THE STEREO RUBBERS

Edited by

WILLIAM M. SALTMAN
The Goodyear Tire & Rubber Company

A WILEY INTERSCIENCE PUBLICATION

JOHN WILEY & SONS, New York • London • Sydney • Toronto

Ph. Teyssié

Institut de Chimie
Université de Liège
au Sart Tilman
4000 Liège, Belgium

F. Dawans

Institut Français du Pétrole
92 Rueil-Malmaison, France

Chapter 3 Theory of Coordination Catalysis

Manuscript received December 1970, revised March 1975.

1 INTRODUCTION

1.1 Scope of the Chapter

A great deal has been achieved since the early discovery by Ziegler of the "Aufbau" reaction (1) and its striking modification in the presence of transition metal derivatives. The tremendous amount of research work in polymer chemistry stimulated by these discoveries provided a very strong support for the rapid development of coordination catalysis and coordination chemistry. In turn, the advances realized from the study of definite complexes in simple organic reactions provided powerful tools for a better understanding of coordination polymerizations. In particular the determinant role of the transition metal complexes is now well documented. The first part of this chapter is devoted to surveying the most important recent advances using monometallic catalysts.

This situation has also allowed a fruitful attack on the unsolved and complex problems regarding the oxidation state of the transition metal; the mono- versus bimetallic mechanism; and the heterogeneous versus homogeneous control of the stereospecificity.

A much better insight into the detailed mechanism of stereospecific coordination polymerization has been obtained. Rather direct and clear correlations have been established between the structure of the active species and its catalytic properties, i.e., activity and stereospecificity (2). In addition, it has been realized that the reaction schemes used to describe α-olefin polymerization by Ziegler type catalysts $M_TX_n + AlR_mX_{3-m} + L$ are very general and applicable to many reactions, and to very different types of substrates and bonding (e.g., to epoxide polymerization; see Section 5).

Other fields of specific polymerization contain one or another aspect of the basic features of coordination complex control; stereocontrol by organolithium derivatives (3, 4) and the alternating copolymerization of hydrocarbon and polar monomers in the presence of metal salts (5) are particularly interesting examples.

1.2 Importance of Coordination Catalysis in Polymerization

The breadth of the field may be indicated by a few examples (6).

Both the efficiency and the versatility of the coordination catalysts can be controlled closely by systematic modification of the catalytic structure, with monometallic and with bimetallic complexes. Very high activities have been obtained, allowing use of minute amounts of catalyst even on an industrial scale, in the parts per million range. Steric, structural, and geometric isomerism have been controlled in practice in most hydrocarbon polymers, leading, for instance, to the preparation of high performance isotactic polyolefins and synthetic equivalents of natural rubber. Still more refined types of stereoregulation (which could be considered as second-order control) have also been realized, for instance by preparing ditactic polymers (erythro- and threotactic polyolefins) or equibinary polydienes, and by performing stereoelective polymerizations where a particular optical isomer of a racemic monomer is preferentially incorporated. Polymerization of different types of monomers has also been achieved, for example by ring opening of cycloolefins or heterocyclic compounds (see Chapter 6). Finally, strong indications have been obtained that direct methods to prepare block copolymers, involving coordination catalysis at least for one type of sequence, could be designed with a sufficient degree of specificity to prepare interesting new products in one operation.

Considering both the quality and the volume of the products resulting from processes based on coordination catalysis, mainly of the Ziegler-Natta type, one must admire the tremendous development that has taken place in less than 25 years.

2 THE DETERMINANT ROLE OF TRANSITION METAL COMPLEXES IN STEREOSPECIFIC POLYMERIZATION OF UNSATURATED HYDROCARBONS

2.1 Present Conceptions

Numerous papers have been concerned with the nature of the active sites and the origin of stereospecific control in the Ziegler-Natta catalysts. Various and sometimes contradictory schemes have been offered to explain the principles underlying their action.

These multicomponent active systems (involving a transition metal derivative M_TX_n, a metal alkyl, e.g., AlR_mX_{3-m}, and perhaps a ligand L) might be grouped into catalysts acting in a homogeneous phase and those acting in a heterogeneous phase, the solubility or insolubility being determined, of course, by the structure and the ratio of the different components which make up the catalyst. In the case of homogeneous catalysis, it is clear that the factors controlling the stereospecificity must be linked to the specific interaction of the monomer and/or the growing chain with the active complex (including metal, counterion, ligands, and solvent). In the case of catalysts acting in a heterogeneous phase, it was speculated that the determinant factor might be the structure of the catalytic surface. Comparison of homogeneous and analogous heterogeneous systems allows one to forecast that there should be no essential difference in their basic mechanism of action. This point is discussed in more detail in Section 3.4.

Although the exact mechanism by which stereospecific catalysts operate is still a matter of controversy, two conclusions have been reached which have adequate experimental foundation and are widely accepted at the present time:

1. Interaction of the components of the bimetallic catalytic systems results in the formation of alkyl derivatives of transition metals which are capable of coordinating unsaturated hydrocarbon molecules.
2. Growth of the polymer chain takes place by repeated insertion of the monomer into a bond between transition metal and one carbon atom belonging to the alkyl group or later to the growing polymer chain.

It is now clear that these polymerization catalysts, in mechanism, represent a particular although very important example of a broad class of complex catalysts for organic reactions, including hydrogenation, carbonylation, oligomerization, isomerization, etc., of unsaturated compounds.

The exact role of the organometallic compound is still debated. Some scientists propose that its function is limited to alkylating the transition metal, the propagation involving two or more coordination sites on this central transition metal (Fig. 1). Others believe the organometallic compound not only alkylates the transition metal but also participates in the formation of the active center (Fig. 2). There are still some who propose that the growing chain is attached to the aluminum atom (8). It seems more accurate to admit that there may well be internal or external transfer reactions to the aluminum alkyl during polymerization, thus leading at some stage to the eventual formation of different metal-polymer bonds. However, the dependence or reactivity ratios in α-olefin copolymerization on the structure of the transition metal derivative and not of the organometallic cocatalyst, has now been accepted for several years to indicate growth on the transition metal atom. This hypothesis, according to which a transition metal-carbon is involved in the propagation step, is further supported by a number of reported experiments, such as the electrodialytic investigation of the soluble catalyst $(CH_3)_2AlCl+(C_5H_5)_2TiCl_2$ (9–12), the dependence of the propagation rate constants on the transition metal component and not on the metal alkyl structure (13), and the kinetic study of ethylene polymerization combined with ESR and magnetic susceptibility measurements on soluble catalysts (14–17).

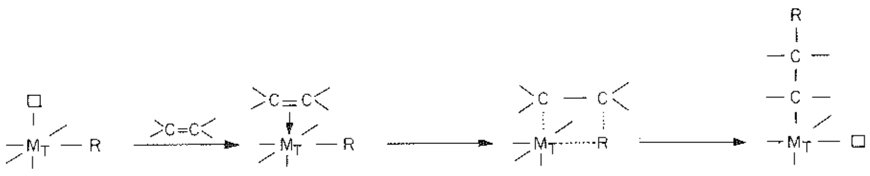


Figure 1

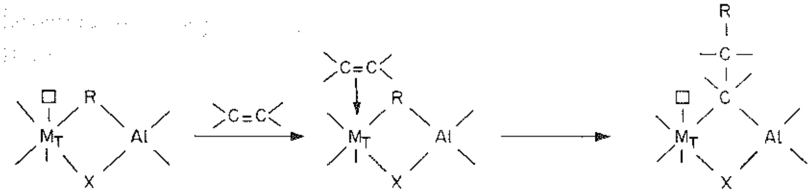


Figure 2

If the role of the alkyl derivative of a metal of the first three groups is limited to alkylating the transition metal compound, proportionality should be expected between the alkylating power of the organometallic compound used for the catalyst preparation and the activity of the catalyst itself. Different studies (18, 19) have shown that this is not the case. Hence in addition to the alkylating power of the organometallic compound, its stronger or weaker tendency to form complexes with the transition metal compound is also important and might even influence the stereospecificity of the entire catalytic system. Thus even admitting that the growth of the polymer chain takes place through repeated insertion of the monomer into a transition metal-carbon bond, it is now evident that active centers are formed whose activity and eventual stereospecificity depend on the nature of other groups bound to this metal, as is the case of many other reactions. In other words, in the presence of metal alkyl compounds and particularly of aluminum alkyls with a high ability to form complexes with transition metal compounds, active centers also containing aluminum may be formed. This observation is further corroborated by the fact that the value of the propagation rate constants for ethylene polymerization by catalysts obtained by the interaction of tetrakis-π-allyl zirconium with an oxide support, changes markedly as the nature of the support is changed (7). This seems to be related to the difference in the composition of the active centers of these catalysts, and is further evidence that an alkylating organometallic cocatalyst is not absolutely required for the formation of highly active catalytic species.

Notwithstanding the large amount of work accomplished in recent years and reported in a number of excellent reviews (6, 20–23), this interesting problem has not yet been completely solved. This is owing mostly to its complexity but above all to the various natures of the numerous combinations which belong to the vast class of Ziegler-Natta catalysts, which are still difficult to represent by a unitary model. Even where studies have been carried out on homogeneous systems, at least two organometallic compounds are involved, making accurate determination of the structure of very small amounts of the propagating species difficult.

These problems are discussed in more detail in the following sections. However, the ability to polymerize, stereospecifically, unsaturated hydrocarbons in the presence of monometallic complexes is now well documented; it has been definitely proved that a second metal is not essential for catalyst formation. Accordingly, the present discussion will center on simple catalytic transition metal complexes having well-defined structures and on the factors, reported mostly during the last 10 years, controlling both the activity and the stereospecificity of monometallic catalysts. The ability to modify the catalyst structure systematically is to be considered as particularly important, since an understanding of the mechanism of action might reveal more of the important features of the chemistry of the active site involved.

These active monometallic catalysts reported for the polymerization of unsaturated monomers (principally butadiene and ethylene) are essentially transition metal salts and complexes (e.g., hydride, alkyl, carbene, cyclopentadienyl, carbonyl, benzyl, and allyl complexes), used as such or more often in the presence of some added electron donor or acceptor. Many catalytic derivatives used appear to be originally associated as binuclear complexes, involving, in some cases, two different transition metals; but even in these cases the catalytic site may be regarded as being formally monometallic, the other metal derivative functioning as a ligand.

2.2 Types of Catalytic Complexes

2.2.1 *Transition Metal Salts*

Noble Metal Salts. Considerable interest was aroused by the discovery that rhodium salts catalyze the stereospecific polymerization of 1,3-butadiene to a high trans-1,4 polymer in protonic media (24); indeed, noble metal salts were the first example of stable and formally simple catalysts inducing a highly stereospecific polymerization. Although this polymerization can be carried out in an aqueous emulsion system, it has been convincingly demonstrated that these systems do not operate by means of a conventional free radical mechanism (25), but they do imply the coordination of the monomer on the metal atom. Consequently, these catalysts enjoy a high versatility and many factors influence the course of the reaction; in particular, the nature of the metal used appears to be the determinant of the stereospecificity. For example, the microstructure of the polybutadiene obtained in the presence of salts and complexes of palladium is predominantly 1,2, whereas high trans-1,4 contents are observed in the polymers produced with rhodium derivatives and, in spite of some controversy, the polybutadiene produced by means of complex cobalt fluorides is reported to be essentially cis-1,4 (220).

Various coordinating compounds such as those containing nitrogen atoms can markedly affect the activity of the rhodium in the polymerization systems, confirming that its $4d$ orbitals are involved in the catalytic process (28). Addition of certain additional diolefins was shown to give superior catalysts (29). The so-called emulsifiers play an important role as ligands that take an active part in polymerization. Only anionic emulsifiers give active catalysts, and at emulsifier/rhodium molar ratios greater than 2 (30). The emulsifier is consumed during the reaction, the polymer produced containing approximately 1 mole of sulfur per chain (31). Studies conducted in homogeneous solution have confirmed that the effective surfactants are of the sulfate or sulfonate types (sodium lauryl sulfate and sodium alkylbenzene sulfonates having alkyl chains greater than C_5) (32).

It has thus become obvious that the rhodium based catalytic systems involve the formation of a complex between the metal, butadiene, and various ligands, including the emulsifier itself. In fact, the close analogies between these reactions and Ziegler-Natta catalysis—the only major difference being the stability of the noble metal catalysts toward protonic media—suggest some similarity in the mechanism of both types of polymerization, most probably implying the formation of an allyl type species, indicative of a coordination propagation proceeding by cis rearrangement. One of the possible paths is shown in Fig. 3, although initiation by a π-crotyl complex arising from an intermediary hydrido-Rh(I) species (33) might also be considered, as well as the incorporation of some chlorine at chain ends.

