those obtained with noncomplexed aluminum alkyls. The mode of action of the ethers is still obscure as is the reason why the properties of the polymers are improved. It is now accepted that all diolefin polymers obtained by coordination catalysts contain, to some extent, cyclized units* (128). It would be of interest to know whether or not the improved polymer properties obtained with etherate catalysts are due to the fact that such polymers contain lower amounts of cyclized units than polymers obtained with noncomplexed catalysts.

Data on the influence of the solvent were reported by Adams et al. (121). Aliphatic solvents, such as petroleum ether and *n*-heptane are preferred, but other solvents can also be used. Polymerizations in benzene and toluene yield polymers very similar to those obtained in heptane. In laboratory tests, ortho-di-chlorobenzene was also found to be a satisfactory solvent. The few available data indicate that the polymerization rate in this solvent is higher than in petroleum ether, but that the polymers obtained contain a slightly higher percentage of *trans*-1,4 units.

The kinetics of the polymerization of isoprene to *cis*-1,4 polymer by AlR_3–$TiCl_4$ systems were studied by Saltman (24) and Yamazaki (125).

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* We wish to point out that the data reported in this chapter concerning the composition of the diolefin polymers do not take into account the presence of cyclized units. Therefore the percentages of trans-1,4, *cis*-1,4, 1,2 units, etc. reported refer only to the unsaturated units and not to the total number of monomeric units in the polymer.

The former employed $Al(i\text{-}C_4H_9)_3$, the latter $AlEt_3$. Both prepared the catalyst *in situ:* the former by separate addition of solutions of $Al(i\text{-}C_4H_9)_3$ and $TiCl_4$ to the isoprene–heptane mixture, the latter by adding $TiCl_4$ to the hexane solution of $AlEt_3$ and isoprene.

Polymerizations carried out at different initial catalyst concentrations indicated a high dependence of the polymerization rate on catalyst concentration. The rate is a function of the product of the initial concentrations of Ti and of Al. Due to the necessity of operating at a constant Al/Ti ratio, this means that the rate is proportional to both $[Al]^2$ and $[Ti]^2$.

The polymerization appears to be first order with respect to monomer. This is demonstrated by the linearity of the plots of $\ln M/M_0$ vs reaction time. In these plots a break was found by some authors (125) who used unaged catalysts, but others who used aged catalysts found a fairly good linearity over a large interval of time (122).

The kinetic equation of the polymerization reaction can be expressed as follows:

$$-dM/dt = K[M][Ti]^2$$

where K is the rate constant. The activation energy of the overall process is 14.4 kcal/mole according to Saltman (24) and about 22 kcal/mole according to Yamazaki (125).

Monomer and catalyst concentrations influence the rate of polymerization, but not the microstructure of the polymer. The latter seems to be determined essentially by the chemical nature of the catalytic complex.

Predominantly *cis*-1,4 polyisoprene was also obtained with catalysts from $TiCl_4$ and $ZnEt_2$ (129), $CdEt_2$ (130), or complexes of the type $(CaH_2)_x\cdot(CaEt_2)_y\cdot ZnEt_2$ (129). It seems that these systems offer no advantages over those obtained from AlR_3.

Detailed data were published (39,40) on the polymerization of isoprene to *cis*-1,4 polymer by catalysts from $TiCl_4$ and various alanes (e.g., $AlHCl_2\cdot O(C_2H_5)_2$, $AlHCl_2\cdot N(CH_3)_3$, $AlH_2Cl\cdot N(CH_3)_3$, $AlH_3\cdot N(CH_3)_3$, and $AlH_2\cdot N(CH_3)_2$). These systems are used in benzene and give good yields of high molecular weight polymers with about 96% *cis*-1,4 content.

b. *Trans*-1,4 Polyisoprenes. The synthesis of an isoprene polymer having a structure practically identical with that of gutta-percha was first reported in a patent of March 1955 (98). The heterogeneous system $Al(C_2H_5)_3$–$TiCl_3$ (violet modification) was used as polymerization catalyst.

Synthetic *trans*-1,4 polyisoprene was obtained with several other catalysts, e.g., $AlEt_3$–$TiCl_4$ (Al/Ti ratio ~0.5) (23), $AlEt_3$–VCl_4 (76), $AlEt_3$–VCl_3 (99), $LiAlH_4$–TiI_4 (88).

The most suitable catalyst for the preparation of synthetic gutta-percha seems to be that obtained from an Al trialkyl and VCl_3. This system gives crude polymerization products consisting of 99–100% *trans*-1,4 units, and having a negligible amorphous fraction (103). Improvements in catalyst performance were obtained by using VCl_3 supported on an inert carrier, such as titanium dioxide, silica, alumina, and barium sulfate (132,133).

The supported VCl_3 can be easily prepared by heating (e.g., to 80°C for about 2 hr) a suspension of the carrier in an inert liquid containing dissolved VCl_4. The latter undergoes thermal decomposition, precipitating VCl_3 on the carrier. The supported catalysts gives higher efficiencies, (i.e., amount of total polymer obtained per gram of VCl_3) and higher polymerization rates.

By using the recipe: benzene 350 g; VCl_3 70–100 mg (10% by weight on TiO_2); $Al(i\text{-}C_4H_9)_3/VCl_3 = 5$; isoprene 80 g; temperature 50°C, it is possible to obtain up to 450–470 g of polymer per gram of VCl_3, with polymerization rates as high as 15–20 g of polymer/g VCl_3/hr.

Further improvements in polymerization rate and catalyst efficiency were obtained by using a homogeneous three-component system AlR_3–VCl_3–$Ti(OR)_4$ where $Al/V = 10/1$ and $V/Ti = 2/1$ (133,134). The efficiency of this homogeneous catalyst is reported to be about 50 times higher than that of the $Ti(OR)_4$ free supported catalyst. The polymerization rate can reach 600–700 g of *trans*-1,4 polyisoprene/g VCl_3/hour.

Other homogeneous catalysts for the *trans*-1,4 polymerization of isoprene were obtained from $AlEt_2Cl$ and $V(acac)_3$ or $VCl_3{\cdot}3THF$ (100). However, these systems seem to be far less efficient than the ternary one containing $Ti(OR)_4$.

The catalysts based on Ti, both the AlR_3–α-$TiCl_3$ (38) and the $LiAlH_4$ (ether suspension)–TiI_4 (88) systems, are less stereospecific than those from VCl_3. These catalysts produce in addition to pure *trans*-1,4 macromolecules, less pure polymer which, although predominantly *trans*-1,4 (>50%) contains 3,4 and *cis*-1,4 units as well.

Kinetic studies have been published on the polymerization of isoprene to *trans*-1,4 polymer with the $AlEt_3$–α-$TiCl_3$ (135) and $AlEt_3$–VCl_3 (136) systems.

c. 3,4 Polyisoprenes. 3,4 Polyisoprenes were first obtained, independently and almost simultaneously, by Wilke and by the School of Milan (106,137).

Both teams used a homogeneous catalyst system obtained from $Al(C_2H_5)_3$ and a titanium tetraalcoholate in an aromatic or aliphatic solvent (108,138). The optimum Al/Ti ratio, both with regard to the yield of polymer and 3,4 content, is about 6–7. Different titanium tetraalcoholates give practically identical results. The Al/Ti ratio strongly influences the molecular weight. This is probably due to transfer between the growing polymer chain and excess aluminum trialkyl used for catalyst preparation. This is suggested by polymerizations carried out in the presence of C^{14}-containing $AlEt_3$, which showed that the radioactivity in the polymer increased with increasing Al/Ti ratio, while the molecular weight decreased (Table XVII). This phenomenon seems to be quite similar to that observed in the polymerization of α-olefins (139).

The 3,4 content of the polymer depends on the polymerization temperature, as indicated in Table XVIII. At 20–25° and with an Al/Ti ratio of 6–7, the products contain 94–95% 3,4 units while at 0° or slightly below the 3,4 content is 97–98%.

The $AlEt_3$–$VO(OR)_3$ system also yields 3,4-polyisoprenes. These products are analogous to those obtained with the $AlEt_3$–$Ti(OR)_4$ system (61). By contrast $AlEt_3$–$V(acac)_3$ does not polymerize isoprene. The systems obtained from $AlEt_3$ and $V(acac)_3$ or $VO(OR)_3$, respectively, which are practically equivalent for the polymerization of butadiene (both yielding 1,2 syndiotactic polymers), are very different in the polymerization of isoprene. This is probably due to the fact that the ace-

TABLE XVII
Polymerization of Isoprene by the $Al(C^{14}{}_2H_5)_3$–$Ti(O\text{-}n\text{-}C_3H_7)_4$ Catalyst System[a]
Variation of Polymer C^{14} Activity on the Al/Ti Ratio (108)

Al/Ti molar ratio	Polymer[b]		Polymer activity (counts/min)
	g	$[\eta]$	
6	1.5	1.27	47
9	2.57	0.56	70
12	2.38	0.37	100
15	2.04	0.35	115

[a] Experimental conditions: 30 ml toluene; 10 ml isoprene (Phillips "polymerization grade"); 0.2 ml $Ti(O\text{-}n\text{-}C_3H_7)_4$ (isoprene was added to the toluene solution of $Al(C_2H_5)_3$, then $Ti(OR)_4$ was introduced). Polymerization 9 hr at 25°C.

[b] IR analysis: 90–95% 3,4 units.

a. ***Trans*-1,4 Polypentadienes.** The synthesis of a crystalline isotactic *trans*-1,4 polypentadiene was first reported in a patent of 1955 (98). The heterogeneous $AlEt_3$–$TiCl_3$ (violet modification) catalyst system was used in heptane, at about 60°C. A mixture of the two isomers of pentadiene was used as the monomer. The crude polymerization product consisted of an amorphous fraction (extractable with boiling diethyl ether) and a crystalline fraction (insoluble in diethyl ether). The percentage of the latter was rather low, probably due to the low purity of the monomer used and the relatively high temperature of polymerization.

Far better results, both with regard to polymer yield and crystalline fraction in the polymer, were obtained with the heterogeneous $AlEt_3$–VCl_3 system in heptane at room temperature (103,141). Both the *cis* and the *trans* monomers are polymerized by this catalyst system, yielding practically identical results (Table XIX). The only difference observed

TABLE XIX
Polymerization of 1,3-Pentadiene with the $Al(C_2H_5)_3$–VCl_3 System[a] (141)

Monomer[b] *trans* isomer, %	Polym. time, hr	Polymer, g	Residue from ether extn., %[c]	Melting temp., °C
100	14	1.23	87	95
100	15	1.5	83.5	95
100	17	1.4	88	—
100	70	2.4	85	95
100	72	2.4	85	—
77	14	1.44	69	92
75	14.30	0.68	66	92
50	14.30	0.64	65	90
50	15	0.95	58	89
50	16	0.87	64	90
28	14.30	0.67	69	89
25	16	1.47	64	91
0	16	0.95	94	95
0	76	1.6	92	95

[a] Polymerization conditions: monomer 4 ml; VCl_3, 0.3 g.; Al/V molar ratio, 2.5; *n*-heptane, 15 ml.