The observations made during a study of butadiene polymerization in homogeneous solution, in the presence of dichloro-2,6,10-dodecatriene-1,12-di-yl-ruthenium, $RuCl_2(C_{12}H_{18})$, and a tertiary phosphine, also suggest a close similarity between the propagation mechanism in this

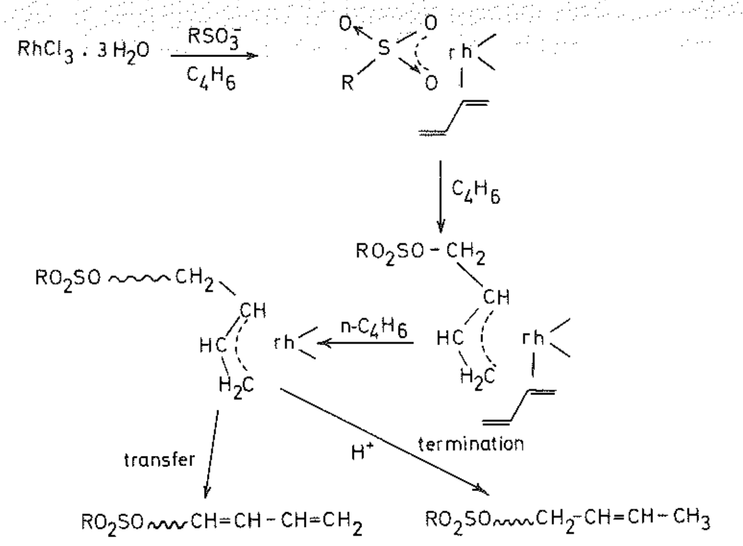


Figure 3 Proposed mechanism for rhodium catalyst coordination propagation proceeding by cis rearrangement. (rh designates a rhodium atom in an octahedral environment but whose ligands are not all determined. RSO_3^- may be replaced by Cl^- or H^-.)

homogeneous solution polymerization and that in the heterogeneous emulsion polymerization with a ruthenium trichloride-triphenylphosphine catalyst. The NMR spectrum of the homogeneous system indicates the coexistence of both π- and σ-allylic structures, considered to be active intermediates for the polymerization of butadiene (34).

Additional strong evidence in favor of coordinated mechanisms is the selective behavior of metal derivatives toward specific monomers; for example, rhodium salts do not catalyze ring opening polymerization of norbornene but they yield addition polymers from cyclobutene (35). On the other hand, ruthenium salts which as such are not good catalysts for the polymerization of butadiene promote the ring opening polymerization of both cyclobutene and norbornene (36–38). A comparative structural study of polynorbornadienes produced by complexes of three different metals (e.g., rhodium, iridium, and palladium) emphasizes the dependence of the polymer structure upon the nature of the metal. Indeed the polymer produced exhibits a unique structure depending on the specific nature of the metal used as catalyst (39). In Fig. 4 rhodium gives a saturated polymer with a nortricyclene repeating unit from a 1,5 polyaddition (scheme *A*); with palladium, a 1,2 addition leads to a polymer containing one unsaturation per repeating unit (scheme *B*), while with

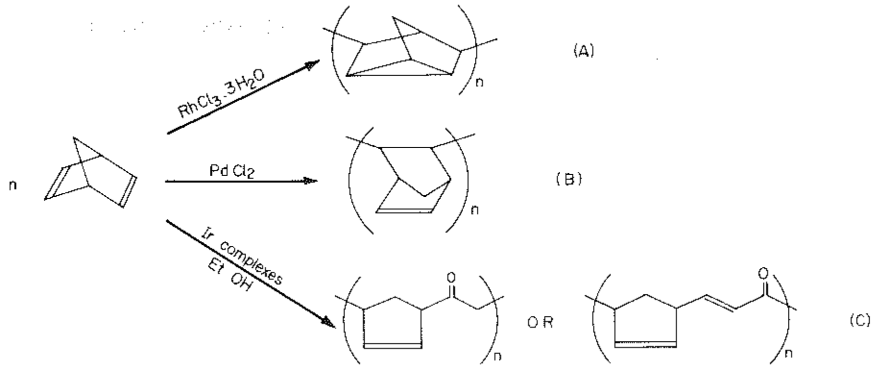


Figure 4

iridium oxygenated polymers containing one oxygen atom per repeating unit are obtained on performing the reaction in an oxygenated solvent (scheme *C*). Some noble metal complexes are thus specific for addition polymerization whereas others are effective only for ring opening polymerization.

Another significant example indicating close interaction between the monomer and the noble metal atom during the propagation reaction is the polymerization of propylene in the presence of palladium cyanide, yielding a copolymer containing 93% 1,3 units and 7% 1,2 units (40). Indeed, since palladium cyanide is completely insoluble in the medium, the reaction probably takes place at the crystal surface involving two adjacent palladium atoms. The peculiar structure of the polymer produced might be due to the intermediary formation of a π-allyl type complex (Fig. 5).

First Row Transition Metal Salts. A propagation reaction mechanism involving coordination of the monomer at the crystal surface may be compared with the catalytic activity promoted through γ-irradiation [see, e.g., Pino (41) and Allegra et al. (42)] or through mechanical activation (ball-milling) (43, 44) of crystalline titanium halides which are, in the absence of organometallic cocatalysts, otherwise very poor catalysts for the polymerization of ethylene. Indeed, when γ-irradiated or ball-milled,

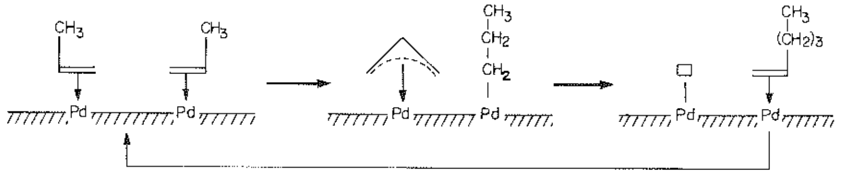
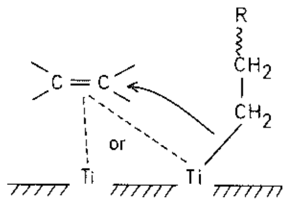


Figure 5

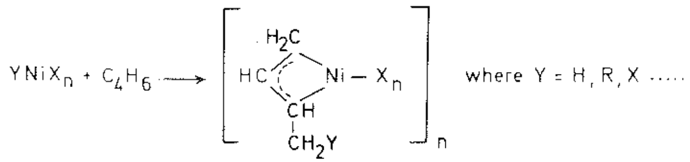
they are converted into active catalysts (e.g., for ethylene) in the absence of organometallic cocatalysts or of metals and their derivatives (such as Al or $AlCl_3$). The polymerization rate was shown to be proportional to surface area, and a direct function of Ti^{2+} content of the catalyst. The proposed reaction scheme postulates an active catalytic alkyl complex, where both initiation and propagation could take place at a single metal atom or alternatively on two adjacent Ti^{2+} ions.



Termination probably proceeds through the formation of hydride species, as suggested by the presence of one terminal double bond per polyethylene chain.

Just as titanium subchlorides were shown to be catalysts for the polymerization of monoolefins, 1,3-butadiene was reported to be polymerized to cis-1,4 polymer on irregularly stacked, halogen deficient crystals of cobalt(II) or nickel(II) halides (45, 46). In this case, halogen is removed from the halides by heating the salts under high vacuum or by photolyzing them in the presence of butadiene, transferring halogen to butadiene. The species responsible for the initiation of butadiene polymerization are probably nickel or cobalt monohalide complexes.

Catalytic subhalides of nickel inducing cis-1,4 polymerization of butadiene may also be obtained by reacting nickel hydride (46, 47) or reduced nickel (48–50) with some Lewis acids and various organic halides. Once again, the results suggest that the cis-1,4 polymerization proceeds by a coordinated mechanism, involving the formation of π-crotyl complexes with the monomer:



More recently, halide derivatives of transition metal haloacetates were found to be efficient catalysts for the stereospecific polymerization of unsaturated monomers; for example, $CF_3COONiCl$ yields a high *cis*-1,4-polybutadiene in hydrocarbon solutions (51, 52). In this case, the transitory formation of a π-chlorobutenyl complex was confirmed, using a ^{36}Cl-labeled nickel salt (208).

Finally, stereospecific polymerization reactions can also be promoted by transition metal subhalides complexed with strong electron donating ligands. For example, $TiCl_3 + N(C_2H_5)_3$ or $P(n\text{-}C_4H_9)_3$ as well as $[(C_6H_5)_3P]_3NiX$ or $(Cl_3P)_4Ni$ complexes, when reacted with Lewis acids, induce the coordinated polymerization of various monomers such as 1,3-butadiene, isoprene, ethylene, allene, or isobutyl vinyl ether (53–56). In the presence of $(Cl_3P)_4Ni + WCl_6$, the ring opening polymerization of cyclopentene to a linear polymer is also promoted (57).

2.2.2 *Alkyl Complexes of Transition Metals*

As summarized in Table 1, numerous catalytic systems containing transition metal alkyl derivatives are known which polymerize α-olefins, cycloolefins, conjugated diolefins, and vinyl or acetylenic monomers, in the absence of any alkyl derivatives of metals of groups IA to IIIA.

For α-olefin polymerization these systems usually contain two compounds of the same metal, namely titanium, which suggests that the active centers might involve two metal atoms. Although it is well known that organoaluminum can impart a high catalytic activity to organometallic compounds of a transition metal, which otherwise would be practically inactive [e.g., $(C_5H_5)_2Ti(C_2H_5)Cl + (C_2H_5)_2AlCl$] or at least poorly active $[(C_6H_5CH_2)_4Ti + (C_6H_5CH_2)_3Al]$, the fact that some of the titanium catalysts containing no aluminum [such as $RTiCl_3$, $(C_6H_5CH_2)_3TiCl$, or $(CH_3)_2Ti(C_5H_5)_2 + TiCl_3$ or $TiCl_4$] give crystalline polypropylene may be considered support for the idea that the *origin* of the stereoregulation is solely in the structure of the transition metal complex.

Another interesting observation concerns the ability of some alkyl complexes of transition metals to induce the polymerization of vinyl polar monomers, avoiding the marked tendency of polar groups to react with the metal and to inhibit completely the polymerization process. Such a specific interaction with alkyl complexes of transition metals was suggested, for example, in the course of the polymerization of acrylonitrile in the presence of diethyldipyridylnickel (81); infrared absorption data indicate that under suitable conditions acrylonitrile may be coordinated to the nickel atom through the vinyl bond and not by the nitrile groups; this interaction causes the weakening of the ethyl-nickel bonds, leading to their scission and the initiation of polymerization by a coordinated mechanism (Fig. 6).

Table 1 Catalysts from Alkyl Complexes of Transition Metals

Monomers	Alkyl Complexes	Cocatalysts	Ref.
α-Olefins[a]	$RTiCl_3$	Cr, V, Ti halides	58–64
	$C_2H_5TiCl_3$	3–25 Megarads	66
	R_2TiCl_2		58–65
	$R_2Ti(C_5H_5)_2$	$TiCl_3$, $TiCl_4$	64, 67–71
	$(CH_3)_2Ti(OR)_2$	$TiCl_3$, $TiCl_4$, VCl_4	72, 73
	$(C_6H_5CH_2)_{4-n}TiCl_n$		74
	$(C_6H_5CH_2)_{4-n}ZrCl_n$		75
	$(C_3H_5)_4Zr$	SiO_2	7, 209–211
	$(C_7H_7)_4Ti$	Al_2O_3	7, 209–211
Vinyl ethers	$RTiCl_3$		76
Vinyl compounds	$(C_5H_5)_2TiCl_2$	Fatty acids	77
Diarylvinylamine	$(CH_3CO_2)_2TiCl_2$		78
Alkoxystyrenes	$(CH_3CO_2)_2TiCl_2$		79
Styrene	$C_6H_5Ti(i\text{-}C_3H_7O)_3$		80
Acrylonitrile	$(C_2H_5)_2Ni$ dipyridyl		81
Alkyl isocyanates	$(C_2H_5)_2Ni$ dipyridyl or $(PPh_3)_4Ni$		205
Allene	$(C_8H_{12})_2Ni$		82, 83
1,2-Butadiene	$(C_8H_{12})_2Ni$		84
1,3-Butadiene	$(C_8H_{12})_2Ni$	Metal halides	85, 86
	$(C_8H_{12})_2Ni$	Protonic acids	87, 88
	$C_8H_{12}NiX$		89
	$(C_6H_5)_3CNiCl$		90
	$(C_5H_5)_2Ni$	Metal halides	47, 91–93
	$(C_5H_5)_2Ni$	F_3CCOOH	94
	$(C_5H_5)_2Ni$	p-Chloranil	47

[a] Most of the reported catalytic systems were applied to ethylene polymerization. Consequently, valuable data on the stereoregularity control by monometallic species are difficult to sort out. However, in the case of propylene polymerization, partially crystalline polymers are obtained only in the presence of VCl_4, $TiCl_4$, or $TiCl_3$ as cocatalysts.

Finally, it may be interesting to point out that some carbene complexes of tungsten were recently shown to enjoy a very high catalytic activity for the ring opening polymerization of cyclopentene in the presence of Lewis acids as cocatalysts (212) (see also Chapter 6).

In butadiene polymerization performed in the presence of hydrocarbon complexes of nickel, the insertion of monomer molecules occurs between the nickel atom and a π-allylic unit formed by direct interaction of 1,3-butadiene with the nickel complex as shown by Wilke and co-workers (95) (Fig. 7). This π-allyl group might also be formed by the reaction of a cocatalyst with the nickel complex, followed by interaction with the monomer (Fig. 8), as proposed by Dolgoplosk and co-workers (47).