[b] A mixture of pure *cis* and pure *trans* isomers was used.

[c] About 95% soluble in boiling benzene; $[\eta]$ 1.3–1.5 dl g^{-1} (determined in toluene at 30°C).

is that the product from the *cis* isomer contains a lower percentage of amorphous fraction (about 4–6% vs 12–15%). Mixtures of the two isomers yield a product containing a considerably higher percentage of amorphous fraction than that obtained from either of the two isomers. In addition, the crystalline fraction obtained from mixtures of the two isomers exhibits a final melting temperature that is a few degrees lower than that of the crystalline fraction obtained from either isomer. This seems to be due to a lower degree of steric order in the configuration of the asymmetric carbon atoms.

The amorphous fraction obtained with the $AlEt_3$–VCl_3 system consists predominantly of *trans*-1,4 units. Although this fraction is amorphous by x-ray analysis, the IR spectrum of the solid polymers shows some bands (e.g., at 12.80; 11.54 μ) that are characteristic of isotactic *trans*-1,4 polypentadiene. Although these bands are very weak, they nonetheless indicate the presence of short isotactic sequences, which are evidently insufficient to give rise to crystallinity detectable by x-rays.

The heterogeneous $AlEt_3$–VCl_3 system seems to be the most stereospecific for the synthesis of isotactic *trans*-1,4 polypentadiene. In addition to this system and to that from violet $TiCl_3$ mentioned above, other heterogeneous catalysts are known which yield crystalline *trans*-1,4 isotactic polypentadienes, e.g., systems obtained from AlR_3 and $TiCl_4$, VCl_4, and $VOCl_3$, respectively (61).

At present, no homogeneous catalyst based on transition metals is known which will give *trans*-1,4 isotactic polymers from pentadiene. The homogeneous catalysts which give highly crystalline *trans*-1,4 polymers from butadiene or isoprene do not usually give polymers with a high *trans*-1,4 content from pentadiene. Thus the systems from AlR_2Cl and $V(acac)_3$ or $VCl_3{\cdot}3THF$, already mentioned for the preparation of 99–100% *trans*-1,4 polybutadiene, yield amorphous polymers, containing about 70% *trans*-1,4 and 30% 1,2 units from pentadiene (100). This does not mean that the presence of a solid catalytic surface is necessary to obtain isotactic *trans*-1,4 polypentadiene. Polymers of this type, having a good degree of crystallinity, were also obtained by butyl lithium in *n*-heptane, from the *cis* isomer of pentadiene (7). The latter catalyst is outside the scope of this chapter, however cf. Chapter 6, p. 537.

b. Cis-1,4 Polypentadienes. *(1) Isotactic cis-1,4 Polypentadiene.* This polymer was prepared by homogeneous systems obtained from an aluminum trialkyl and a titanium tetraalcoholate $Ti(OR)_4$ (142,143). Data concerning the polymerization of both the *cis* and the *trans* isomers of pentadiene by these systems are shown in Table XX. The optimum

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100	17	1.4	88	—
100	70	2.4	85	95
100	72	2.4	85	—
77	14	1.44	69	92
75	14.30	0.68	66	92
50	14.30	0.64	65	90
50	15	0.95	58	89
50	16	0.87	64	90
28	14.30	0.67	69	89
25	16	1.47	64	91
0	16	0.95	94	95
0	76	1.6	92	95

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The heterogeneous $AlEt_3$–VCl_3 system seems to be the most stereospecific for the synthesis of isotactic *trans*-1,4 polypentadiene. In addition to this system and to that from violet $TiCl_3$ mentioned above, other heterogeneous catalysts are known which yield crystalline *trans*-1,4 isotactic polypentadienes, e.g., systems obtained from AlR_3 and $TiCl_4$, VCl_4, and $VOCl_3$, respectively (61).

At present, no homogeneous catalyst based on transition metals is known which will give *trans*-1,4 isotactic polymers from pentadiene. The homogeneous catalysts which give highly crystalline *trans*-1,4 polymers from butadiene or isoprene do not usually give polymers with a high *trans*-1,4 content from pentadiene. Thus the systems from AlR_2Cl and $V(acac)_3$ or $VCl_3 \cdot 3THF$, already mentioned for the preparation of 99–100% *trans*-1,4 polybutadiene, yield amorphous polymers, containing about 70% *trans*-1,4 and 30% 1,2 units from pentadiene (100). This does not mean that the presence of a solid catalytic surface is necessary to obtain isotactic *trans*-1,4 polypentadiene. Polymers of this type, having a good degree of crystallinity, were also obtained by butyl lithium in *n*-heptane, from the *cis* isomer of pentadiene (7). The latter catalyst is outside the scope of this chapter, however cf. Chapter 6, p. 537.

b. Cis-1,4 Polypentadienes. (*1*) *Isotactic cis-1,4 Polypentadiene.* This polymer was prepared by homogeneous systems obtained from an aluminum trialkyl and a titanium tetraalcoholate $Ti(OR)_4$ (142,143). Data concerning the polymerization of both the *cis* and the *trans* isomers of pentadiene by these systems are shown in Table XX. The optimum

Al/Ti ratio, both with regard to polymer yield and the stereoregularity, was found to be about 7. Although both the *trans* and the *cis* isomers can be polymerized, the polymers obtained from the *trans* isomer are far more stereoregular than those obtained from the *cis* one. The *trans* isomer gives products that appear crystalline by x-rays, even in the crude state. From these, it is possible to separate an amorphous fraction (about 60% of the total product) and a fraction exhibiting a high degree of crystallinity. The latter fraction has 85–90% *cis*-1,4 units and a melting temperature of about 45°C. The *cis*-1,4 content in the amorphous fraction is lower (about 60–70%).

The products obtained from the *cis* isomer have a *cis*-1,4 content practically identical with that of the polymers obtained from the *trans* isomer (about 80–85% in the crude polymerization products). However, they are amorphous by x-rays, and only after careful fractionation was it possible to isolate a small fraction exhibiting low crystallinity of the isotactic type. However evidence exists that the fraction appearing amorphous by x-rays exhibits a certain degree of stereoregularity of the isotactic type (62).

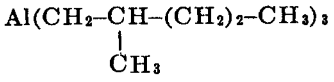
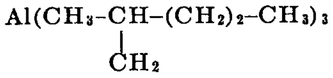
It was observed that the AlR_3–$Ti(OR)_4$ catalyst can isomerize the *cis* isomer of 1,3-pentadiene to the *trans* isomer. This was demonstrated by terminating polymerizations of the pure *cis* isomer at 10–15% conversion: the recovered unconverted monomer was a mixture of the *cis* and *trans* isomers, the latter being the predominant one. It is not known whether the polymerization occurs only with the *trans* monomer obtained by ismerization, or with both the *trans* and *cis* monomers.

The AlR_3–$Ti(OR)_4$ catalyst systems are not the only ones able to give *cis*-1,4 isotactic polypentadienes. Polymers that show crystallinity by x-ray and IR analysis due to isotactic *cis*-1,4 sequences were also obtained with the heterogeneous $AlEt_3$–$TiCl_4$ system from the *trans* isomer of pentadiene (61). The polymers obtained at an Al/Ti ratio of about 1 exhibit weak crystallinity but those obtained at a ratio of 2 appear as crystalline as the polymers obtained with the AlR_3–$Ti(OR)_4$ system. The products obtained with the $TiCl_4$ catalysts, even the purest fractions isolated, have a *cis*-1,4 content not higher than about 70%. Therefore, crystallinity in these products indicates that they contain sufficiently long *cis*-1,4 sequences interspersed with other units.

(*2*) *Syndiotactic cis-1,4 Polypentadiene.* Syndiotactic *cis*-1,4 polymers of 1,3-pentadiene were obtained with homogeneous catalysts prepared from an aluminum alkylhalide and a Co compound in aromatic solvent (144,145). These catalysts are the same as those used for the *cis*-1,4

TABLE XX

Polymerization of 1,3-Pentadiene by Catalysts Obtained from Aluminum Alkyls and Titanium Alkoxides[a] (143)

Run	Aluminum alkyl	10^3 moles	Ti compound	Al/Ti, molar ratio	Monomer,[b] g	Polymerization: Temp, °C	Polymerization: Time, hr	Crude polymer: Yield, g	Crude polymer: IR analysis,[d] %: *cis*	Crude polymer: IR analysis,[d] %: *trans*	Crude polymer: IR analysis,[d] %: 3,4	MEK insoluble fraction[c]: IR analysis,[d] %: *cis*	MEK insoluble fraction[c]: IR analysis,[d] %: *trans*	MEK insoluble fraction[c]: IR analysis,[d] %: 3,4	MEK insoluble fraction[c]: X-ray exam
1	$Al(C_2H_5)_3$	4.2	$Ti(O\text{-}n\text{-}C_4H_9)_4$	3	5	0	26	0.2	66	25	9	—	—	—	—
2	$Al(i\text{-}C_4H_9)_3$	12	$Ti(O\text{-}i\text{-}C_3H_7)_4$	4	5.5	0	40	5.1	67	24	9	82	11	7	Cryst.
3	$Al(C_2H_5)_3$	6	$Ti(O\text{-}n\text{-}C_4H_9)_4$	5	14	0	30	1.0	70	20	10	85	10	5	Cryst.
4	 $Al(CH_2\text{-}\underset{CH_3}{\underset{\vert}{CH}}\text{-}(CH_2)_2\text{-}CH_3)_3$	7	$Ti(O\text{-}n\text{-}C_4H_9)_4$	5	15	−15	45	6.9	78	16	6	87	9	4	Cryst.
5	$Al(C_2H_5)_3$	8	$Ti(O\text{-}n\text{-}C_4H_9)_4$	5	16	0	35	6	80	14	6	85	10	5	Cryst.
6	 $Al(CH_3\text{-}\underset{CH_2}{\underset{\vert}{CH}}\text{-}(CH_2)_2\text{-}CH_3)_3$	6.4	$Ti(O\text{-}n\text{-}C_4H_9)_3$	5	18	0	70	2.2	77	17	6	81	13	6	Cryst.
7	$Al(C_2H_5)_3$	15	$Ti(O\text{-}i\text{-}C_5H_{11})_4$	7	12	0	14	5	70	23	7	81	13	6	Cryst.
8	$Al(C_2H_5)_3$	20	$Ti(O\text{-}n\text{-}C_4H_9)_4$	7	10	0	40	4.6	54	30	16	60	25	15	Amorph.
9	$Al(C_2H_5)_3$	14	$Ti(O\text{-}n\text{-}C_4H_9)_4$	10	14.5	0	26	4.6	55	34	11	71	17	12	Cryst.
10	$Al(C_2H_5)_3$	7	$Ti(O\text{-}n\text{-}C_4H_9)_4$	5	17.5	0	60	1.5	75	15	10	79	13	8	Amorph.
11	$Al(C_2H_5)_3$	16	$Ti(O\text{-}n\text{-}C_4H_9)_4$	7	11.2	−15	30	1.2	76	15	9	84	10	6	Trace of crystal

---

[a] Solvent (benzene) 100 ml; in runs 3, 5, 6, 10 the catalyst was aged at room temperature for about 20 min; in the other runs the monomer was added immediately after catalyst formation.