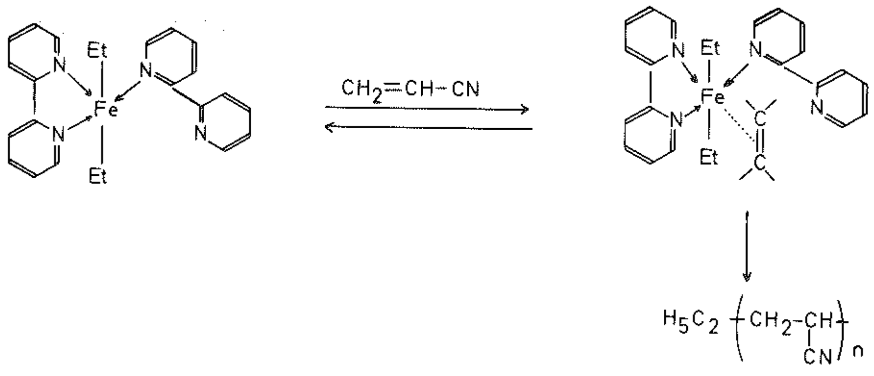


Figure 6

2.2.3 *Carbonyl Complexes of Transition Metals*

Manganese carbonyl, $Mn_2(CO)_{10}$, induces the ring opening polymerization of propylene oxide to yield a tactic polymer (107, 108). In addition to this reaction, an important series of catalysts involving carbonyl complexes of transition metals was discovered by Otsuka and Kawakami (96) for the stereospecific polymerization of 1,3-butadiene. They found that the reaction product of $Co_2(CO)_8$ with $MoCl_5$ polymerizes butadiene in benzene to an amorphous 1,2 polymer, while the system $Ni(CO)_4 + MoCl_5$ gives a high (more than 85%) *cis*-1,4-polybutadiene. Since that time, other nickel and cobalt carbonyl complexes, which as such do not exhibit any catalytic activity in butadiene polymerization, have been tested further together with numerous Lewis acids as cocatalysts (see Table 2). The interaction between carbonyls and Lewis acids results in carbon monoxide evolution and precipitation of products insoluble in hydrocarbons. The rate and stoichiometry of the reaction are influenced by the nature of the Lewis acid used, vanadium and tungsten derivatives

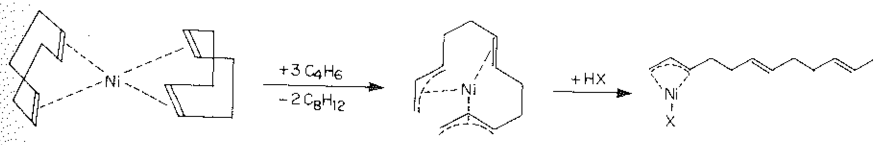


Figure 7

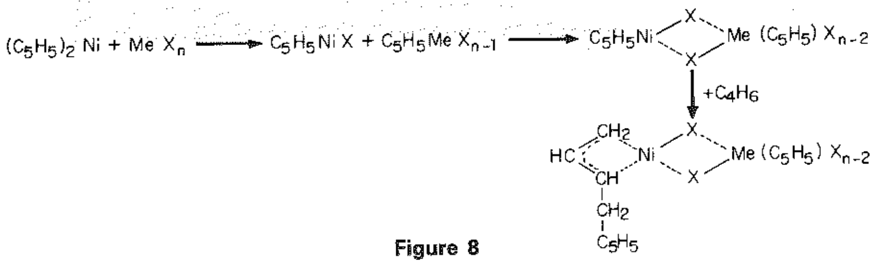


Figure 8

being the most active. The polymers produced all exhibit high cis-1,4 contents (around 90%). Cyclopentadienylnickel carbonyl behaves as $Ni(CO)_4$ but substitution of one carbonyl group by triphenylphosphine in $Ni(CO)_4$ results in a complete loss of activity of the products formed by reaction with Lewis acids (47). Catalysts produced by reaction of nickel carbonyl with Lewis acids in aromatic solvents were shown to be arene-nickel complexes:

$$Ni(CO)_4 + MeX_n + ArH \longrightarrow Ni(ArH)_2 \cdot (MeX_n)_m$$

The activity of these catalysts is considered to be associated with their π complex nature, and therefore dependent on the ability of aromatic ligands to be substituted by butadiene, i.e., on the lability of the arene-metal bond; in fact, butadiene polymerization is completely suppressed in the presence of mesitylene or hexamethylbenzene.

Table 2 Catalysts from Carbonyl Complexes of Transition Metals for 1,3-Butadiene Polymerization

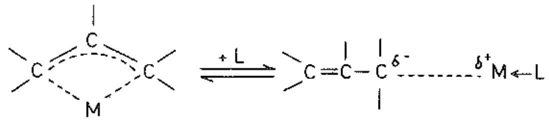
		Polybutadiene Structure (%)			
Carbonyl Complex	Cocatalyst	Cis-1,4	Trans-1,4	1,2	Ref.
$Ni(CO)_4$	Various metal halides	75–95	3–20	1–6	47, 96–105
$Ni(CO)_4$	$AlCl_3 + KCN$	59	37	4	103
$Ni(CO)_4$	$AlCl_3 + KI$	3	95	2	103
$(C_5H_5NiCO)_2$	$TiCl_4$, $VOCl_3$	91–94	4–6	2–3	47, 97
$[Co(CO)_4]_2$	$MoCl_4$, $MoCl_5$	2	3	95	47, 96 97, 102 106
$[Co(CO)_4]_2$	WCl_6	56	35	9	102
$[Co(CO)_4]_2$	$AlCl_3$ + thiophene	96	2	2	105
$[Rh(CO)_2Br]_2$ $[RhNH_3(CO)_2Cl]$ $[Rh(CO)Br_2]_2 \cdot [N(C_4H_9)_4]_2$ $[Rh(CO)_2Cl_2] \cdot [N(C_4H_9)_4]$			78–84		46

On the other hand, halide derivatives of rhodium carbonyl are catalysts for the stereospecific polymerization of butadiene in hydrocarbon media, to yield 1,4-trans polymers (46).

Butadiene polymerizations induced by carbonyl complexes on the one hand, and by other transition metal π complexes, especially alkyl, arene, and cyclopentadienyl complexes, on the other, present striking similarities. This similar behavior can be ascribed to the intermediate formation in all cases, of π-allylic complexes resulting from the interaction of the monomer with the transition metal compound and its cocatalyst. Reactions of this type are well documented in organometallic chemistry. In other words, the catalytic activity does not necessarily depend on the existence of a preformed transition metal-carbon bond. This bond may be generated by the action of the monomer on the complex, as is also suggested in the case of the metal salts.

2.2.4 *π-Allylic Complexes of Transition Metals*

It has been shown experimentally that dienes react with a number of group VIII metal derivatives to give complexes having a π-allyl type of structure. NMR spectroscopy indicates that the metal–ligand bond involves three carbon atoms with delocalized π electrons; the π-allylic group is thus considered to be a bidentate ligand that can be converted, under the influence of another suitable ligand, to a σ-allyl group able to behave like an alkylated initiating center.



Since many recent results indicate the formation of intermediate π-allylic types of structures, the polymerization of conjugated diolefins by simple π-allyl derivatives of transition metals is of great interest. This subject has been recently reviewed (109). Such π-allyl groups represent good models of the active site structure. Since the first examples of stereospecific polymerization of 1,3-butadiene by π-allylic complexes of nickel and cobalt were reported independently by Natta and Wilke, numerous studies have been concerned with polymerizations in the presence of π-allyl derivatives of transition metals, as summarized in Tables 3 and 4.

Without a cocatalyst, only very few π-allyl type catalysts achieve the activity of the bimetallic Ziegler-Natta types, nor do they produce the same quality polymers (discussed in Section 4). As is evident from part A

Table 3 Catalysts from π-Allyl Transition Metal Complexes for 1,3-Butadiene Polymerization in Hydrocarbon Solutions

		Polybutadiene Structure (%)			
π-Allyl Complex	Cocatalysts	cis-1,4	trans-1,4	1,2	Ref.
A. (π-Allyl)$_x$M$_T$					
$(C_3H_5)_2Ni$, $(C_4H_7)_2Ni$		1,5,9-Cyclododecatriene			95
$(C_3H_5)_3Co$, $(C_4H_7)_3Co$		Linear oligomers			46, 95, 110
$(C_3H_5)_3Cr$, $(C_4H_7)_3Cr$			19–10	81–90	46, 47, 110–112
$(C_4H_7)_3Nb$				up to 97	46, 113
$(C_4H_7)_3Ti$		0	17	83	46
$(C_4H_7)_3Rh$		0	94	6	46
B. (π-Allyl)$_x$M$_T$ + MeX$_n$					
$(C_3H_5)_2Ni$	$SnCl_4$	30	68	2	91, 92
	SnI_4	0	95	5	47, 91
	$SnCl_2$	52	46	2	91
$(C_4H_7)_2Ni$	$AlCl_3$, $MoCl_5$, $TiCl_4$ $NiCl_2$, $SnCl_4$, $SnCl_2$ $AgClO_4$, $Mg(ClO_4)_2$	81–95	3–18	1–3	46, 47, 90
	NiF_2	28	66	6	47
	$NiBr_2$	14	82	4	47
	NiI_2	0	95	5	47
	$NiCl_2 + 10THF$	71	24	5	47
	$NiCl_2 + 1P(C_6H_5)_3$				
	$NiCl_2 + 100H_2O$	0	95	5	47
	$NiCl_2 + 1Bu_2S$	87	11	2	47
$(C_4H_7)_3Cr$	$CrCl_3$	10	15	75	47
	$NiCl_2$	92	2	6	46, 47
	$NiBr_2$	0	95	5	47
	TiI_4	90	6	4	46, 47, 114
	$TiCl_4$	45	50	5	114
	$Cr(AcAc)_3$	35	0	65	114
	$Zn(OOCCCl_3)_2$	82	5	13	46
	$Mn(OOCCCl_3)_2$	64	11	25	46
$(C_4H_7)_3Co$	$CoCl_2$	40	13	47	46
$(C_4H_7)_3Fe$	$NiCl_2$	92	6	2	46
$[(C_4H_7)_2Mo]_2$	$MoCl_5$	15	4	81	47
	$TiCl_4$	61	15	24	47
$(C_4H_7)_3Ti$	$NiCl_2$, TiI_4	85–88	5–8	4–10	46
$(C_3H_5)_4Zr$	$TiCl_4$	45	45	10	114
$(C_4H_7)_3Rh$	$AlCl_3$, $SnCl_4$	0	90–98	2–10	46

Table 3 (Continued)

C. (π-allyl)$_x$M$_T$ + HX or X$_2$					
$(C_3H_5)_2Ni$	$1CF_3COOH$	71–77	22–28	1	115
	$2CF_3COOH$	48–53	46–50	1–2	115
	$C_7H_7SO_3H$	48–50	48	2–4	115
	$CH_{3-n}Cl_nCOOH$	92–95	4–6	1–2	47
	$C_6H_3(NO_2)_2OH$	93	5	2	46
$(C_4H_7)Ni(C_5H_5)$	$C_6H_2(NO_2)_3OH$	90	8	2	116
$C_{12}H_{18}Ni$	HCl	84	13	3	87, 88, 117,
	HBr	72	25	3	87, 88, 117 118
	HI	0	100	0	87, 88, 117, 118
	Cl_2	74	23	3	117, 118
	I_2	12	86	2	117, 118
	$CH_{3-n}Cl_nCOOH$	89–91	4–6	3–5	87, 88, 117, 118
	$1CF_3COOH$	92	4	4	87, 88, 117, 118
	Up to $3CF_3COOH$ or $CF_2ClCOOH$	50	50	0	121, 122
	$C_6H_2(NO_2)_3OH$	93	4	3	87, 88, 117, 118
$(C_4H_7)_3Cr$	1HCl	14	19	67	46
	2HCl	90	5	5	46, 113, 114
	CCl_3COOH	93	4	3	46, 47, 113
$(C_3H_5)_3Co$, $(C_4H_7)_3Co$	1HCl	36	14	50	46
	2HCl	88	2	10	46, 113
	CCl_3COOH	78	8	14	47
$(C_4H_7)_3Co$	I_2	45	12	43	46, 111, 112
$(C_3H_5)_3Co$	I_2	90	2	8	110
$[(C_3H_5)_2Mo]_2$	HCl or HI	0–4	6–7	90–93	47
$(C_4H_7)_3Rh$	HCl	10	88	2	46
$(C_4H_7)_3Nb$	HCl	91	5	4	46, 113
D. (π-Allyl)$_x$M$_T$ + quinones					
(π-Allyl, methallyl, crotyl)$_2$Ni	p-Chloranil or p-bromanil	88–94	3–9	3	119, 120
$[(C_3H_5)_2Mo]_2$	p-Chloranil or benzoquinone	0	1–5	95–99	47, 116
E. (π-Allyl M$_T$X)$_n$					
C_3H_5– or C_4H_7NiCl		92	6	2	46, 47, 125–127
C_3H_5– or C_4H_7NiBr		45–72	25–53	2–3	46, 47, 125–127

Table 3 (Continued)