[b] Run 1–7, 9: *trans* isomer (98–99 %); run 8: mixture of *trans* (50 %) and *cis* (50 %) isomers; run 10–11: *cis* isomer (99.9 %).

[c] 30–35 % of the crude polymer; $[\eta]$ 5–7 dl/g (100 ml/g; in toluene at 30°C).

[d] According to NMR analysis the *trans* double bonds are partly *trans*-1,4 and partly 1,2, while the *cis* double bonds are almost exclusively *cis*-1,4.

polymerization of butadiene. In the case of pentadiene, they polymerize only the *trans* isomer and not the *cis* form. The latter seems to remain unchanged (62).

The characteristics of the polymerization of pentadiene by Co catalysts are similar to those of the polymerization of butadiene. In the polymerization of butadiene the Co catalysts can be prepared in combination with $AlEt_2Cl$, $AlCl_2Et$, and $Al_2Et_3Cl_3$. Differences among the catalysts obtained from the various aluminum alkyls affect the kinetics of the polymerization and the molecular weights, but not the stereospecificity of the process. With pentadiene the catalysts from $AlEt_2Cl$ yield predominantly *cis*-1,4 polymers, while those from $AlEtCl_2$ or $Al_2Cl_3Et_3$ yield low molecular weight cationic polymers predominantly consisting of 1,2 units. These polymers are identical with those obtained from $AlEtCl_2$ alone in the absence of Co compound. The different behavior of pentadiene in comparison with butadiene is due to its much higher reactivity under cationic conditions.

However, by adding a Lewis base, such as thiophene or pyridine to $AlEtCl_2$, catalysts are obtained that yield high *cis*-1,4 polypentadienes.

Some data on the polymerization of pentadiene by the $AlEtCl_2$·thiophene–$Co(acac)_2$ and $AlEtCl_2$·pyridine–$Co(acac)_2$ systems are shown in Table XXI. In these systems, the thiophene/aluminum ratio can be varied within fairly wide limits, from 5 to about 0.5, while the pyridine/aluminum ratio can be varied within a narrower range, from about 0.5 to 0.9. This is related to the different basicities of the two electron donors. The crude polymers obtained by these two systems contain about 75–80% *cis*-1,4 units and show a fairly good degree of crystallinity by x-rays. By fractionation of the crude polymer it is possible to obtain fractions with about 85–90% *cis*-1,4 content. This means that the polymers are heterogeneous in the sense that they consist of macromolecules ranging from about 55 to about 90% *cis*-1,4. This is another difference between the polymerizations of pentadiene and butadiene by Co catalysts. *Cis*-1,4 polybutadienes obtained with these catalysts are more homogeneous and the *cis*-1,4 content in the various molecular weight fractions vary within far narrower limits. The heterogeneity of the *cis*-1,4 polypentadienes cannot be attributed to the existence of different catalytic centers, because, if this were the case, macromolecules with different *cis*-1,4 contents should be obtained also from butadiene.

c. 1,2 Syndiotactic Polypentadiene. When used in *n*-heptane or other aliphatic solvents, the catalysts prepared from AlR_2Cl and a Co compound yield polypentadienes containing predominantly 1,2 units (up to about 94%) (146).

TABLE XXI
Polymerization of 1,3-Pentadiene by Catalysts Prepared from Cobalt Diacetylacetonate, $Co(acac)_2$, and $Al(C_2H_5)Cl_2$ Complexed with Thiophene[a] or Pyridine[b]

				Polymerization		Crude polymer		MEK insoluble fraction[e]	
Run	$Co(acac)_2$[c], moles 10^5	Benzene, ml	Monomer,[d] g	Temp., °C	Time, hr	Yield, g	IR analysis *cis*-1,4, %	IR analysis *cis*-1,4, %[f]	[η], dl g^{-1}
1	5.1	350	28	20	24	23	77	84	2.8
2	1.5	50	10.5	20	6	8	72	85	—
3	0.34	15	3.1	20	12	2.3	73	83	2.9
4	0.68	30	5	0	20	4	81	86	2.3
5	0.5	30	3	20	8	2.6	77	83	1.9
6	0.15	15	3.5	0	48	3.2	71	85	—
7	0.5	30	4	20	12	3.1	69	85	2.5
8	0.5	30	3	0	12	1.7	76	86	—

[a] Runs 1–6; Al/thiophene molar ratio: 1.

[b] Runs 7 and 8; Al/pyridine molar ratio: 0.53.

[c] Al/Co molar ratio: ~500. Catalyst prepared by introducing first the Co compound and the Lewis base, then the $Al(C_2H_5)Cl_2$ and finally, after a few minutes, the monomer.

[d] *trans* Isomer, 99.5 % pure.

[e] Crystalline by x-ray examination (polymer annealed 4 hr at 35°C). [η] was determined in toluene at 30°C.

[f] The remaining units are characterized by *trans* double bonds and are probably a mixture of 1,2 and *trans*-1,4 units.

Table XXII shows data on the polymerization of pentadiene by the $AlEt_2Cl$–$Co(acac)_3$ system in *n*-heptane. The polymers obtained are amorphous by x-rays at room temperature. However, they crystallize on stretching and show an identity period of about 5.1 Å as measured from the fiber spectrum. On the basis of this, a 1,2 syndiotactic structure was attributed to the polymers.

It should be remembered that in the polymerization of butadiene, the $AlEt_2Cl$–$Co(acac)_3$ system yields predominantly *cis*-1,4 polymers even in *n*-heptane (although the *cis*-1,4 content is lower than in polymers obtained, by the same system, in benzene).

E. Properties of the Diolefin Polymers

Although a detailed examination of the physical and elastomeric properties of the polymers of butadiene, isoprene, and 1,3-pentadiene obtained with coordination catalysts is beyond the scope of this chapter, we shall discuss briefly some of the characteristics of these polymers.

TABLE XXII

Polymerization of 1,3-Pentadiene (*trans* Isomer) by Catalysts from $Co(acac)_3$ and $Al(C_2H_5)_2Cl$ in *n*-Heptane[a] (61)

			Polymerization		Polymer			
						IR analysis		
n-Heptane, ml	$Co(acac)_3$, moles 10^6	Al/Co molar ratio	Temp., °C	Time, hr	Yield, g	*cis*-1,4, %	1,2,[c] %	$[\eta]$,[b] dl g^{-1}
20	2.2	800	−10	48	1	14.5	82	2.35
20	2.03	400	0	24	3.5	4.8	91	3.2
20	3.6	400	0	24	3.5	3.5	92	2.22
20	1.2	200	0	144	1	4	92	—
30	3.65	400	24	12	3	2	94	2.12
30	3.93	5000	24	6	2.5	3	93	2.31
25	3.9	400	24	24	1.2	2	94	—

[a] Catalysts prepared by introducing first $Co(acac)_3$, then $Al(C_2H_5)_2Cl$ and finally 5 ml of pentadiene.

[b] Determined in toluene at 30°C.

[c] The remaining units are *trans*-1,4.

In general, the physical properties of a polymer from a given monomer depend on the type and degree of tacticity. Table XXIII shows melting temperatures, identity periods, and densities of the polybutadienes, polyisoprenes, and polypentadienes so far obtained.

Among the polybutadienes, the *trans*-1,4 polymer ($>99\%$ *trans*-1,4 content) melts at about 145°C. Hence this polymer has no elastomeric properties. The same holds true for the highly crystalline 1,2 isotactic and 1,2 syndiotactic polybutadienes, which melt at 127 and 156°C, respectively. However, stereoisomers of 1,2 polybutadiene are known which have such a low degree of stereoregularity that they are amorphous at room temperature by x-ray analysis. These polymers, which include the diethyl ether soluble fractions of the products described under Sect. I-D-1c, have elastomeric properties.

The high *cis*-1,4 polybutadiene melts at about +3°C, which is only slightly lower than the melting point of natural rubber. Among the butadiene polymers, only the *cis*-1,4 possesses highly satisfactory elastomeric properties.

The *cis*-1,4 and *trans*-1,4 polyisoprenes are very similar to the corresponding natural products in their properties (157,158,127,131).

Although it may have a 3,4 content as high as 97–98%, the 3,4 polyisoprene obtained so far is amorphous because of a lack or a low degree of stereoregularity.

Among the polypentadienes, the *trans*-1,4 isotactic polymer melts at about 95°C, and hence it is not an elastomer at room temperature. The isotactic and syndiotactic, *cis*-1,4 polymers, melt at about 42 and 52.5°C, respectively. These melting temperatures refer to the purest polymers (85–90% *cis*-1,4 content) obtained. Higher melting temperatures are expected for polypentadienes having a higher *cis*-1,4 content or a higher degree of stereoregularity than those obtained so far. Of the two *cis*-1,4 polypentadienes presently available, the syndiotactic shows properties which are intermediate between those of gutta-percha and

TABLE XXIII

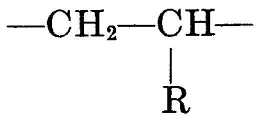
Physical Properties of Butadiene, Isoprene, and Pentadiene Polymers Obtained with Stereospecific Catalysts

Polymer	Melting temp., °C	Identity period, Å	Density	Ref.
trans-1,4 Polybutadiene[a]	70–75° (transition temp.)	4.85 mod. I	1.02	103, 147 148, 149
	145°C (melting temp.)	4.7 mod. II	0.93	
cis-1,4 Polybutadiene	3	8.60	1.01	68, 150, 151
Isotactic 1,2 polybutadiene	128	6.5	0.96	152, 153
Syndiotactic 1,2 polybutadiene	156	5.14	0.96	154
cis-1,4 Polyisoprene	20–30	8.10	1.00	150, 155, 156
trans-1,4 Polyisoprene	65	4.77 8.75 9.2	1.04	148, 155, 160
3,4 Polyisoprene	Amorphous	—	—	
trans-1,4 Polypentadiene	95	4.82	0.98	141
Isotactic *cis*-1,4 polypentadiene	42	8.15	n.d.	142, 143
Syndiotactic *cis*-1,4 polypentadiene	52–3	8.5	n.d.	145
1,2 Polypentadiene	10–20	515	n.d.	146

[a] *trans*-1,4 Polybutadiene can exist in two crystalline modifications; one (mod. I) is stable below about 75°C, the other from 75 to 145°C. The two modifications have different identity periods and different equatorial encumberment per each chain (the latter being greater for mod. II). Only the equatorial encumberment is greater for mod. II. Identity period is greater for mod. I, as reported under the third column.

natural rubber, while the isotactic has a lower melting temperature and in general is more similar to *cis*-1,4 polybutadiene or polyisoprene.

Among the elastomeric polybutadienes, polyisoprenes, or polypentadienes, the 1,4 polymers show dynamic properties superior to those of the 1,2 polymers. These properties are better for 1,4 polybutadienes and polyisoprenes than for 1,4 polypentadienes. This is due to the higher freedom of rotation around the $-CH_2-CH=$ or even the $-CH_2-CH_2-$ bonds, than around the $-CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-$ bonds.



From the practical point of view *cis*-1,4 polybutadiene and *cis*-1,4 polyisoprene are by far the most important of the various polydienes obtained by coordination catalysts. They are also being produced industrially. The physical properties of the elastomers derived from these two polymers have been examined in detail elsewhere (127,131, 157–159).

F. Mechanism of Polymerization

After twelve years of research on stereospecific polymerization of diolefins a great number of new polymers have been obtained, some of which have a high degree of structural regularity. The present state of knowledge concerning the mechanism of formation of these polymers will now be examined.

1. Nature of the Polymerization

The nature of the polymerizations initiated by catalysts based on transition metals has been discussed to a considerable extent. In the case of catalysts prepared from Ti, V, Cr, or Mo compounds, there is general agreement that polymerization occurs by monomer incorporation at the polarized $Me^{\delta+}-C^{\delta-}$ bond between the transition metal and the alpha carbon of the last polymerized unit. This conclusion has been reached not only from the study of the polymerization of diolefins, but also from that of ethylene and α-olefins.

For catalysts based on metals of Group VIII, in particular of Co or Ni, there is much less agreement as to the nature of the active catalyst. Therefore, the two cases will be examined separately.

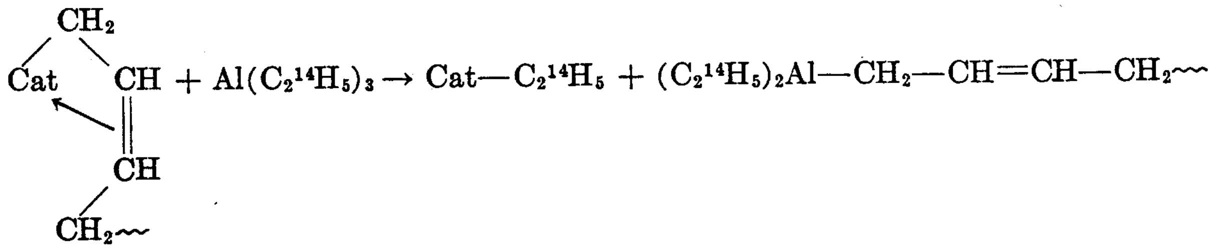
a. Polymerization by Catalysts from Ti, V, Cr, or Mo. The hypotheses regarding the mechanism of these catalysts are based on the following evidence.

1. Polymerizations terminated by CH_3OH^3 give tritium-containing polymer which evidently derives, at least in part, from a reaction of the type

$$\text{Cat—CH}_2\text{—CH=CH—CH}_2\sim + \text{CH}_3\text{OH}^3 \rightarrow \text{Cat—OCH}_3 + \text{H}^3\text{CH}_2\text{—CH=CH—CH}_2\sim$$

Experiments of this type were carried out with the $AlEt_3$–$Ti(OR)_4$ catalyst system in the polymerization of isoprene or pentadiene (61) and with the $Al(i\text{-}C_4H_9)_3$–TiI_4 system in the polymerization of butadiene (161). With the latter system, the termination with $C^{14}O_2$ has also been tested and radioactive polymer was obtained (161).

2. Catalysts from $Al(C_2{}^{14}H_5)_3$ give radioactive polymer. This is due to the fact that the monomer is incorporated at the metal–$C_2{}^{14}H_5$ bond. This bond could form by reaction between $Al(C_2{}^{14}H_5)_3$ and the transition metal compound or during the polymerization by transfer between the growing polymer chain and the aluminum alkyl:



$$\text{Cat}(\text{CH}_2\text{—CH=CH—CH}_2\sim) + \text{Al}(\text{C}_2{}^{14}\text{H}_5)_3 \rightarrow \text{Cat—C}_2{}^{14}\text{H}_5 + (\text{C}_2{}^{14}\text{H}_5)_2\text{Al—CH}_2\text{—CH=CH—CH}_2\sim$$

This problem has been widely discussed in connection with the polymerization of propylene by the $AlEt_3$–α-$TiCl_3$ system (139). With diolefins, transfer between aluminum alkyl and the growing chain has been observed in the polymerization of butadiene and isoprene by the $AlEt_3$–VCl_3 system (61,136); with butadiene by the $Al(i\text{-}C_4H_9)_3$–TiI_4 system (86); with 1,3-pentadiene and isoprene by the $AlEt_3$–$Ti(OR)_4$ system (61,108,143).

3. Overall activation energies of polymerization in the cases examined so far are much lower than those observed in radical polymerizations which is evidence for an ionic mechanism. Thus, for the polymerization of isoprene by AlR_3–$TiCl_4$, $E_a = 14.4$ kcal/mole (24); of butadiene by the $AlHCl_2 \cdot O(C_2H_5)_2$–$AlI_5$–$TiCl_4$ system, $E_a = 8.75$ kcal/mole (87); and of propylene by the $AlEt_3$–α-$TiCl_3$ system, $E_a = 12.4$ kcal/mole (162).

4. For some catalysts obtained from AlR_3 and Ti, V, Cr, or Mo compounds a cationic mechanism can certainly be excluded since systems like AlR_3–$Ti(OR)_4$, AlR_3–$V(acac)_3$, AlR_3–$Mo(acac)_3$ are unlikely to exhibit cationic activity. This conclusion is supported by the fact that polymerizations by these catalysts can be performed in solvents such as thiophene which destroy the activity of strong Lewis acids such as $AlCl_3$, $AlBr_3$, etc. (61). For other systems, e.g., the AlR_3–$TiCl_3$ system, this conclusion may not seem so obvious, but it seems reasonable to assume that all these catalysts belong to the same class.

Some of the findings reported in items 1–4 are not conclusive. Thus, the validity of the method of termination by CH_3OH^3 has been questioned in regard to the possibility of isotopic exchange (161). Taken as a whole, however, these arguments clearly suggest that the active catalyst site is a polarized $Me^{\delta+}$—$C^{\delta-}$ bond.

It has been discussed whether the growing polymer chain is bonded to the Al (or to another metal of Group II or III present in the alkyl metal used) or to the transition metal component. At present there is little doubt that the polymer grows on the transition metal. Evidence for this conclusion is that stereospecific catalysts have been obtained by transition metal compounds alone, in the absence of Al. For example, in the field of diolefins, $TiCl_2(CH_3)_2$ (31) gives 1,4 polybutadienes similar to those obtained with AlR_3–$TiCl_4$, Al/Ti = 2, and $(\pi\text{-allyl})_3Cr$ gives 1,2 polybutadienes (163), a fraction of which shows crystallinity of the syndiotactic type (61).

Commonly this type of polymerization is called "coordinated anionic." The term "anionic" may seem incorrect considering that the growing chain, at least in most of the cases, is not a free ion but is bonded to the transition metal by an essentially covalent bond. In the case of diolefins this bond is of the π-allylic type. However, this term is to be understood in the sense that in the polarized metal–carbon bond involved in the polymerization, the positive charge is on the metal and the negative on the carbon of the growing chain. The term "coordinated" is used because the monomer coordinates to the transition metal before it is incorporated into the growing chain. This topic will be discussed later (see Section V-2-a).

b. Polymerization by Co Catalysts. According to some authors the Co catalysts used for the *cis*-1,4 polymerization of butadiene are different from those examined in the previous section.

Arguments in favor of this are as follows:

1. When the growing polymer chain is terminated by CH_3OH^3, tritium is not found in the polymer.

2. The $AlEt_2Cl$–Co compound systems are inactive without the addition of an activator e.g., H_2O.

3. Catalysts obtained from $Al(C_2{}^{14}H_5)_2Cl$ yield polymers that do not contain C^{14}.

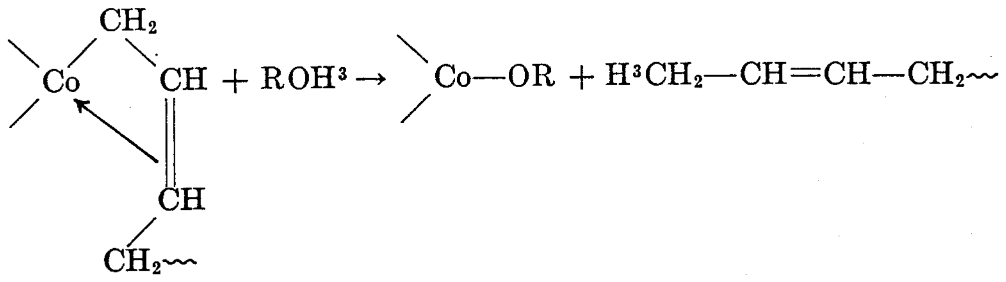
4. High *cis*-1,4 polybutadienes can also be obtained with catalysts from $AlCl_3$ and $CoCl_2$ in the absence of any metal alkyl. It seems highly improbable, according to some authors, that the polymerization by these systems proceeds by monomer incorporation at a metal–carbon bond, since bonds of this type are not present in the catalyst system.

These items will be discussed separately.

(*1*) *Termination of the Growing Chains by Labeled Alcohols.* This is a much debated point. Childers found (164) that polybutadienes initiated by $AlEt_2Cl$–Co octoate were radioactive if terminated by C^{14}-containing butanol while they were inactive if terminated by CH_3OH^3. He deduced from this that the polymerization was cationic. Cooper repeated Childers' experiments and obtained opposite results (165): he thus deduced that the polymerization was anionic. Natta and co-workers found (166) activity in the polymers terminated by CH_3OH^3 but showed that the activity is partly derived from secondary reactions. Also they cast some doubts on the validity of the method with catalysts based on metals of Group VIII. Bresler has recently reexamined (161) the problem and his data are substantially in agreement with those of Childers'.

These discrepancies demonstrate the complexities of these measurements. This is partly due to the very low amount of catalyst used and also to the possibility of secondary reactions. For instance, Cooper found (105) that upon terminating with inactive alcohol polymerizations initiated by the $AlEt_2Cl^{36}$–Co octoate–H_2O system, the polymer contained radioactive Cl^{36}. Evidently, in the termination by alcohol, HCl^{36} is evolved which may add to the polymer double bonds. Thus the polymer may become radioactive. This was probably one of the sources of contamination observed by G. Natta and co-workers in their experiments (166). It is difficult to explain why Childers and Bresler have not found radioactivity deriving from secondary reactions of this type in the polymers terminated by CH_3OH^3.