π-Allyl Complex	Cocatalysts	Polybutadiene Structure (%)			Ref.
		cis-1,4	trans-1,4	1,2	
π-C_4H_7NiI		4	93	3	46, 47, 125–127
$C_3H_5NiOOCCH_{3-n}Cl_n$		92–97	2–6	1	113, 123, 124
π-Allyl, methallyl, or crotyl $NiOOCCF_3$		91–98	1–8	1	52, 113, 123, 124, 170
$C_3H_5NiOC_6H_2(NO_2)_3$		97	3	0	52
$C_3H_5NiOC_6H_2Br_3$		0	96	4	47, 113
$C_3H_5NiO_3SC_6H_4CH_3$		48	48	4	47, 52, 113
$C_{12}H_{19}NiOOCCF_3$		98	2	0	94, 128
F. (π-Allyl $M_TX)_n$ + MeX_m					
C_3H_5 or C_4H_7NiX X = Cl, Br, I	Ti, V, Mo, W, Sn, Mg, Co, Ni, Zn, B, Al halides	80–95	4–20	1–6	46, 47, 91, 113, 115, 116, 126, 127
	Mg, K sulfates, KCNS, K_2CO_3, $AgNO_3$ $Mg(ClO_4)_2$ Ni, Co, Mn, Mg, Zn trichloro- or trifluoroacetates				
C_4H_7NiCl	$SnCl_2$	43	56	1	91
C_4H_7NiCNS	$TiCl_4$	79	19	2	129
$C_4H_7NiOOCCH_3$	$TiCl_4$	91	6	3	129
C_4H_7NiI	SnI_4	85	13	2	46
G. (π-Allyl $M_TX)_n$ + Halogen or Organic Electron Acceptors					
C_4H_7NiCl	I_2	94	4	2	47
C_4H_7NiI	I_2	84	15	1	46
C_4H_7NiX X = Cl or I	$CHCl_2COOH$, CCl_3COOH, $C_6H_2(NO_2)_3OH$, CF_3COOH CCl_3COH, $(CCl_3)_2CO$ CCl_3COCl $C_2H_5OOCCCl_3$	87–95	1–7	2–12	46, 47, 113 115, 116
C_4H_7NiCl	C_6H_5COOH	82	13	5	127
$C_4H_7NiOOCCl_3$	CF_3COOH	94	3	3	115
$C_4H_7NiOOCCF_3$	CCl_3COOH	90	7	3	115
C_3H_5 or $C_4H_7NiOOCCF_3$	CF_3COOH	50	49	1	115, 130
C_4H_7NiCl	p-Benzoquinone, dichloro- or bromoquinones p-chloranil, p-iodanil, p-fluoranil	95–98	1–3	1–2	47, 113, 116 119, 120
C_4H_7NiBr	p-Chloranil	92	6	2	47, 116, 119, 120
C_4H_7NiI or –CNS	p-Chloranil	49–51	46–48	3	116, 119, 120
$C_4H_7NiOOCCH_3$ or $OOCCF_3$	p-Chloranil	83–94	3–14	3	115, 116, 129
C_4H_7CoI	p-Chloranil	96	3	1	116
π-Methallyl CoCl	p-Chloranil	70	7	23	119
H. (π-Allyl $M_TX)_n$ + Electron Donors					
C_4H_7NiCl	O_2, benzoyl or t-butyl peroxides, acetylacetone, thiophene, $(C_2H_5)_2O$	71–90	7–24	3–5	47, 127, 131
	Na_2O_2	52	44	4	127
	AIBN	45	43	12	127
	Tetrahydrofuran	54	41	5	47
	C_2H_5OH	30	70	0	130
	H_2O+KI	14	82	4	130
C_3H_5NiBr	O_2, benzoyl peroxide	84–88	7–11	5	131
C_4H_7NiBr	$(C_2H_5)_2O$	60	36	4	131
	C_2H_5OH	32	66	2	131
	H_2O or H_2O+KI	4–6	92–94	2	131
C_4H_7NiI	Benzoyl peroxide	0	96	4	132
	p-Nitrobenzoyl peroxide	84	11	5	132
	O_2	57	38	5	132
	$(C_2H_5)_2O$, C_2H_5OH, H_2O H_2O+KI, HCOOH, CH_3COOH	4–18	80–94	2–3	131
$C_3H_5NiOOCCF_3$	Aromatic derivatives	49	49	2	130
$C_{12}H_{19}NiOOCCF_3$	C_2H_5OH, $(C_6H_5O)_3P$	0	96	4	133

Table 4 Catalysts from π-Allyl Transition Metal Complexes for the Polymerization of Monomers Other Than 1,3-Butadiene

Monomers	π-Allyl Complex	Cocatalysts	Polymer Structure	Ref.
Isoprene	$(C_4H_7)_3Cr$		35% 1,4; 28% 1,2; 37% 3,4	46
	C_4H_7NiCl	$TiCl_4$	50% cis-1,4; 38% trans-1,4; 12% 3,4	46
		$ZnCl_2$, $Ni(OOCCCl_3)_2$ Cl_3CCOOH	23–30% cis-1,4; 52–59% trans-1,4; 10–20% 3,4; 0–2% 1,2	46
		p-Chloranil	46% cis-1,4; 39% trans-1,4; 15% 3,4	46
	$C_{12}H_{19}NiOOCCF_3$		68–79% cis-1,4; 15–26% trans-1,4; 6% 3,4	135
	$C_3H_5NiOOCCF_3$	*o*-$Cl_2C_6H_4$	51–55% cis-1,4; 45–49% trans-1,4	135
Ethylene	$(C_3H_5)_3Cr$,			110, 114
	$(C_3H_5)_2CrI$		Linear, high density	136, 137
	$[(C_3H_5)_2Cr]_2$	$TiCl_4$	Linear, high density	
	$(C_3H_5)_4Zr$		Linear, high density	136
	$(C_4H_7)_4Ti$, $(C_3H_5)_2Ti(OC_2H_5)_2$		Linear, high density	136, 137
	$(C_3H_5)_4Ti$, $(C_3H_5)_4Nb$	$TiCl_4$	Linear, high density	139
Propylene	$(C_3H_5)_3Cr$, $(C_3H_5)_2CrCl$	$TiCl_3$, $TiCl_4$	Partially crystalline	114
	$(C_3H_5)_4Mo$, $(C_3H_5)_4Zr$	$TiCl_3$, $TiCl_4$	Partially crystalline	114
	$[(C_3H_5)_2Cr]_2$	$TiCl_3$	85% crystalline	139
Chloroprene	(Allyl or methallyl)$_3$Cr			138
Acetylene	C_3H_5NiCl	Phosphine, isonitrile		140
Allene 1,2-Butadiene	C_3H_5NiBr		1,2 polymer	82, 83, 84
Styrene	C_3H_5NiCl		Low molecular weight	127, 141, 142
	$C_3H_5NiOOCCF_3$		atactic polymers	52
	$C_{12}H_{19}NiOOCCF_3$			135
	$(C_3H_5)_3Cr$	$TiCl_4$		114
Methyl methacrylate	$(C_3H_5)_3Cr$, $(C_4H_7)_3Cr$		About 20% isotactic, 35% heterotactic, and 45% syndiotactic	138, 143
	$(C_3H_5)_2CrAcAc$			138
	$(C_3H_5)_3Rh$, $(C_4H_7)_4Ti$			138, 143
	$(C_3H_5)_4Mo$			138
Methacrylonitrile	$(C_3H_5)_3Cr$, $(C_4H_7)_3Cr$			138, 143
	$(C_3H_5)_4Zr$			138, 143
Butyl vinyl ether	C_4H_7NiCl	Benzoyl peroxide	Atactic	127
Cyclobutene	$(C_4H_7)_2Ni$, C_4H_7NiX	$AlBr_3$, $TiCl_4$	Polycyclobutene	144
	$[(C_4H_7)_2Mo]_2$, $(C_4H_7)_4W$	$AlBr_3$, $TiCl_4$, $MoCl_5$, WCl_6	80–90% *cis*-1,4-, 10–20% *trans*-1,4-polybutadiene	144
Cyclopentene	$(C_4H_7)_2Ni$, C_4H_7NiX	$AlBr_3$, $TiCl_4$ $MoCl_5$	Polycyclopentene	144
	$[(C_4H_7)_2Mo]_2$	$AlBr_3$, WCl_6	35–40% *cis*-1,4-, 60–65% *trans*-1,4-polypentenamer	144

of Table 3, only a few π-allylic complexes of transition metals are able to promote polymerization; most of them first induce oligomerization reactions and become active polymerization catalysts only when halides or other anions are bound in the coordination sphere, most often through addition of various cocatalysts to the reaction medium (as in parts B, C, and D of Table 3).

This influence of the counterion in the catalytic π-allyl complexes is a determinant not only of the overall activity but also of the stereospecificity (see part E, Table 3). The addition of various metallic or organic electron acceptors to π-allyl M_TX complexes, resulting in some cases in the formation of charge transfer complexes, results in enhanced catalytic activity and, for most polybutadienes, a further increase in the cis-1,4 content (parts F and G, Table 3). The addition of electron donating ligands usually results in decreased catalytic activities with a simultaneous modification of the stereospecificity (part H, Table 3). The significance of these effects is considered in more detail in Section 4, when discussing the factors influencing the stereoregulation process in diolefin polymerization.

As shown in Table 4, π-allylic complexes of transition metals are able to initiate the polymerization not only of other conjugated diolefins such as isoprene and chloroprene, but also of monoolefinic, acetylenic, and polar vinyl monomers. Partially crystalline polypropylene was also obtained by means of these complexes, with titanium tetrachloride or trichloride as cocatalysts. It is possible that, in the latter case, polymerization actually takes place on titanium catalytic species formed by reaction of the cocatalysts with the π-allylic complexes. Polymerization of cyclobutene and cyclopentene in the presence of π-crotyl complexes of molybdenum, tungsten, or nickel (eventually combined with Lewis acids) has also been reported (198). For example, catalytic systems based on bis(π-crotyl)nickel and π-crotylnickel halides polymerize cyclobutene and cyclopentene exclusively through the double bond, whereas ring opening is observed in the presence of catalysts containing π-crotyl complexes of molybdenum or tungsten.

3 THE EVOLUTION OF IDEAS ON THE MECHANISM OF OLEFIN COORDINATION POLYMERIZATION

The evolution of ideas on reaction mechanism has undoubtedly been dominated by the mechanism proposed by Cossee a few years ago. By then a general consensus had been reached on several essential points, and these key points were included in the Cossee hypotheses. These were determinant role of the transition metal; formation of an alkyl derivative of this metal foreshadowing the polymeric chain on the catalyst; accessibility of at least one free coordination position on the complex to allow a proper positioning of the monomer; and existence in this complex of steric factors responsible for the stereospecificity of the propagation reaction. Cossee's proposal left several questions unanswered. In particular, it did not detail the role of the alkyl metal derivative of groups I–III (especially aluminum) in controlling the stereospecificity and activity of the catalyst, nor the exact importance of the heterogeneous or homogeneous state of this catalyst. With our current knowledge, these questions are no longer as crucially important as they once were, but these aspects will be discussed later.

3.1 The Cossee-Arlman Mechanism: Cis Rearrangement

In the Ziegler-Natta bimetallic catalysts, a dominant role is played by the transition metal derivative in controlling the stereospecific polymerization reaction. The influence of the aluminum compound is much less essential than had been frequently proposed for historical reasons [Aufbau reaction (1) of ethylene to low molecular weight polymers by aluminum alkyls]. The assumptions as to the greater importance of the transition metal have now been experimentally proved by performing the polymerization of α-olefins in the presence of monometallic catalysts (containing only one type of metal, although sometimes binuclear) displaying good activities and stereospecificity.

Emphasizing the prominent role of the transition metal, and more specifically of its *d* orbitals, in 1964 Cossee and Arlman presented in a very lucid series of papers a mechanism for the stereospecific polymerization of unsaturated hydrocarbons on a previously alkylated monometallic complex, for instance, of titanium (145–148) as shown in Fig. 9. Their reaction scheme specifically involves the following important considerations.

3.1.1 *Formation of the Active Center (Steps 1 and 2 of Fig. 9)*

The essential role of the alkylaluminum compound is to alkylate the titanium by substituting one of the chloride ions of a pentacoordinated metal atom exposed at the surface and displaying a chloride vacancy. Of these five chloride ions, three are completely embedded in the interior of the crystal; of the two remaining, the first is still attached to two metal ions, and only the other is considered to be loose enough to undergo the alkyl exchange easily. The alkyl group introduced by this reaction foreshadows the growing polymer chain. From crystallographic models

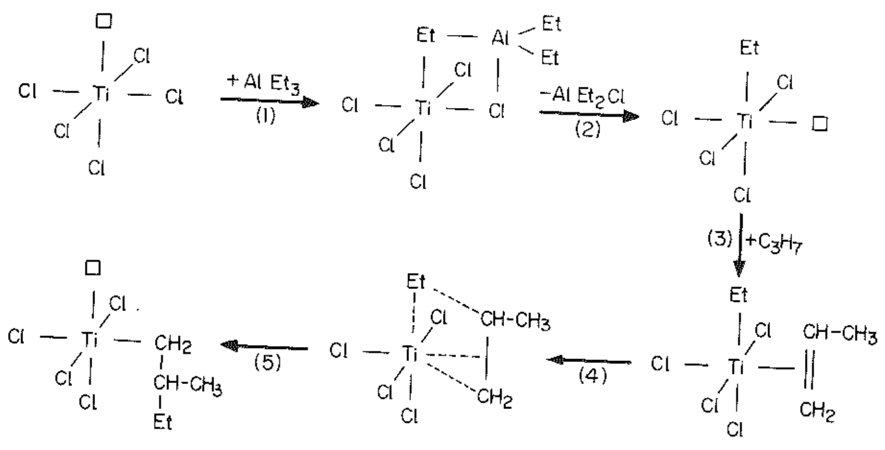


Figure 9

and calculations of the energies needed to remove a chlorine atom from the surface of α-$TiCl_3$ crystals, Arlman showed that the vacancies should be found on the edges of the elementary planes in the crystal. The number of such vacancies, potentially giving active sites, was shown to correspond reasonably to the number of the centers experimentally determined by kinetic estimates and by use of radiotracers. These deductions have been substantiated (see Section 3.2) by electron micrographs taken by Rodriguez et al. (12, 149), which indeed show dramatically that the growing chains are not in a 001 face, but are located along a spiral, most probably the edge of a crystal growth spiral.