It should be added that the validity of these termination processes for the AlR_2Cl–Co compound catalyst has never been thoroughly investigated. According to the mechanism of anionic polymerizations the polymer chain is bonded to Co by a π-allylic bond. There is no experimental evidence showing that in a reaction between the catalyst complex and CH_3OH^3, the bond between Co and the last polymerized unit would react quantitatively with the alcohol according to:



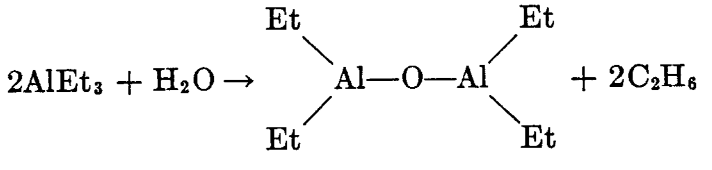
$$>\mathrm{Co}(\pi\text{-}\mathrm{CH_2{-}CH{=}CH{-}CH_2}\sim) + \mathrm{ROH^3} \rightarrow\ >\mathrm{Co{-}OR} + \mathrm{H^3CH_2{-}CH{=}CH{-}CH_2}\sim$$

It is known that π-allyl-Ni halides are stable in alcohols and can initiate the polymerization of butadiene in alcohol solvent (102). It has been established that this polymerization is anionic in the sense discussed above. Thus termination with labelled alcohols is not of general validity, particularly when applied to the polymerization of diolefins by catalysts based on metals of the Group VIII.

These considerations cast doubt on the conclusions derived from termination experiments with CH_3OH^3.

(*2*) *Activation of the Catalysts by* H_2O. Although the question of catalyst activation for the *cis*-1,4 polybutadiene process remains controversial, it has been established that the addition of particular substances (e.g., H_2O) strongly influence both the rate of polymerization and the molecular weight. However, this is no evidence for the hypothesis that Co catalysts are of a different nature than those obtained from, e.g., $TiCl_3$, $TiCl_4$, etc.

Since H_2O is always added in small amounts with respect to the aluminum alkyl, compounds containing the $>\mathrm{Al{-}O{-}Al}<$ group might arise by the following reaction:

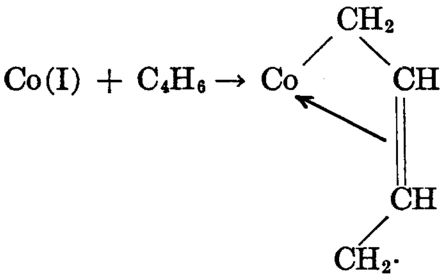


$$2\mathrm{AlEt_3} + \mathrm{H_2O} \rightarrow \mathrm{Et_2Al{-}O{-}AlEt_2} + 2\mathrm{C_2H_6}$$

A possible explanation for the activation by H_2O is that compounds containing the $>\mathrm{Al{-}O{-}Al}<$ group, or mixtures of such compounds with AlR_2Cl, may be much more active in the polymerization than the initial organoaluminum compounds.

(*3*) *Absence of Radioactivity in Polymers Obtained with* $Al(C_2{}^{14}H_5)_2Cl$–$Co(acac)_2$. The fact that polymers obtained with the $Al(C_2{}^{14}H_5)_2Cl$–$Co(acac)_2$ system were inactive (167) might suggest that the Co—C bond is not involved in the polymerization. This fact was considered by some authors as further evidence that the polymerization by Co catalysts is cationic (164).

Actually the absence of C^{14} in the polymer is quite consistent with the hypothesis that the polymer grows on a Co—C bond. It has been established that the reaction between $AlEt_2Cl$ and a Co compound leads to the formation of a complex which contains Co(I) (58,60). However, Co—C bonds could form by the reaction of butadiene with the complex containing Co(I), e.g.,



Two radicals of this type could couple rapidly giving rise to a chain growing at the two ends. Transfer reactions with monomer would lead to chains bonded only to one Co and therefore growing only at one end.

Initiation of this type takes place in the polymerization of dienes with metallic lithium (168). In this case a Li—C bond is formed (and consequently a formal oxidation from metallic lithium to Li(I) occurs) as a result of the reaction of Li with C_4H_6 (cf. Chapter 6, p. 496).

Various reactions between diolefins and transition metal compounds are known to lead to the formation of π-allyl bonds. Thus, dichloro(dodeca-2,6,10-triene-1,2-diyl)Ru(IV) containing two π-allyl bonds was obtained from $RuCl_3$ and butadiene (169), dichloro(2,7-dimethylocta-2,6-diene-1,8-diyl)Ru(IV) was obtained from $RuCl_3$ and isoprene (170), and a $Rh_2Cl_4C_{12}H_8$ complex which probably contains π-allyl bonds was obtained from $RhCl_3$ and butadiene (171).

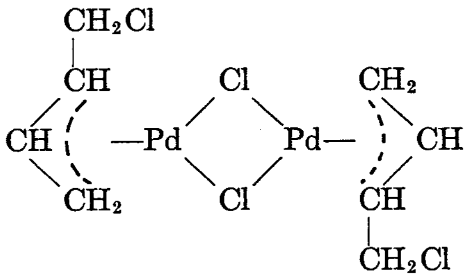
These facts indicate that the existence of a Co—C bond is not a necessary prerequisite for anionic polymerization since such a bond can be easily formed by the action of the monomer on the complex obtained from $AlEt_2Cl$ and the Co compound. This type of initiation can explain the absence of radioactivity in polymers obtained by the system $Al(C_2{}^{14}H_5)_2Cl$–$Co(acac)_2$.

The hypothesis that the polymer chain grows on a Co—C bond is further supported by the following facts: a) cobalt–allyl–monoiodide can polymerize butadiene to a predominantly *cis*-1,4 polymer (163), b) π-allyl–Ni–Cl is capable of producing low polymers of butadiene having predominantly *cis*-1,4 structures (102,172). There is also evidence which indicates that the chain grows by incorporation of the monomer at the Ni—C bond.

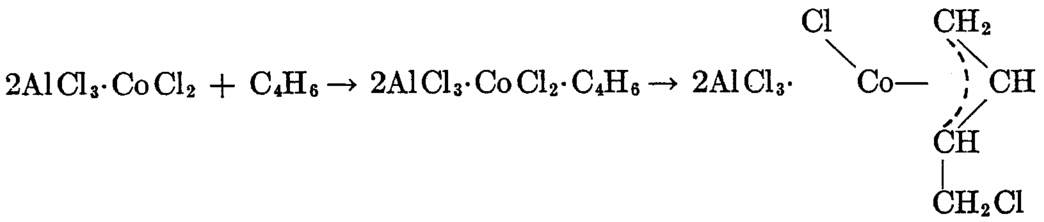
(*4*) *Catalysts from* $AlCl_3$ *and* Co *Compounds.* The catalysts obtained from $AlCl_3$ (or $AlBr_3$) and Co compounds (in particular $CoCl_2$) might be considered to belong to a different class from that obtained from $AlEt_2Cl$. Here we must distinguish between the complexes obtained in the presence of metallic Al (63) and those obtained in the absence of any reducing agent (65,66). The former complexes contain Co(I) (64) and may initiate in the same way as complexes obtained from $AlEt_2Cl$.

It is conceivable that the catalysts obtained in the absence of a reducing agent, i.e., from aluminum trihalide and a Co compound, are similar to $AlEt_2Cl$–$CoCl_2$ systems. In other words, the active species could contain a Co—C bond formed by the reaction between the monomer and the initial complex, also in the case of the $AlCl_3\cdot CoCl_2$ system. The complex obtained from $AlBr_3$ and $CoBr_2$ in aromatic solvent has been examined by Fisher (64). This author showed the existence of $[(\text{arene})_2\text{Co}]^{2+}$ which under particular conditions could be isolated as a salt with the anion $(PtCl_6)^{2-}$. It is extremely interesting, however, that this cation can undergo disproportionation very easily to give the more stable monovalent cation $[(\text{arene})_2\text{Co}]^{+}$. It is possible that a disproportionation of this type also occurs during the catalyst formation. If so, the initiation by these catalysts should also fall within the case examined under (*3*).

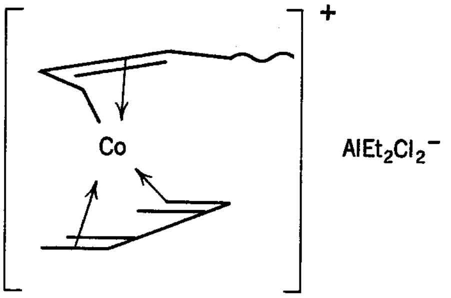
The formation of a Co—C bond via a radical anion is not the only possible explanation. For instance, it is known that the complex between butadiene and $PdCl_2$, $C_4H_6\cdot PdCl_2$, exists in solution as



a π-allyl complex (173). Similarly, butadiene may coordinate to the Co of the $2AlCl_3\cdot CoCl_2$ complex to form a π-allyl bond:


$$2AlCl_3\cdot CoCl_2 + C_4H_6 \rightarrow 2AlCl_3\cdot CoCl_2\cdot C_4H_6 \rightarrow 2AlCl_3\cdot$$

In conclusion it seems that Co catalysts also operate by a coordinated anionic mechanism, as do other catalysts obtained from aluminum alkyls and Ti, V, Cr, Mo compounds. Co-containing catalysts are probably ionic complexes in which the Al is part of an anion, and the Co is part of a cation. In the presence of the monomer the following complex can be visualized:



The growing chain is bonded to the Co by a π-allyl bond, while the incoming monomer is coordinated by the two double bonds. Obviously this figure is an oversimplification, as the catalyst is a rapidly changing species during polymerization and cannot be represented by a single formula or figure.

2. Factors Determining or Influencing the Type of Addition of the Monomeric Units

Although the mechanism of polymerization of conjugated diolefins by stereospecific catalysts is still rather obscure it is now possible, after twelve years of research in this field, to single out some of the factors which determine or influence the type of addition of the monomeric units. This aspect of the problem will now be examined.

a. Coordination of the Monomer to the Catalyst. It is now generally accepted that the incoming monomer coordinates to the transition metal of the catalyst before being incorporated into the growing chain. Some authors have expressed reservations with this hypothesis because of kinetic results (175) or other considerations (176). Several facts, however, indicate that coordination actually does occur. The transition metal in the catalyst complex is in a low valence state and is electron-deficient, therefore the monomer should be able to coordinate to it.

Evidence for the coordinating capability of the transition metal in the catalytic complex exists with the Co catalysts. As already mentioned (see I-C-4) $AlEt_2Cl$ and a cobalt compound in aromatic solvent give a cation, $[(\text{arene})_2\text{Co}]^+$, which can be isolated. If the arene coordinates to Co, the monomer, also an electron donor, is also expected to coordinate to Co. The coordination of the monomer evidently occurs by displacement of the arene. This explains why the addition of hexamethylbenzene to the benzene solution of the catalyst inactivates the catalyst (62). Hexamethylbenzene is a strong electron donor and therefore coordinates so strongly to Co that it cannot be displaced by the monomer.

The mode of coordination of the monomer to the transition metal may determine the type of addition of the monomer unit. If the coordination occurs through both double bonds with the monomer in the *cis* conformation, it appears plausible that a *cis*-1,4 unit will be formed. This occurs most probably in the polymerization by Co catalysts.

The formation of a 1,2 unit is probably preceded by coordination involving only one unsaturated group. That the monomer coordinates by only one unsaturated group is determined by the number of vacant coordination sites around the transition metal.

Various arguments, however, suggest that a diolefin coordinated by only one unsaturated group can lead, after incorporation, not only to 1,2 but also to *trans*-1,4 units. Evidence suggesting that in the case of homogeneous catalysts the formation of *trans*-1,4 units is preceded by a coordination of the monomer with only one unsaturated group are as follows:

1. It seems unlikely that a diolefin can coordinate to a metal with both double bonds in the *trans* conformation. No example exists in organometallic chemistry for a coordination of this type.

2. Two typical homogeneous catalysts which yield *cis*-1,4 polybutadiene in benzene, i.e., $LiAlH_4$–TiI_4 and $AlEt_2Cl$–Co compound (see I-D-1a), yield *trans*-1,4 polybutadiene when a small amount of Lewis base is added to the system (Section I-D-1b). This can be explained by assuming that the Lewis base occupies one coordination site so that the monomer can no longer coordinate through both double bonds but only by one (105).

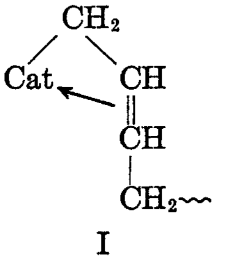
On the other hand, if coordination by only one unsaturated group can lead to *trans*-1,4 units, it seems that at least in one case (62) this type of coordination can also lead to *cis*-1,4 units (see I-F-3).

In conclusion, while coordination through both double bonds leads to *cis*-1,4 units, coordination through only one vinyl group may lead to 1,2 as well as to *trans*-1,4 or *cis*-1,4 units. The factors determining the type of unit obtained in the latter case are in general obscure and, as we will see later, are known only in particular cases.

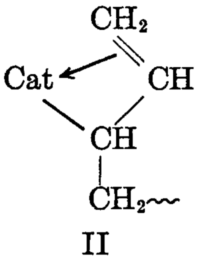
b. Effect of the Chemical Structure of the Catalyst. 1,2 vs. 1,4 Polybutadienes. In general, catalysts from transition metal halides yield 1,4 polymers from butadiene while those halogen free compounds yield 1,2 polymers. Thus, catalysts from AlR_3 and $TiCl_4$, VCl_4, $TiCl_3$, or VCl_3 yield 1,4 polymers, whereas those from AlR_3 and $Ti(OR)_4$ or $V(acac)_3$ yield 1,2 polymers. However, catalysts from AlR_2X (X = halogen) and halogen free transition metal compounds, such as $Ti(OR)_4$, $V(acac)_3$, $Co(acac)_2$ also give 1,4 polymers. This is due to the fact that the groups bonded to the transition metal are replaced by the halogen of the Al compound. The two systems AlR_3–$MoCl_5$ and AlR_3–$CoCl_2$, which are prepared from halogen containing compounds but yield 1,2 polymers (Section I-D-1c), may appear to be exceptions. However, in these systems practically all the chlorine is removed from the transition metal during the reaction with AlR_3.

In some cases the formation of 1,4 units is favored by catalyst heterogeneity. For example, the heterogeneous AlR_3–VCl_3 system, gives 95–98% *trans*-1,4 polymers from pentadiene, while the homogeneous AlR_2Cl–$VCl_3 \cdot 3THF$ system gives about 70% *trans*-1,4 and 30% 1,2 polypentadienes (Section I-D-3a).

With homogeneous systems, however, the chemical nature of the catalytic complex determines the type of enchainment, i.e., 1,2 or 1,4. Let us consider, e.g., the two homogeneous systems AlR_3–V $(acac)_3$, which yields 1,2 polybutadiene, and $AlEt_2Cl$–$V(acac)_3$, which yields *trans*-1,4 polybutadiene. In both cases the polymer grows on an allylic bond between V and the terminal polymer unit. The mode of coordination of the monomer does not seem to be a determining factor since in both cases the monomer probably coordinates only through the vinyl group. A possible explanation for the different modes of monomer addition is that the allylic unit, depending on the nature of the groups bonded to the transition metal, can react either as I (which gives rise to 1,4 units) or as II (which gives rise to 1,2 units).



I



II

These questions cannot be resolved at present since very little is known about how substituents on the transition metal affect the properties of π-allyl bonds.

c. Effects of Monomer Substituents. Different monomers can yield different polymer structures by the same catalyst system. This can be

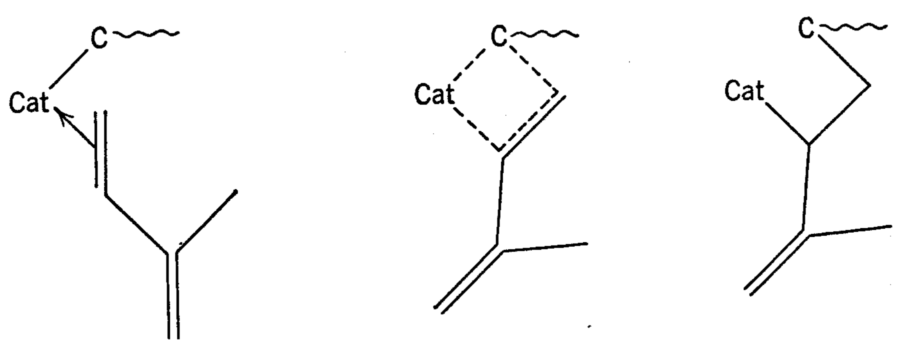


Fig. 7. Possible scheme for the formation of 3,4 units from isoprene.

explained by steric, inductive, or conformational factors depending on the nature and position of the substituents in the monomer.

(*1*) *1,2 Polymers from 4-Methyl-1,3-Pentadiene.* 4-Methyl-1,3-pentadiene is easily polymerized by catalysts from AlR_3 and $TiCl_3$, $TiCl_4$, VCl_3, or VCl_4 to predominantly 1,2 polymers (177). The above systems give almost completely 1,4 polymers with butadiene, isoprene, or pentadiene. The different behavior of 4-methyl-1,3-pentadiene has been attributed to a steric effect due to the presence of the methyl group in the 4 position.

(*2*) *1,4 Polypentadienes and 3,4 Polyisoprenes by the* AlR_3–$Ti(OR)_4$ *System.* The homogeneous AlR_3–$Ti(OR)_4$ system yields 1,2 polymers from butadiene (Section I-D-1c), 3,4 polymers from isoprene (Section I-D-2c) and *cis*-1,4 polymers from 1,3-pentadiene (Section I-D-3b).

The reason why 1,4 units are obtained from 1,3-pentadiene and 3,4 units from isoprene has been attributed to the different electronic distribution in the two monomers due to the different position of the methyl group. Figures 7 and 8 show possible schemes for the formation of 3,4 units from isoprene and 1,4 units from 1,3-pentadiene (62,108).

(*3*) *1,4 Polybutadienes and 1,2 Polypentadienes by* $AlEt_2Cl$–$Co(acac)_3$ *in n-heptane.* The $AlEt_2Cl$–$Co(acac)_3$ system in *n*-heptane yields *cis*-1,4 polybutadienes (Section I-D-1a), and 1,2 polypentadienes (Section I-D-3c).

These facts may be explained as follows. With Co catalysts, a *cis*-1,4 unit is obtained presumably by a coordination of the monomer to Co through both double bonds. Such coordination probably occurs in two steps: first, coordination through only one of the two double bonds and, second, coordination with the other. There is some experimental evidence in support of this hypothesis. $PdCl_2$ forms a complex with 1,5-cyclooctadiene, $C_8H_{12}\cdot PdCl_2$, and also with butadiene, $C_4H_6\cdot PdCl_2$.

In these complexes the diolefin is coordinated to Pd by both double bonds. When operating at low temperatures, however, an intermediate has been observed in which the diolefin is coordinated to Pd by only one double bond (179).

Thus it is suggested that the mechanism of the formation of a *cis*-1,4 unit by Co catalysts is that shown by route I in Fig. 9. Coordination through only one of the vinyl groups leads to a 1,2 unit by route II. According to this scheme the structure of the polymer is determined by the relative rates of the reactions by routes I and II. With $AlEt_2Cl$–$Co(acac)_3$ in *n*-heptane, 1,3-pentadiene would react faster by route II, while butadiene would react faster by route I.

(*4*) *1,4 Polypentadienes by* AlR_3–$TiCl_4$ *Catalyst.* Polypentadienes obtained by this system have predominantly *trans*-1,4 structures when prepared from the *cis* isomer, and predominantly *cis*-1,4 structures when prepared from the *trans* isomer (61). This is probably due to conformational factors relating to the monomer. The *trans* isomer can assume both the *trans* and the *cis* conformation and yields *cis*-1,4 polypentadiene with this catalyst, which preferentially yields *cis*-1,4 polymers. For steric reasons the *cis* isomer cannot assume the *cis* conformation and therefore polymerizes to a predominantly *trans*-1,4 polymer.

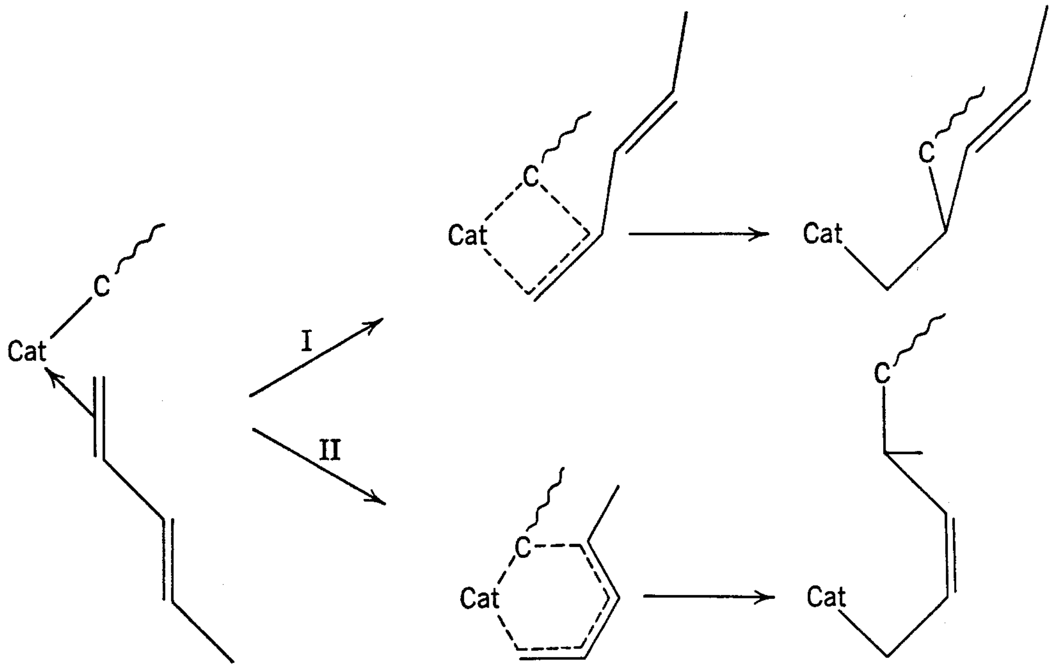


Fig. 8. Possible scheme for the formation of *cis*-1,4 (II) or 1,2 (I) units from 1,3-pentadiene.