The alkylation reaction (steps 1 and 2) itself has been put in evidence first on a model system devoid of side reactions, $ScCl_3$–$Zn(Et)_2$, where both zinc and ethyl groups could be labeled (150); a further detailed study of the $TiCl_3$–$Al(CH_3)_3$ system was also performed by Rodriguez et al. (151).

3.1.2 *Reaction of Monomer at the Active Center (Steps 3–5)*

This reaction implies the preliminary bonding of the olefinic monomer to the free coordination position of the alkylated octahedral titanium complex, $TiCl_4R\square$. Step 3 occurs through π bonding (152), a type of bonding that is now well documented; the knowledge gained from studies of different olefin-transition metal complexes is readily applied to polymerization catalysts. The heats of formation of the complexes are usually small and almost the same as their heats of solution (see, e.g., ref. 157); also, small complex formation constants have been indicated by several thermodynamic and kinetic studies. Molecular models reveal that there is no special steric hindrance to a very close approach of the monomer to this sixth coordination position on the $TiCl_3$ crystal.

The greatest merit of this scheme is most certainly the avoidance of any important nuclear displacement during the reaction of the coordinated monomer with the alkyl group; only the first CH_2 group of the growing chain attached to the transition metal has to undergo a limited translation of about 1.9 Å. This displacement starts with the angular vibration of the Ti–CH_2 bond. In transition metal complexes, owing to an additional overlap of the CH_2 group with the metal d_{yz} orbital, the amplitude of this vibration in the nonequilibrium position may be larger than in a nontransition metal complex. This situation also allows a much greater overlap of the two potential wells corresponding to the equilibrium positions of the R groups and the coordinated olefin's orbitals. The energy of activation for the rearrangement (step 5) is consequently lowered, and the migrating group finds simultaneously a combination of overlapping orbitals all along its reaction path (Fig. 10).

In this reaction sequence, it is claimed that the overall measured activation energy is essentially representative of the energy involved in the rearrangement, since the heats (ΔH) of complex formation are usually small.

The cis migration mechanism presented here explains very well many essential features of the olefin's specific polymerization by transition metal complexes. An elegant illustration of its versatility came from observations made in the course of vinylcyclopropane polymerization (158); indeed, the simultaneous occurrence of 1,2 and 1,5 additions implies a mechanism involving both normal and abnormal alkylation of the coordinated monomer during cis migration (Fig. 11). In fact, it is of much broader scope than for polymerization only, and has been applied to a number of reactions catalyzed by transition metal complexes, for example in the dimerization of ethylene in the presence of rhodium salts, which has been shown to involve a $[C_2H_5\text{–}RhCl_3(C_2H_4)(\text{solvent})]^-$ complex. Some catalytic hydrogenations are claimed to proceed by a similar migration of the metal bonded hydrogen to the coordinated olefinic substrate. Several carbonylation reactions (e.g., hydroformylation) have also been explained by this type of rearrangement.

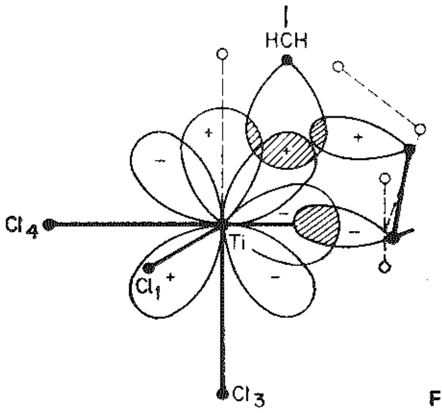


Figure 10

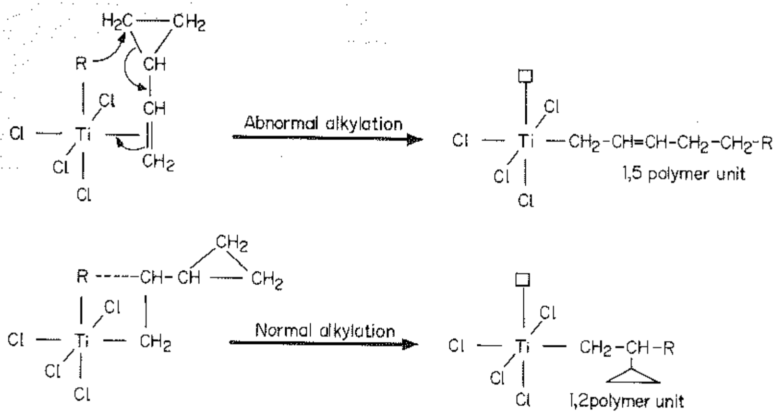


Figure 11

The general nature of this reaction, corroborated by new examples discovered every year, was also demonstrated by the specific activation and reaction of other interesting substrates including, e.g., molecular oxygen or nitrogen.

3.1.3 *Quantitative Aspects of the Rearrangements*

In an attempt to get a more precise picture of the reaction (148), it has been proposed that in the nonequilibrium position the important factor is the mixing of ϕ with ψ_2 orbitals; orbital d_{yz} (originally in the common $3d$ level) is the one that connects π^* and σ_R (or performs the mixing). This will occur to an appreciable extent only when the energy spacings (π^*, σ_R and d_{yz}) are not too large; i.e., the best catalytic activity will be attained when the metal $3d$ level is somewhere between π^* and σ_R (Fig. 12). It is also clear that these levels, and consequently the relative activity, will be influenced not only by the nature of the metal but also by that of the more or less electron attracting surrounding ligands.

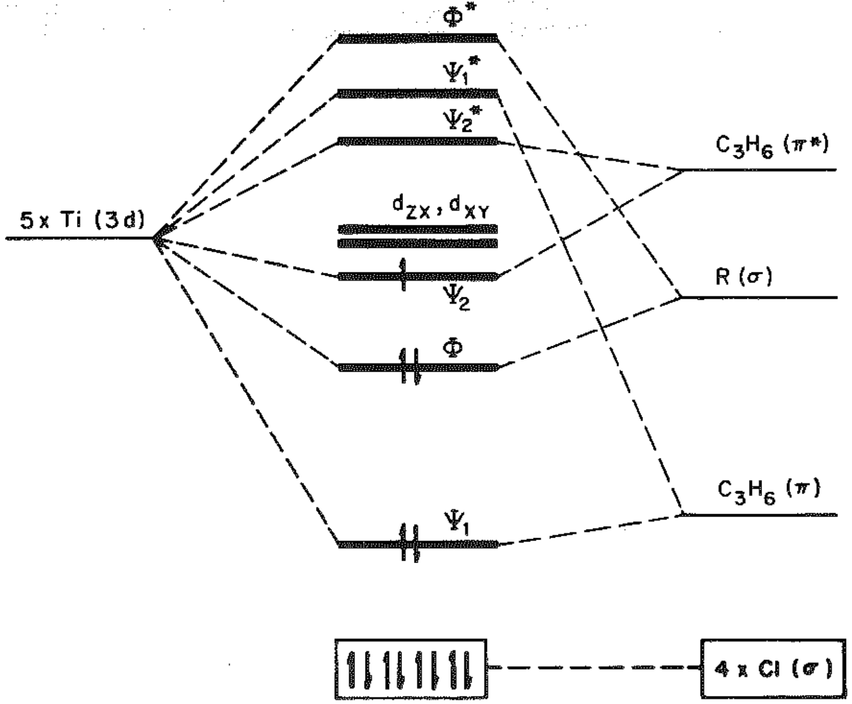


Figure 12

Quantum mechanical calculations allowed a more quantitative evaluation of this cis rearrangement (in a complex carrying a methyl group to simplify the problems) through an "iterative extended Hückel" approach (153). Results were obtained for several situations along the reaction coordinate; the energy diagrams of a number of relevant orbitals, their composition, and the evolution of charges and bond orders give a fairly detailed picture of this catalytic reaction. The calculations confirm the qualitative picture that the d level is between π and π^* of C_2H_4, and the C–Ti bond is located 16,000 cm^{-1} below that of the nonbonding d_{xy} and d_{yz} of the metal; they also show, in the initial titanium alkyl, the small electronegativity difference in the Ti–C bond, and the reason for the low kinetic stability of this bond (short distance between the M_T–C bond orbital and the empty d orbitals). Moreover, the total splitting of the d levels is of a very reasonable order of magnitude (28,700 cm^{-1}), and the chloride ions also show some π bonding to the metal.

In the complex with ethylene, d_{xy} is depressed by the olefin antibonding orbital and the distance $\sigma\text{-}CH_3 \leftrightarrow d_{xy}$ is thereby reduced from 14,900 to 11,100 cm^{-1}. If this is indeed a measure of the M_T–C bond lability, we have a quantitative indication of the path of action of the transition metal ion in catalysis. Simultaneously the π-π^* distance in ethylene increases from 48,500 to 53,200 cm^{-1}. An interesting conclusion is the unsymmetrical bonding of the two carbon atoms of the olefin, the one closer to the methyl group being somewhat more weakly bonded.

During the reaction (moving the CH_3 group), which is accompanied by delocalization, the charge on the Ti atom (as well as on the four Cl ions) remains practically constant despite the temporary storage of some negative charge. The important conclusion is that the alkyl group *does not move as an anion*, as was often suggested in the early studies on the Ziegler-Natta catalysts.

A comparison has been made among Ti, V, and Cr indicating that the lability of the methyl group increases in this series (from Ti to Cr), while there is a corresponding decrease in the M_T–ethylene interaction. This lability could be a favorable factor in the propagation, which fits Pasquon and Zambelli's determination of the absolute activity of active sites in Ti and V catalysts; however, it also becomes a limiting factor for the formation of a sufficient number of M_T–R bonds, which may explain the very poor performance of Cr in Ziegler-Natta catalysts as well as the improved performances in better ligand environment as in oxide type catalysts.

3.1.4 *Stereospecificity*

The isotacticity of many polyolefins obtained with the Ziegler-Natta $TiCl_3$–AlR_3 catalyst has also been explained by Cossee and Arlman on the basis of a monometallic complex.

Considering the octahedral [$(RTiCl_4\ \square)$] in the surface of the crystalline lattice, they came to two important conclusions: (*a*) This octahedron is placed unsymmetrically, and does not contain a plane of symmetry; and (*b*) the positions of the alkyl group and the coordination vacancy in the lattice are not equivalent, either sterically or ionically.

This situation might completely predetermine the configuration of the new asymmetric carbon being formed (i.e., only one orientation of the coordinated olefin is allowed), explaining the tacticity of the chain (ref. 148, pp. 154 and 162).

There are still two possible paths for the reaction:

1. After the rearrangement, the alkyl group stays on its new position, the monomer is coordinated on the newly formed vacancy, and the same process is repeated, giving an alternating type propagation and a syndiotactic polymer. This eventuality will be favored by a substantial

lowering of the temperature (decreasing the rate of both alkyl back-shift and alkyl migration, but increasing complex formation on the new vacancy).

2. In most cases, however, the extended alkyl group moves back to its original position before a second monomer is incorporated. This ensures that the insertion of every monomer unit in the chain is repeated in a stereospecifically identical manner and an isotactic polyolefin is produced. This scheme fits in with the nonequivalence of the two positions involved, and also with the kinetic analysis of the reaction. This back-shift will proceed by the same mechanism as the migration in the insertion step, with the help of metal t_{2g} orbitals. Consequently, the preference for an isotactic or syndiotactic placement will be governed essentially by the ratio of the rates of the alkyl back-shift and the insertion in the growing chain.

When using a monomer with two potentially asymmetric carbon atoms, e.g., a 1-deuterated α-olefin, a ditactic polymer is obtained whose formation can be exactly explained by the spatial control of the monomer coordination.

Finally, the formation of stereoblocks, i.e., isotactic homopolymers containing sequences of, say, *d* configurations followed by other sequences of the mirror image *l* configuration, can also be easily visualized. The growing chain may exchange with a metal alkyl molecule in the solution and exchange again with another active titanium site from which position growth resumes but possibly with the opposite configuration. It would be interesting to see if these stereoblock structures are absent when using a monometallic catalyst that was prepared using no metal alkyl.

3.2 The Modified Model for Titanium Trichloride

Despite its outstanding merits, the Cossee-Arlman scheme still leaves a series of questions unanswered. For instance, (*a*) why does the aluminum alkyl, in some cases, influence the activity and even the stereospecificity of the catalyst (e.g., AlR_2I); (*b*) why do the organozinc derivatives, which are good alkylating agents, yield less active and stereospecific catalysts; (*c*) why do electron donor ligands (e.g., amines) significantly improve the stereospecificity of a given catalyst; (*d*) why do only a small proportion of the alkylated transition metal sites give rise to polymer chains, as shown by a comparison of the degree of alkylation with the dispersion of growing chains along crystal growth spirals or faults, as indicated by electron microscopic observations; and (*e*) why does β-$TiCl_3$ still promote

the formation of a significant proportion of isotactic polypropylene, despite its great number of symmetrical active sites with two vacancies?

These points were considered in a modified scheme presented by Rodriguez and Van Looy (149). Keeping the basic features of Cossee's proposal (in particular the cis rearrangement reaction), these authors suggest that the active site is a tetracoordinated alkylated titanium atom carrying two coordination vacancies. One vacancy is occupied by the halogenated aluminum alkyl (or eventually another ligand) and forms a bridged bimetallic complex with the titanium atom; the other is filled by the monomer. The resulting catalytic sequence is schematized in Fig. 13.