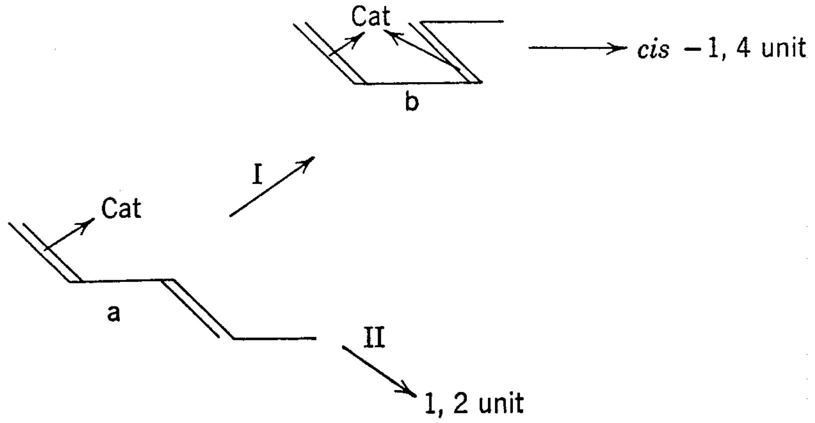


Fig. 9. 1,2 versus *cis*-1,4 polymerization of 1,3-pentadiene.

3. *Forces of Stereoregulation*

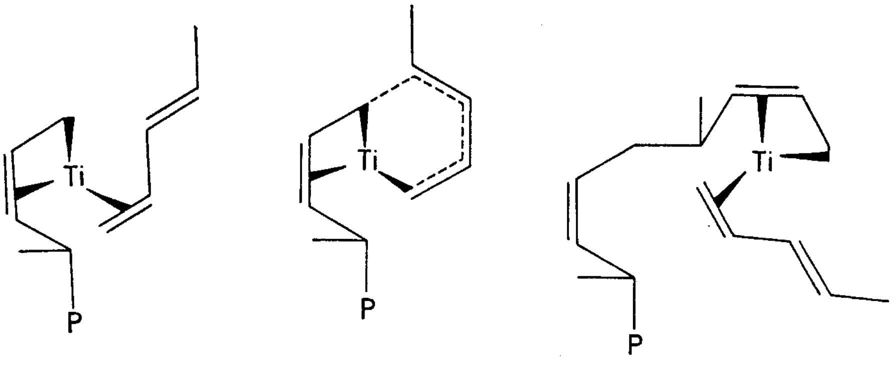
Five of the polymers previously discussed exhibit configurational regularity with respect to the asymmetric carbon atoms in the chain, namely isotactic and syndiotactic 1,2 polybutadiene, isotactic and syndiotactic *cis*-1,4 polypentadiene, and isotactic *trans*-1,4 polypentadiene. All these polymers can be obtained by homogeneous catalysts. Thus with diolefins, a solid catalytic surface is not a necessary condition for stereoregulation. This has been clearly recognized since 1955–1956, when the first isotactic and syndiotactic 1,2 polybutadienes were obtained with homogeneous catalysts. Although the presence of a solid catalytic surface is not necessary it can influence the stereospecificity. Thus, isotactic *trans*-1,4 polypentadiene obtained with $AlEt_3$–VCl_3 is more crystalline (and of higher molecular weight) than that obtained with butyl lithium in a homogeneous phase. Furthermore, isotactic *cis*-1,4 polypentadiene obtained with the hetereogeneous $AlEt_3$–$TiCl_4$ system ($Al/Ti \sim 2$; *trans* isomer of pentadiene) exhibits higher crystallinity (61) than polymers obtained with the homogeneous $AlEt_3$–$Ti(OR)_4$ system, although the latters have higher *cis*-1,4 contents. Evidently, the polymers obtained with the heterogeneous $AlEt_3$–$TiCl_4$ system contain more stereoregular isotactic sequences than those obtained with the homogeneous system.

In the case of diolefin polymerization, the catalytic complex (which, for simplicity, we shall consider as symmetric) and the terminal monomer unit constitute an asymmetric system, independently of the nature of the diolefin (butadiene, isoprene or pentadiene) and of the structure of the terminal unit (1,2, *trans*-1,4, or *cis*-1,4). In fact, a system consisting of a diene bonded to a metal by a π-allylic bond does not have a plane of symmetry. The formation of a stereoregular sequence by the incorporation of the coordinated monomer into the Me—C bond (Me = transition metal) is determined by two factors: (1) the relative configuration assumed by the incoming monomer with respect to the asymmetric system consisting of the catalytic center and the terminal monomer unit; (2) the mode of monomer incorporation, i.e., *cis* or *trans* opening of the double bonds.

Provided the chemical nature of the catalyst remains the same during polymerization, the mode of the double bond opening also remains the same throughout the process. Since the latter should remain the same as long as the chemical nature of the catalyst does not change, it may be concluded that point (*1*) determines the formation of a stereoregular sequence.

Little is known about the factors that determine the configuration of the incoming monomer with respect to the asymmetric system consisting of the transition metal and the terminal monomer unit. The only case for which plausible hypotheses have been put forward is that of the polymerization of 1,3-pentadiene to isotactic and syndiotactic *cis*-1,4 polymers.

In the schemes proposed (Figs. 10 and 11) pentadiene coordinates through the vinyl group only in the AlR_3–$Ti(OR)_4$ system, while it coordinates through both double bonds in the $AlEt_2Cl$–$Co(acac)_2$ system. Figs. 10(a) and 11(a) show the transition metal with the terminal monomer unit bonded to it, and a coordinated monomer molecule; Figs. 10(b) and 11(b) represent the transition state; Figs. 10(c) and 11(c) show the transition metal with the monomer that was coordinated in (a) already incorporated, and a new coordinated monomer molecule. It can easily



(*a*) (*b*) (*c*)

Fig. 10. Possible scheme for the formation of *cis*-1,4 isotactic polypentadiene.

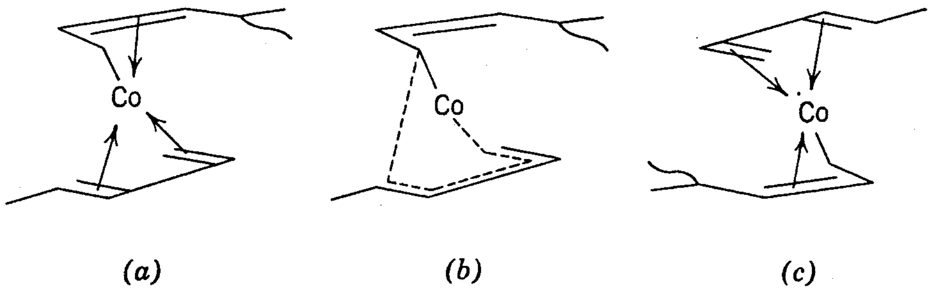


Fig. 11. Possible scheme for the formation of *cis*-1,4 syndiotactic polypentadiene.

be seen that Fig. 10(c) represents a situation identical to that shown in Fig. 10(a). Therefore, after incorporation, the coordinated monomer in (c) will give a unit with the same configuration as the preceding one. By this mechanism, *cis*-1,4 isotactic sequences will be formed.

On the other hand, Fig. 11(c) shows a situation that is enantiomorphous to that depicted in Fig. 11(a). Therefore, after incorporation, the coordinated monomer in (c) will give a unit with configuration opposite to the preceding one. Hence, *cis*-1,4 syndiotactic sequences will be formed by this mechanism. Obviously, these schemes are grossly oversimplified and the phenomena actually occurring during polymerization are much more complex.

II. COPOLYMERS OF BUTADIENE, ISOPRENE, AND PIPERYLENE

A. Introduction

Most studies of the polymerization of conjugated diolefins with catalysts based on transition metals have been concerned with the preparation of homopolymers. Relatively little effort has been devoted to the copolymerization of diolefins. Apart from disclosures in the patent literature, information is available concerning the following types of copolymers:

1. Butadiene–2-phenyl-butadiene copolymers obtained with Ti catalysts containing iodine (181).
2. Butadiene–pentadiene copolymers, obtained (*a*) with the heterogeneous $AlEt_3$–VCl_3 system (182), and (*b*) with the homogeneous $AlEt_2Cl$–$V(acac)_3$ system (182,183).

3. Butadiene–isoprene copolymers, obtained (*a*) with the AlR_3–$TiCl_4$ system (184,185), and (*b*) with the alkylaluminumchloride–Co compound system (184,186).

The copolymerization of conjugated diolefins with ethylene and/or α-olefins has been investigated extensively, but this subject falls outside the scope of this chapter.

B. Copolymers of Butadiene and 2-Phenyl-Butadiene

Copolymers of butadiene and 2-phenyl-butadiene have been prepared with the $AlHCl_2 \cdot O(C_2H_5)_2$–$AlI_3$–$TiCl_4$ system ($AlHCl_2/AlI_3/TiCl_4$ molar ratio = 5:1:1). This catalyst yields homopolymers with predominantly *cis*-1,4 structure from both butadiene and 2-phenyl-butadiene. In the copolymers both monomer units have *cis*-1,4 structure. The formation of true copolymers has been confirmed through fractionation, solvent extraction, and determination of glass transition temperatures. The copolymers are apparently random.

The reactivity ratios were found to be

$$r_{C_4} = 1.85\text{–}1.90 \qquad r_{PhC_4} = 2.58\text{–}2.6$$

Technological evaluation showed that the copolymers possess outstanding elastomeric properties. Greatly improved stress-strain properties, tear strengths and friction coefficients have been demonstrated. The introduction of up to about 25% by weight of 2-phenyl-butadiene into the *cis*-1,4 polybutadiene chain showed only a slight influence on the heat build-up. Thus butadiene–2-phenyl-butadiene copolymers (181), show particularly interesting properties for general purpose elastomer applications.

C. Copolymers of Butadiene and Piperylene

1. *Copolymers Obtained with the Heterogeneous* $AlEt_3$–VCl_3 *System*

The heterogeneous $AlEt_3$–VCl_3 system yields butadiene-1,3-pentadiene copolymers in which both the butadiene and the pentadiene units have a *trans*-1,4 structure (182). It is known (see Sections I-D-1b and I-D-3a) that the homopolymers of both butadiene and pentadiene obtained with the same system also have a 99–100% *trans*-1,4 structure. Either the *trans* or the *cis* isomer of pentadiene can be used as the comonomer.

TABLE XXIV
Melting Temperatures of *trans*-1,4-Butadiene-Pentadiene Copolymers (182)

Copolymer composition, C_4, mole %	T_m, °C
100	145
86	130
63	128
46	107
33	99
23	97
0	95

trans-1,4 Butadiene-pentadiene copolymers obtained with the $AlEt_3$–VCl_3 catalyst are crystalline over the whole composition range examined (from about 20 to 100% C_4). The final melting temperatures (T_m) are between those of the homopolymers over the entire composition range (Table XXIV). The type of crystallinity in the copolymers depends on their composition. Copolymers rich in butadiene (85–100%) exhibit crystallinity typical of modification I of *trans*-1,4 polybutadiene, while copolymers having lower butadiene content exhibit the crystallinity typical of modification II of *trans*-1,4 polybutadiene.

Copolymers properties have been explained by assuming that, due to the pendant methyl groups, the *trans*-1,4 pentadiene units are not (or only to a slight extent) isomorphous with the butadiene units of mod. I of *trans*-1,4 polybutadiene while they are isomorphous with mod. II, which is characterized by a higher equatorial encumberment for each chain.

2. Copolymers Obtained with the Homogeneous $AlEt_2Cl$–$V(acac)_3$ *System*

In copolymers obtained with the homogeneous $AlEt_2Cl$–$V(acac)_3$ catalyst, the butadiene units have *trans*-1,4 structure while the pentadiene units are partly *trans*-1,4 and partly 1,2. Only the *trans* isomer of pentadiene can be polymerized by this catalyst (182,183).

In these copolymers the melting temperature (T_m) decreases rapidly with increasing pentadiene content. The transition temperature (T_t) from mod. I to mod. II also decreases, but much less rapidly than T_m. Table XXV shows the values of T_m and T_t for various copolymers as a function of composition.

The difference in properties between these butadiene-pentadiene copolymers and those obtained with the $AlEt_3$–VCl_3 catalyst have been attributed to the side chains of the 1,2 pentadiene units which prevent the former copolymers from being isomorphous with mod. II of *trans*-1,4 polybutadiene (and, hence, even less with mod. I).

As shown by the data in Table XXV, a relatively small amount of C_5 units strongly decreases the T_m. This is due to the low enthalpy of fusion of mod. II of *trans*-1,4 polybutadiene, which is about 1000 cal/monomer unit (188).

The properties of the copolymers depend on the composition. Copolymers with a low pentadiene content and hence a high melting temperature are plastomers. On the other hand, copolymers which have a T_m close to room temperature are elastomeric. Thus, a continuous spectrum of products can be obtained by incorporating varying amounts of pentadiene into the *trans*-1,4 polybutadiene chain.

The elastomers obtained from the copolymers with T_m about 20°C have good hysteresis properties and are also able to crystallize on stretching. The type of crystallinity appearing on stretching at room temperature is that of mod. II of *trans*-1,4 polybutadiene (i.e., the modification of pure *trans*-1,4 polybutadiene which is stable above ~75°C).

The capacity of these copolymers to crystallize on stretching is therefore related to the isomorphism in *trans*-1,4 polybutadiene. More precisely, it is due to the existence of mod. II, which is characterized by an irregular chain conformation and therefore can exist even when a certain number of extraneous units have been introduced into the chains (183).

TABLE XXV

Transition and Melting Temperatures of Butadiene-Pentadiene Copolymers Obtained with the Homogeneous $Al(C_2H_5)_2Cl$–$V(acac)_3$ and $Al(C_2H_5)_2Cl$–$VCl_3 \cdot 3THF$ Systems (183)

Copolymer composition, C_5, mole %	T_t, °C	T_m, °C
0	75	145
5	65	120
10	53	95
13	47	81
15	40	67
19	27	46
22	—	20

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15	40	67
19	27	46
22	—	20

D. Copolymers of Butadiene and Isoprene

1. Copolymers Obtained with the Heterogeneous AlR_3–$TiCl_4$ *System*

Butadiene-isoprene copolymerization by the AlR_3–$TiCl_4$ catalysts has been studied by Bresler et al. (184) and by Suminoe et al. (185). It is known (see Sections I-D-1a and I-D-2a) that such catalysts are highly stereospecific for the polymerization of isoprene, yielding polymers with 95–97% *cis*-1,4 content, while they are considerably less stereospecific for the polymerization of butadiene, giving only about 70% *cis*-1,4 addition.

In the copolymers obtained either with $Al(i\text{-}C_4H_9)_3$–$TiCl_4$ (Al/Ti molar ratio 1.1:1) or with $Al(C_2H_5)_3$–$TiCl_4$ (Al/Ti molar ratio: 1.5:1), both the isoprene and the butadiene units have the same structure as in the homopolymers. That true copolymers, rather than mixtures of homopolymers, have been obtained was demonstrated by fractionation and by determination of the glass transition temperature (T_g). The latter varies linearly with composition from about −72°C to about −110°C for copolymers containing from 0 to 100% butadiene.

The reactivity ratios for the two monomers are $r_{C_4} = r_{C_5} = 1$. Hence, the composition of the copolymers corresponds exactly to the composition of the monomer charge.

2. Copolymers Obtained with the Homogeneous AlR_2Cl–Co *Compound System*

These types of copolymers have been studied by Bresler et al. (184), and by Pasquon et al. (186). The former authors (184) used $Al(i\text{-}C_4H_9)_2$-Cl–$CoCl_2 \cdot C_2H_5OH$ in benzene, the latter (186) $AlEt_2Cl$–$Co(acac)_2$ in toluene. It is known (see Section I-D-1a) that these systems are highly stereospecific for the polymerization of butadiene, yielding polymers with 97–98% *cis*-1,4 content, while they are less stereospecific for the polymerization of isoprene, yielding polymers with about 65–70% *cis*-1,4 units, the remaining ones being 3,4.

In the copolymers the microstructure of the butadiene and isoprene units depends on the copolymer composition. The ratio of *cis*-1,4 isoprene units/total C_5 units increases with increasing butadiene content, while the amount of 3,4 isoprene units simultaneously decreases. On the other hand, the ratio *cis*-1,4 butadiene units/total C_4 units decreases with increasing amounts of isoprene in the copolymer, while the 1,2

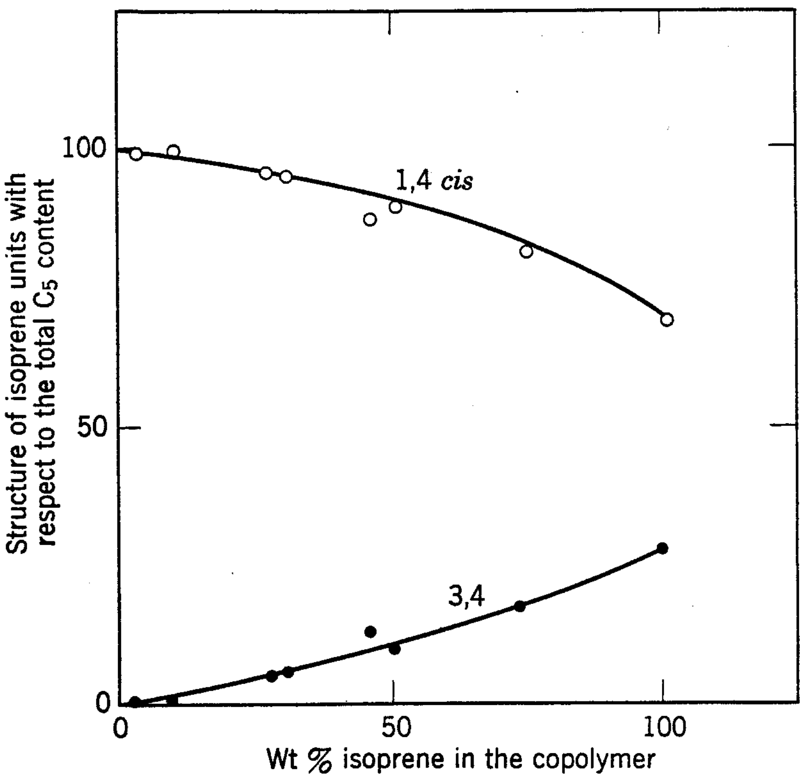

Fig. 12. Structure of isoprene units as a function of copolymer composition.

butadiene units simultaneously increase (Figs. 12 and 13). These facts suggest that the structure of a new unit is, at least in part, influenced by the nature and structure of the terminal monomer unit. Phenomena of this type have been observed in other types of copolymers (189).

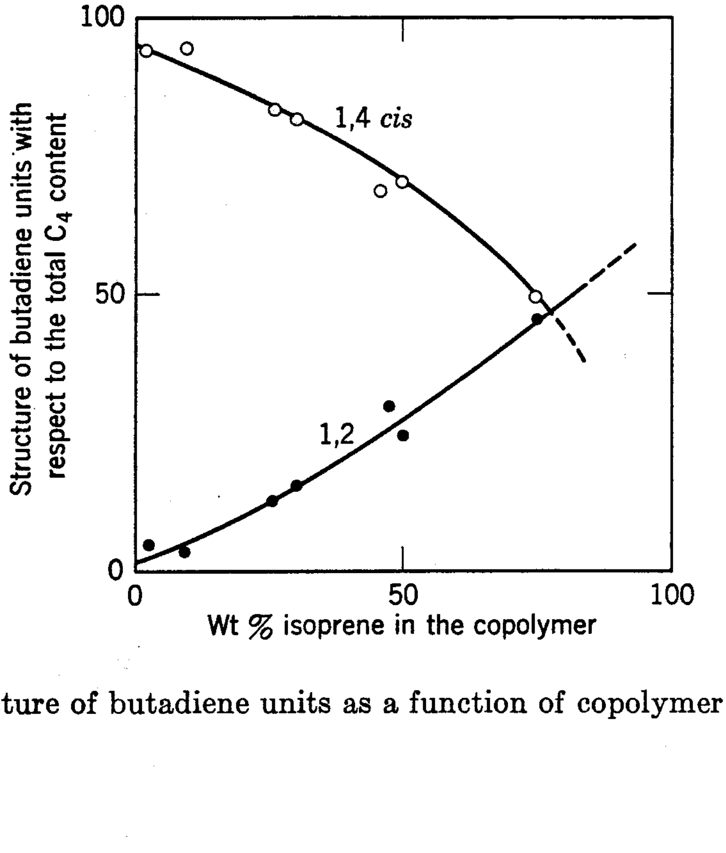

Fig. 13. Structure of butadiene units as a function of copolymer composition.

The reactivity ratios for the two monomers are $r_{C_4} = r_{C_5} = 1$ for copolymerization in toluene by $AlEt_2Cl$–$Co(acac)_2$, and $r_{C_4} = 2.3$, $r_{C_5} = 1.15$ for copolymerization in benzene by $Al(i\text{-}C_4H_9)_2Cl$–$CoCl_2 \cdot C_2H_5OH$.

The physical properties of the copolymers are determined by the composition. In particular, the melting temperature (which is about +3°C for 99% *cis*-1,4 polybutadiene) decreases with increasing isoprene content. These copolymers are therefore elastomers which may be suitable for low temperature applications.

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