After the rearrangement (breaking the initial bimetallic bridge), the formation of a new bridge under the influence of the aluminum atom is the driving force that will restore the active site to its initial configuration. This will give rise to an isotactic polymerization. Such a mechanism may furnish a satisfactory answer to the questions raised above (at least for β-$TiCl_3$). It explains in particular the influence of external ligands (amines) acting in place of the aluminum alkyl; the inhibitory effect of strongly coordinating entities such as $ZnCl_2$; the stereospecificity of $TiCl_2$–$Al(CH_3)_3$; and the influence of aluminum alkyls. For the α form of $TiCl_3$, one has to admit that although the pentacoordinated form is predominant, there are still a few tetracoordinated sites arising from lack of stoichiometry in the crystal and from a double chlorine vacancy permitted by the relatively small differences of retention energies within the edges of this crystal. The latter observation would explain the small number of active sites indicated by electron micrographs.

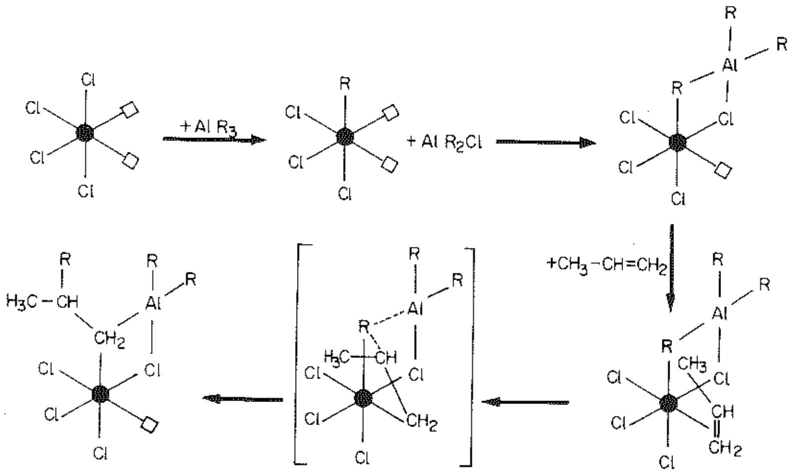


Figure 13

The proposal does not imply that Cossee's pentacoordinated center must be inactive, since the aluminum alkyl coordination is reversible, but its stereospecificity is not guaranteed. It reconciles the antagonistic views of the supporters of the mono- or bimetallic mechanisms (see the following section), since the aluminum alkyl is playing the role of a ligand to the determinant transition metal complex. It must be admitted that the essential role of the titanium-carbon-aluminum bridge is questionable in view of the relative instability of such structures (154) compared to the corresponding chloride bridges. It represents a very good working hypothesis to use to compare the results described below for the homogeneous polymerization of ethylene and propylene.

3.3 Soluble Bimetallic Catalysts

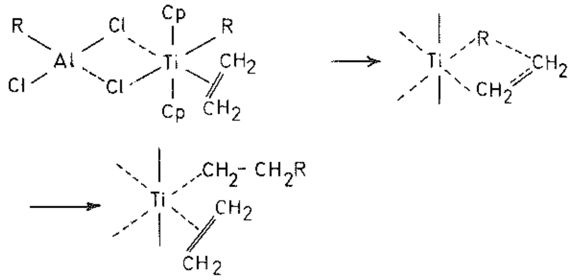
The polymerization of olefins by two families of *soluble* Ziegler-Natta catalysts has been investigated in detail. These give a better insight into the polymerization mechanism and support the main ideas arising from studies of heterogeneous catalysts. These investigations include the polymerization of ethylene by biscyclopentadienyl titanium dichloride catalysts, and the syndiotactic polymerization of propylene by vanadium catalysts in the presence of an electron donor molecule.

3.3.1 *Cp_2TiCl_2—$EtAlCl_2$ for Ethylene Polymerization*

This interesting system, very suitable for a systematic investigation because of its solubility and its rather well-defined chemistry, has been extensively studied by Henrici-Olivé and Olivé (14). Combining EPR and kinetic measurements, they came to the conclusion that the active species was again an alkylated octahedral titanium complex on which polymerization took place through a scheme very similar to the one proposed by Cossee:

$$Cp_2TiCl_2 \xrightarrow{AlR_nCl_{3-n}} Cp_2TiClR$$

$$Cp_2TiClR + AlRCl_2 + C_2H_4 \longrightarrow$$



The studies also emphasized a number of interesting features:

1. *Oxidation state and geometry.* The active center contained Ti(IV) exclusively in an octahedral arrangement, which is especially interesting in view of the time-honored discussions on the importance of the oxidation state of the transition metal, and particularly since most heterogeneous catalysts involve Ti(III).

Hence it becomes clear that the key factor is the *geometry* of the complex. For *soluble* species, only the Ti(IV) oxidation state ensures the octahedral geometry with a vacancy for the monomer coordination in the suitable cis position relative to the R group (growing chain), while the corresponding Ti(III) gives an inactive tetrahedral complex. In heterogeneous catalysts, the crystalline $TiCl_3$ lattice itself ensures this same octahedral structure.

2. *Stability of the* Ti–R *bond and reactivity of the complex.* Taking as a criterion either the rate of reduction from Ti(IV) to Ti(III) or the rate of ethylene polymerization, it was also proved experimentally that the Ti–R bond was destabilized both by the alkyl groups of the aluminum ligand (acting presumably through its bridge in the position trans with respect to the R group) and by the coordinated monomer. This particular point, detailed by simplified molecular orbital calculations, was also confirmed by experiments involving nonpolymerizable olefins and strongly supports the predictions of Cossee.

The stability of this Ti–R bond, which is directly related to the catalytic activity of the complex, can accordingly be "tailored" to a certain extent by modifying the donor-acceptor properties of the surrounding ligands, e.g., the aluminum compound. In similar fashion the π-allylnickel complexes exhibit tremendous changes in the butadiene polymerization rate when the electronegativity of the counteranion is modified (123). This explains how the alkyl metal part of the catalyst can influence the polymerization course, and *closely fits the ideas of Rodriguez and Van Looy summarized above.*

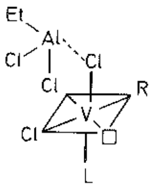
In summary, catalysis results from three cooperative influences: destabilization of the Ti–R bond by coordination of the monomer and by the bridged aluminum alkyl, enhancement of the olefin double bond reactivity by π coordination to titanium, and a suitable spatial arrangement in the complex for the "cis migration" of the alkyl group (or growing chain) by only a small "in plane" vibrational displacement as stressed by Cossee. All these features are related to an octahedral geometry of the complex.

Chain termination is also satisfactorily accounted for as owing to the bimolecular mutual deactivation of two catalyst molecules with loss of the R group (growing chain).

3.3.2 VCl_4–$Al(C_2H_5)_2Cl$ for Syndiotactic Propylene Polymerization

Boor and Youngman (155) as well as Zambelli and Natta (156) and their co-workers have studied these systems, and although suggesting slightly different active centers, both groups came to the conclusion that again, polymerization took place on an octahedral complex, on two vicinal positions occupied, respectively, by the chain and the monomer.

Zambelli used a Lewis base L (particularly anisole) as an additional ligand replacing one of the organometallic molecules, and obtained a complex to which the following structure was ascribed:



This species is more stable than in the absence of anisole since polypropylene yield and molecular weight both increase, indicating a considerable decrease in the termination process.

The stereospecificity of the syndiotactic polymerization of this monomer is favored both by low reaction temperatures (−78°C) and the presence of the Lewis base. In the proposed catalyst structure, the vanadium atom is asymmetrical, and the syndiotactic type of stereospecificity is explained by an inversion of configuration every time a previously coordinated monomer molecule enters the vanadium-alkyl bond. From a steric point of view this asymmetry does not seem important enough to justify a preferential presentation of the monomer. The explanation can probably be found in Boor's proposal that the free rotation of the last added unit is sterically hindered. The addition of a new monomer molecule would then be faster if it approaches the growing chain end from a direction imposed by the presence of the counterions in the most favorable position, i.e., presenting the side of the molecule having a configuration opposite to that of the last unit to minimize the interaction of the methyl groups. A rise of the reaction temperature will obviously lower this rotation barrier and consequently reduce the stereospecificity of the process.

It was also shown that the exchange of ligands (when favored by the reaction conditions), or their dissociation leading to two coordination vacancies (in particular when using a metal alkyl having a lower tendency to coordinate than the aluminum compound), introduces steric irregularities in the growing chain, e.g., isotactic diads or even sterically disordered sequences.

3.4 Homogeneous and Heterogeneous Coordination Catalysis

The importance of the insolubility or solubility of the catalyst in the polymerization medium has been a disputed point for years.

The fact that until recently, it has been impossible to prepare *isotactic* unhindered polyolefins with a soluble catalytic system has been considered an indication that π bonding of the monomer in itself is not sufficient to ensure this type of stereoregulation even on a sterically crowded complex. Moreover, this is in agreement with what we know about the chemistry and mechanism of such reactions. It corroborates the hypotheses of Cossee and Rodriguez that an additional factor, such as the severe steric requirements of the crystalline matrix or the control exerted by the bridged aluminum alkyl, is essential to ensure at every step the insertion of the olefin in an identical stereoconfiguration.

One apparent exception to this is the report by Mazzanti (44) of a soluble catalyst able to perform the polymerization of 4-methylpentene into an isotactic high polymer. It is not yet certain, however, that the catalytic species is a truly isolated complex in solution, or an aggregate that reproduces locally, under apparently homogeneous conditions, on a microscopic scale, the same steric requirements as the matrix of the insoluble systems. In another apparent exception Ballard (211) has recently reported that soluble $Zr(allyl)_4$ and $Zr(allyl)_3Cl$ can produce soluble isotactic polypropylene. It is reasonable to assume that this is a homogeneous process. Thus, a single transition metal atom appears to be able to form isotactic polymers and does not require the environment of a solid surface. Even in this case, the environmental changes of the metal atom afforded by adding insoluble cocatalysts lead to increased rates of polymerization.

The beneficial effects of a second factor for steric control in the orientation of the monomer, besides coordination of the double bond to produce isotactic polymers, have also been demonstrated in anionic coordination polymerization. It is worthwhile to remember that lithium alkyls polymerize styrene to atactic macromolecules unless the lithium compound is incorporated in a crystalline lattice such as LiBr, yielding then a highly isotactic polystyrene (159). When the monomer itself contains a second suitably located group, its orientation may be predetermined enough to yield isotactic products even in completely homogeneous solution; this is the case for the polymerization of *o*-methoxystyrene by butyllithium (160), and of methyl methacrylate by 9-fluorenyllithium in toluene (161).

In summary, one can consider the influence of the homogeneous or heterogeneous state of the catalyst as purely incidental; it does not at all affect the basic coordination polymerization mechanism, as confirmed by the fact that individual transition metal atoms can generate isotactic placements. However, if not essential, it is important in controlling the steric environment of the active center (and sometimes the electronic environment too, when the matrix acts as a delocalized ligand); in this respect, the presence of a crystalline lattice or any kind of rigid hindered environment contributes to ensure the isotacticity of a chain composed of monomeric units that do not have more than one binding point to the catalyst.

Interesting new developments (162, 164) indicate that the solid catalytic phase can govern the morphology of the polymer formed; in such cases, we have a direct and specific action of the solid surface. Some systematic control of this effect could represent a new and valuable procedure for modifying polymer properties.

3.5 Conclusion

The cis rearrangement reaction in an alkylated octahedral transition metal complex offering a coordination vacancy to the monomer, affords a clear and useful picture of the actual active center in both heterogeneous and homogeneous stereospecific polymerization of α-olefins. Taking into account recent additional considerations, one obtains a better idea of the relative importance of factors such as the oxidation state of the metal atom, the solubility of the catalyst, and principally the role of the alkylaluminum derivative. This last problem has been the subject of many controversies, but can be rationalized by considering that, besides its alkylating role, the *aluminum alkyl can also act as a ligand* in the coordination sphere. In this manner it exerts a control over the electronic distribution responsible for the reaction rate, and sometimes to a lesser extent steric influence over the course of the polymerization.

These descriptions have been of great help in tailoring the catalyst structure for an ever more precise and elaborate control of both activity and structure, at the molecular and hopefully supermolecular level. Elastomer synthesis represents a special aspect of monoolefin coordination polymerization, since one usually tries to avoid too much crystallinity and starts with different monomers, usually dienes. With dienes stereoregularity involves not only isotactic and syndiotactic placements but also cis, trans, vinyl, and related isomerism. In the preparation of elastomeric polyenamers from cycloolefins some new data recently gathered about the control of olefin metathesis suggest, once again, a process involving a cis rearrangement through the intermediate formation of carbene species (165). Although recently these species were successfully isolated (221), the results can also be explained by hypothesizing transient metallocyclopentanes instead of metallocyclobutanes.

4 ADVANCES IN DIOLEFIN COORDINATION POLYMERIZATION

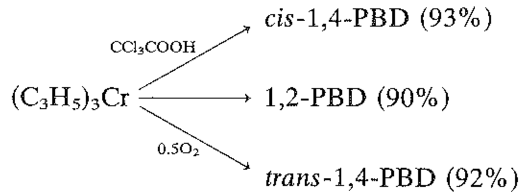
The ability to initiate stereospecific polymerizations by means of well-defined monometallic catalysts that can be modified systematically (particularly the π-allyl complexes; see Table 3) and to characterize the microstructure of the corresponding polymers (by x-ray diffraction, infrared, and NMR spectroscopy) has helped to establish correlations between the composition of the catalytic species and both its overall activity and stereospecificity. The recent advances in stereospecific polymerization of conjugated diolefins appear to be most enlightening as to the propagation control mechanism, the more so as several geometric isomers are possible. Subtleties in behavior are observable which are absent in olefin polymerization.

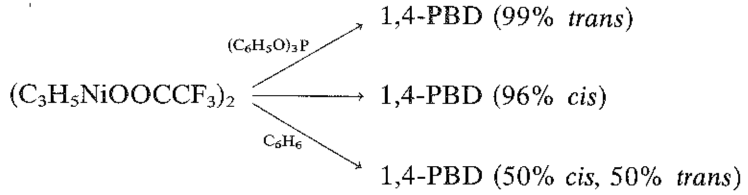
4.1 Factors Influencing Stereospecificity

The structure of polydienes is determined not only by the transition metal itself but also by the nature of the active center as a whole, influenced by the ligands bound into the coordination sphere. These include monomer, the counterion, the solvent, and any electron donating or withdrawing additives used. Three major functions of a complexing agent or ligand have to be considered:

1. The ligand can help to stabilize the transition metal in a lower oxidation state where d-p_π bonding is highly favored.
2. The ligand is very important in directing traffic in the coordination sphere. This can be done by physically blocking one or more coordination sites and/or by changing the electron density in the d orbitals which are available for bonding to an incoming substrate.
3. Some ligands are better leaving groups than others and can facilitate the substitution of olefin or diolefin reactants on the transition metal, consequently influencing the overall kinetics of the process, as will be shown later.

A significant illustration of ligand influence on the structural course of polymerization comes from appropriate modifications of π-allylic catalysts. It is possible to prepare by such modifications not only the different isomeric structures of polybutadiene (46) but also three different isomeric compositions of 1,4-polybutadiene (130):





4.1.1 *The Transition Metal*

As already mentioned, when transition metal compounds having unfilled *d* orbitals form complexes with unsaturated hydrocarbons, there is an overlapping of the filled π orbitals of the olefin with the free *d* orbitals of the metal, and an opposite overlap of the filled *d* orbitals of the metal with the vacant antibonding orbitals of the olefin. Depending on the nature of the orbitals involved, the degree of overlapping of these orbitals, and the atomic radius of the metal, monomer-transition metal complexes will be formed which differ in their structure and consequently exhibit different stereospecificities. On this basis, it should be expected that the structural course of the reaction will be determined primarily by the nature of the transition metal, as widely confirmed in organometallic chemistry. For example, investigations of butadiene trimerization by simple π-allylic complexes indicated the specific formation of either cyclic or linear trimers, implying the same intermediate complex, when bis-π-allylnickel or palladium, respectively, is used as catalyst (95) (Fig. 14).

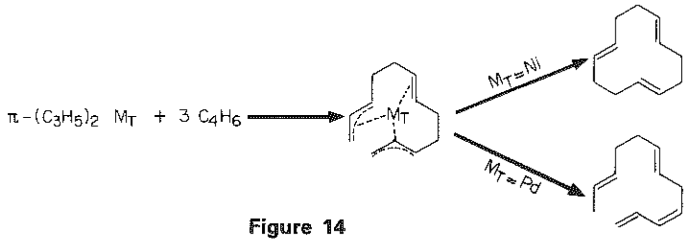


Figure 14

The nature of the transition metal is also a determining factor in stereospecific polymerizations with homogeneous Ziegler-Natta catalysts, as detailed with the aid of molecular orbital theory (see ref. 166). As appears from Table 3, the results obtained with monometallic catalysts of the π-allyl type confirm that metals belonging to the right side of the transition series in the periodic system (e.g., cobalt, nickel, iron, or rhodium) are the most appropriate for the preparation of 1,4-polybutadienes, whereas metals from the center left yield predominantly 1,2-polybutadiene and promote the polymerization of monoolefins (e.g., chromium, molybdenum, niobium). However, the original specificity due to the metal may be completely modified by counteranions; e.g., the addition of hydrogen chloride to chromium or niobium π-allylic complexes results in the formation of *cis*-1,4-polybutadiene instead of a vinylic polymer (46, 113). This indicates that the counterion present in the coordination sphere of the catalyst may be another determinant in controlling the stereospecificity.

4.1.2 *The Counterion*

The microstructure of polybutadienes produced by π-allylic catalysts depends closely on the nature of the anion in the complexes, i.e., chloro complexes give the cis-1,4 isomer whereas iodo complexes favor the formation of the trans-1,4, and bromo complexes produce polymers of mixed intermediate structure. All these products are essentially free from vinyl structure (see Table 3, part E). In fact, since the decrease of the electron density on the transition metal atom becomes more pronounced as the halogen electron affinity increases, we can ascribe the relatively high cis-1,4 contents of polybutadienes obtained with the chloro catalysts to the lower electron density of transition metal orbitals, relative to that in the bromo or iodo systems.

The cis content is still higher when a more electron withdrawing anion, such as a trihaloacetate, is used. Even slight modifications in the counterion used can result in change of microstructure in the polymers obtained, e.g., high *cis*-1,4-polybutadiene is produced in the presence of π-allylnickel picrate whereas the tribromophenate derivative yields a high trans-1,4 polymer (47, 52).

In fact, the observations made with different counterions support the concept that the change of stereospecificity is probably not due exclusively to a steric influence, but mostly to the inductive effect of the counterion present in the coordination sphere of the catalytic complex. Moreover, the role of the counterion appears to be a determinant in controlling not only the stereospecificity but also the overall rate of polymerization, as is shown in Section 4.2.1.

4.1.3 *Ligands*

The ligands bound to the transition metal may strongly influence the steric course of the polymerization, depending on their electron donating or accepting properties; for example, stereoregular 1,4-polybutadienes with high cis-1,4 contents are obtained in the presence of nickel complexes stabilized by carbonyl, cyclopentadiene, cyclooctadiene, or π-allylic ligands with various acids as cocatalysts, whereas when starting from tetrakis triphenyl phosphite nickel, a crystalline *trans*-1,4-polybutadiene is formed (133).

The addition of electron donating ligands to a complex giving the cis-1,4 polymer originally completely modifies its stereospecificity and usually leads to an increase in the amount of trans-1,4 (or even, in a few cases, of 1,2) units as has also been demonstrated with several Ziegler-Natta catalytic systems. This is clearly illustrated by the addition of stoichiometric amounts of ethanol or triphenyl phosphite to π-allylnickel trifluoroacetate, leading to a high *trans*-1,4-polybutadiene instead of a high cis-1,4 polymer (130). Cryoscopic determinations performed on the catalytic species indicate these changes in stereospecificity are due to the occupation of vacant coordination positions on the metal atom by these additional polar ligands. These observations strongly support Arlman's mechanistic assumptions in the case of diolefin stereospecific propagation on α- and β-$TiCl_3$ catalysts (146, 178).

In contrast to the electron donors, the majority of electron accepting molecules used as additives have practically no effect on the microstructure of the polymer chain when starting from catalysts originally yielding a cis-1,4 structure, such as π-allylnickel chloride or the haloacetates. But when starting from π-allylnickel bromide or iodide, electron accepting compounds change the stereospecificity, favoring the cis-1,4 structure formation (see Table 3, part G). In this case, it is obvious that the change in stereospecificity cannot be attributed to a halogen exchange reaction between catalyst components, since systems containing only iodine [e.g., $(C_4H_7NiI)_2 + SnI_4$ or I_2] give predominantly *cis*-1,4-polybutadiene while the corresponding original π-allylnickel iodide brings about the formation of the trans-1,4 polymer. Therefore variations in stereospecificity in the presence of additional electron acceptors appear to be due essentially to the formation of charge transfer complexes in which the electropositive charge on the transition metal atom is increased.

Other ligands have been found with a specific behavior that is different from those discussed above, and not yet observed with the usual bimetallic catalytic systems; indeed, a new kind of stereoregular polymer, namely the "equibinary polydienes" containing equimolecular amounts of two different structural units, were synthesized by modifying, with suitable additional ligands, catalytic species yielding polymers containing only one type of structural unit. Such an elaborate control of the propagation reaction may be very helpful in getting a more intimate view of the stereoregulation processes, since it appears to be a general phenomenon. Various equibinary polydienes have been synthesized by similarly modifying different catalysts; for example, equibinary poly(*cis*-1,4–3,4)- or (1,2-3,4)-isoprenes have been prepared with modified cobalt catalysts (19, 167, 168), and equibinary poly(*cis*-1,4-*trans*-1,4)-butadiene (121, 130, 133) or isoprene (135) in the presence of modified nickel catalysts. An interesting characteristic of the catalysts promoting the formation of equibinary polydienes is their reversible character. The removal of the ligand or the addition of electron accepting or donating compounds promotes the formation of polymers having an all cis-1,4 or crystalline trans-1,4 structure, respectively; consequently, the binary selectivity appears to enjoy some of the versatility usually observed for monoisomeric stereospecificity. A study devoted to the catalytic species involved in the formation of equibinary poly(*cis, trans*)-butadiene, strongly suggests a competitive modification of the initial symmetry of the catalytic complexes when coordinating the additional ligand (130). A tentative scheme for the formation of these equibinary polydienes is proposed (213) on the basis of a binuclear complex in which the insertion of cis and trans units in the two bound growing chains is coupled and complementary.

A most interesting mechanistic indication is the possibility to control to a large extent the distribution of the two isomeric units in the polymeric chains, without disturbing their equimolecular composition; for instance, equibinary 1,4-polybutadienes (containing practically 50% cis and 50% trans) have been obtained in which the isomer placement switches, depending on the nature of the polymerization solvent, from a purely random one (in benzene) to a highly alternate one (in CH_2Cl_2) (214). A tentative interpretation of this behavior might involve kinetic control of the lifetime of the σ form (allowing butadiene insertion) versus the π form of the bound chain.

4.2 Factors Controlling the Kinetics of Coordinated Polymerization

The nature of the ligands bound in the coordination sphere of the transition metal may influence not only the stereospecificity but also the catalytic activity; i.e., changes in the nature of the counterions as well as of the ligands (including monomers) in the catalytic complexes, result in drastic modifications of the overall polymerization rate.

4.2.1 *The Counterion*

An increase of the counterion electron withdrawing character in monometallic catalytic complexes, for instance, the substitution of the halogen in π-allyl derivatives of transition metals by anions of halogenocarboxylic acids, leads to a noticeable increase in activity. Moreover, the behavior of a series of π-allylnickel haloacetates, all of which are highly stereospecific catalysts for the cis-1,4 polymerization of butadiene, indicates an interesting correlation between the overall polymerization rate and this electron withdrawing character of the coordinated counter anion. The catalytic activity increases sharply in the sequence $CH_3COO^- < CH_2ClCOO^- < CHCl_2COO^- < CCl_3COO^- < CF_3COO^-$, and the overall polymerization rate with the trifluoroacetate complex is about 150 times as great as that in the presence of the corresponding monochloroacetate (124). In addition to their high catalytic activity, the trifluoroacetate complexes produce high molecular weight *cis*-1,4-polybutadiene displaying characteristics similar to those of elastomeric polybutadiene obtained with Ziegler-Natta catalysts. These data confirm the interesting possibility of preparing, by the use of appropriate counterions, stable monometallic transition metal complexes that enjoy catalytic properties similar to those of bimetallic systems without the addition of any cocatalyst.

4.2.2 *Ligands*

Ligands Originally Bound to the Transition Metal. Since the first step in coordinated polymerization is the formation of a π complex between the monomer and the transition metal, it should be expected that the ligands bound originally to the catalytic complexes may strongly influence the initiation step and also the overall polymerization rate. Many monometallic catalysts (i.e., π-allylic derivatives) are normally associated as binuclear complexes. Often, the active centers for chain growth are not the dimeric molecules of the original complexes but a mononuclear species, and the first step will be a dissociative equilibrium involving monomer (Section 4.2.3) which might also determine the overall rate of the polymerization process depending on the types of ligands primarily bound to the transition metal. Only a few accurate data have been reported on these points, partly because of the variable degree of purity of the complexes studied.

In a series of hydrocarbon-nickel π complexes, the catalytic activity for the polymerization of butadiene was found to decrease in the sequence (133) 2,6,10-dodecatriene-1,12-diyl $\geqslant$ 1,5,9-cyclododecatriene $>$ 1,5-cyclooctadiene $\gg$ cyclopentadiene $>$ cyclooctatetraene.

Furthermore, in a homogeneous series of π-allylic nickel halides (169) or haloacetates (170), the overall rate constants appear to vary with the type of substitution of the π-allylic ligands in the order allyl > methallyl > crotyl. This parallels the effective activation energies of the hydrogenolysis of these π-allylic complexes (171), indicative of the respective heats of dissociation of the corresponding binuclear complexes.

Monomers. The influence of π-allylic ligands bound to the transition metal may be related to the specificity of such catalysts toward the polymerizing monomer and also to the practical impossibility to obtain a true copolymerization with most of them; this is the case, for example, with butadiene, since the coordination or the insertion into the chain of a different monomer molecule, e.g., of vinyl type, will modify the structure of the catalytic complex and thereby its relative stability. For instance, as observed long ago with cobalt based Ziegler-Natta catalysts, by adding suitable amounts of monoolefins to butadiene, it is possible to control closely the mean molecular weight of the polybutadiene produced. Indeed, insertion of the monoolefin yields a growing chain that must be bonded to the transition metal by a σ type bond, and the σ-cobalt (or nickel) to carbon bonds are known to be much more unstable at room temperature than π-allylic bonds. In some cases copolymers were obtained, e.g., from styrene with butadiene, using π-allylic nickel derivatives as catalysts. The determination of the monomer reactivity ratios indicated that butadiene is much more reactive than styrene; moreover, the overall polymerization rate, the copolymer intrinsic viscosity, and the *cis*-1,4-polybutadiene content decreased sharply with an increase of the styrene content in the starting mixture.

Homopolymerization of styrene by π-allylic nickel complexes yields oligomers having an average degree of polymerization ranging from 8 to 10 and, in some cases, only diphenylbutene-1 (216). These results again confirm that the bond formed by nickel with styryl radical is less stable than the π-allylic bond formed from a butadiene molecule (52, 126, 141, 142, 172). This also seems the reason why nickel and cobalt complexes polymerize diolefins other than 1,3-butadiene (e.g., isoprene, 1,2-butadiene, or allene, as shown in Tables 1 and 4), but not α-olefins. This coordinated polymerization of monoolefins is promoted by the presence of chromium, zirconium, and titanium complexes, supporting the aforementioned concept that the reaction is controlled essentially by the transition metal. Monometallic transition metal compounds were even found to be active catalysts for the polymerization of vinyl polar monomers, i.e., methyl methacrylate or acrylonitrile (144). However, these compounds show considerable variations in activity, and not all polar monomers can be polymerized because of their marked tendency to react with the metal complex to form a new organometallic compound.

Additional Ligands. The coordination of additional electron accepting or donating molecules in the coordination sphere of the transition metal may influence not only the stereospecificity, as mentioned above, but also the overall activity.

For instance, higher catalytic activities are achieved by adding various electron acceptors (e.g., metallic salts, iodine, derivatives of haloacetic acids, or quinones) to the π-allyl complexes of transition metals. In either case, this interaction leads to an increase of the effective charge on the transition metal atom and to an increase in its coordinating ability for monomer, together with the enhanced activity in polymerization.

In the presence of metal halides polymerization proceeds in a heterogeneous manner which implies a change not only in catalyst molecular structure but also in phase constitution. A similar initial situation is encountered when adding organic electron accepting molecules but, in this case, the polymerization proceeds essentially in a homogeneous medium, since the catalytic precipitate usually redissolves in the presence of butadiene when the reaction reaches a few percent conversion. For a series of trichloroacetic derivatives added to π-crotylnickel chloride, the activity increases as one goes from trichloroacetic acid to chloral and still further to the trichloroacetic acid chloride and nickel salt; this corresponds qualitatively to the increasing electron accepting ability of these ligands. Similar observations were made on substituted quinones; their half-wave electron addition potentials, which are a measure of the electron affinity of the acceptor, are +0.01, −0.18, and −0.51 V for *p*-chloranil, dichloro- or dibromo-*p*-benzoquinone, and unsubstituted benzoquinone, respectively. This sequence indicates their decreasing complexing ability as well as their decreasing efficiency in enhancing polymerization rates.

On the other hand, addition of electron donor materials usually leads to decreased catalytic activities and cis-1,4 contents, as shown previously. In fact, when bases coordinate with transition metal ions, they donate electrons to hybrid σ orbitals of the metal ions, but at the same time, part of the resultant negative charge on the metal is back-donated to the ligands in order to keep the metal atom nearly neutral. In other words, the *d* electron density of the metals is expected to be more reduced through back-donation when the basicity of the coordinated ligand is higher. If, as generally admitted, the *d* orbitals play an important role in the coordination of the monomer and the chain to transition metal atoms, the overall activity as well as the cis content of polybutadiene should depend on the coordination of these bases (e.g., ethers, phosphines, phosphites) to the transition metal atom in the active species, as indicated in Table 3, part H.

4.2.3 *Kinetic Data on Polymerization by π-Allylic Complexes of Transition Metals*

The rates of butadiene polymerization by various π-allylic complexes of transition metals are given by

$$-\frac{dM}{dt}=kC^{0.5}M^{1}$$

for bis(π-allylic nickel halides (47, 169, 173) or bis(π-crotylpalladium chloride) (174); by

$$-\frac{dM}{dt}=kC^{1}M^{1}$$

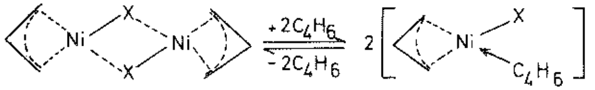
for bis(π-allylic nickel haloacetates) (47, 130) or bis(π-allylic nickel halides) plus electron acceptors (46, 112, 175); and

$$-\frac{dM}{dt}=kC^{2}M^{0}$$

for tris(π-allylic chromium) (46).

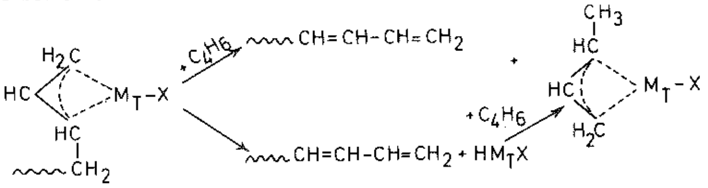
The overall activation energy (ranging from 16 to 14.5 kcal/mole) is surprisingly constant for all the bis(π-allylnickel halides) independently of the nature of both halogen and allylic groups; it ranges from 13 to 10 kcal/mole in the case of bis(π-allylnickel haloacetates), and is decreased from 13 to 6 kcal/mole, depending on the nature of the electron acceptor added.

Cryoscopic determinations have shown that π-allylnickel trifluoroacetate is normally associated as a binuclear complex, but in the experimental conditions yielding *cis*-1,4-polybutadiene, the coordination of stoichiometric amounts of butadiene converts this binuclear species into a mononuclear one (130, 176). These data indicate that, at least in this case, the active centers for chain growth are not the dimeric molecules of the original complexes but that, as already suggested, the first step in the polymerization reaction is a dissociative equilibrium involving the monomer:



It has also been considered (13) that in some coordination polymerizations, the rate determining step could be the coordination of the olefin to the transition metal. However, as mentioned above, some complementary data have recently shown that the polymerization can also be carried out on a binuclear species, e.g., to obtain the equibinary *cis,trans*-1,4-polybutadiene (213).

In fact, most of the observations made in the course of kinetic studies of coordinated polymerizations by monometallic catalytic complexes fit the scheme of dissociation of the initial complex, followed by propagation through an iterative cis rearrangement, and termination by a variety of reactions. Using labeled atoms, some details of this termination mechanism in the coordinated polymerization with π-allylic complexes have been elucidated. In principle, the following routes may be proposed for the termination of growing chains: thermal deactivation by disproportionation, coupling in the deactivation stage, termination onto monomer with chain transfer, or addition of the growing chain to compounds from the allylic substrate (e.g., hexadiene) which might be present in the reaction mixture. Analysis of the experimental data obtained with ^{14}C-labeled π-crotyl complexes shows that the last route is not realized under the usual polymerization conditions. The polymers formed contained one or two crotyl radicals from the catalyst in every macromolecule, supporting the two first routes considered (174, 177). Chain transfer reactions that determine the molecular weight of the polymer produced apparently occur as follows:



and the formation of two conjugated double bonds at the end of the polymer chains has been confirmed by reaction with maleic anhydride (47).

4.3 Possible Stereospecific Polymerization Mechanisms

The enormous amount of sometimes contradictory experimental data pertaining to the same polymerization process, increasingly indicates the difficulty of describing a universal mechanism for stereospecific synthesis. The study of the intimate behavior of transition metal π complexes is of interest because most of these complexes are relatively stable and well-defined species; in addition, these structures, mainly of the π-allyl type, are probably general intermediates in the stereospecific polymerization of conjugated dienes.

In fact, the stereoregularity of polybutadiene should be determined by the conformation that the butadiene molecule or the end of the growing polymeric chain assumes when coordinated to the catalyst metal atom in the transition state of the polymerization reaction. Many reaction mechanisms find it difficult to explain cis-trans isomerism.

One of the most comprehensive hypotheses was proposed several years ago by Arlman (178) as an extension of Cossee's scheme for α-olefin polymerization on heterogeneous catalysts. Its salient features may be summarized as follows. When the transition metal atom carries two vacancies, the monomer is coordinated as a bidentate ligand by its two double bonds, and is incorporated in the growing chain R (by the cis rearrangement reaction) in the same configuration, i.e., as a cis-1,4 unit. If only one vacancy is available, the coordination of the same monomer by one double bond allows it to take its more probable transoid conformation, giving rise to a trans-1,4 unit. These views have been substantiated by the preparation of *trans*-1,4-polybutadiene on α-TiCl$_3$, and of a resolvable mixture of both *trans*-1,4- and *cis*-1,4-polybutadiene on β-TiCl$_3$ where both types of sites coexist. The formation of 1,2 units would be dependent on the relative distance from the C$_2$ or the C$_4$ carbon of the monocoordinated monomer to the first carbon of the R group carried on the same transition metal (growing chain). A shorter C$_2$–R distance (depending on metal radius and complex geometry) would favor this vinyl structure.

It should be stressed that the whole mechanism involves a σ bond between chain and metal in the transition state, whether or not this chain is stabilized through a π-allyl bond (involving its first double bond) between every insertion step. Indeed, the recently reviewed (206) σ-π rearrangements of organotransition metal compounds are well known to play an important role in many processes, including polymerization, isomerization, and hydroformylation of unsaturated hydrocarbons.

Moreover, in elucidating the mechanism of 1,3-diene insertion into the allylic palladium bonds of the complexes (π-allyl-PdX) by means of NMR spectra, Hughes and Powell (217) have confirmed that the 1,3-diene, acting as a monodentate ligand, coordinates to the palladium through the least substituted double bond to give a σ-allylic intermediate [(σ-allyl)(diene)PdX]. The key step of the successive electrocyclic insertions of

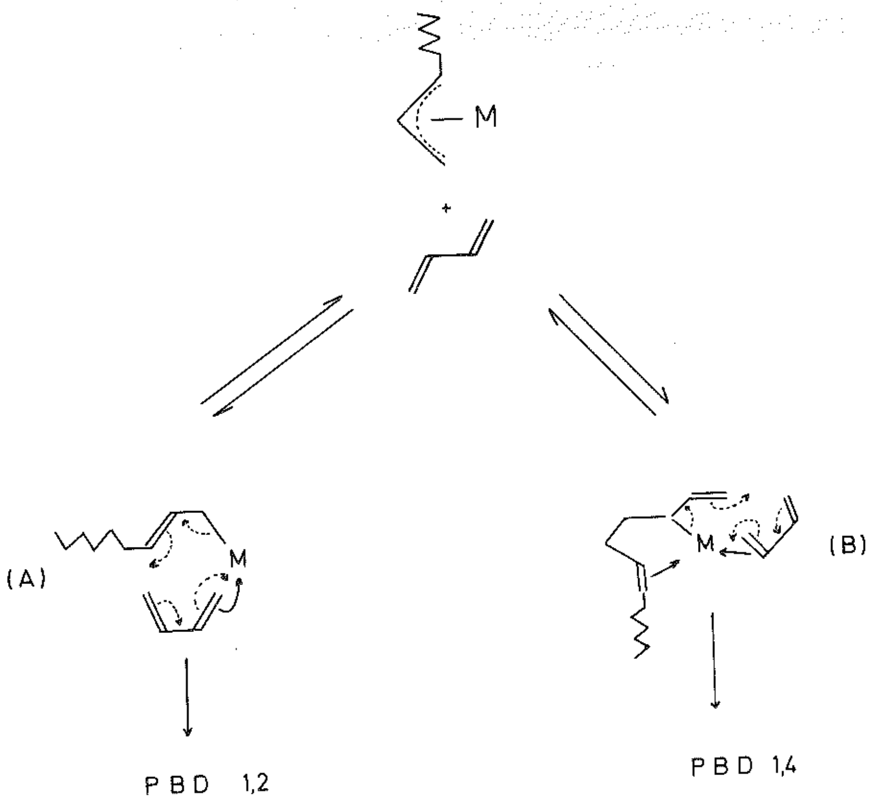
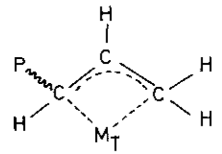


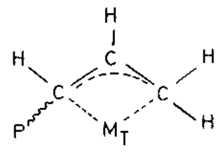
Figure 15

1,3-dienes into allyl-transition metal bonds is a ready $\pi \rightarrow \sigma \rightarrow \pi$ process via an intermediate such as A in Fig. 15, providing a plausible mechanism for 1,2 polymerization of 1,3-dienes. It should be noted, however, that this type of mechanism differs essentially from a cis rearrangement process; it is more like an allylic transposition reaction. Changes in catalytic systems which lead to an increased number of available coordination sites were shown to generally change the mode of polymerization from 1,2 to 1,4. The electrocyclic insertion mechanism may thus conceivably lead to a 1,4 polymeric chain, according to the Hughes-Powell report, via anchimerically assisted formation of an intermediate (B). However, this interpretation raises several difficulties since it implies less probable types of substitution and coordination for the allylic group and the monomer molecule.

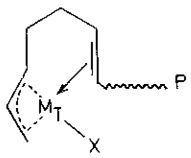
In the case of polymerization by π-allyl complexes, another mechanism frequently proposed in the past (see, e.g., refs. 47, 101, 173, 179) was associated essentially with the isomerism of the growing chain end in the form of a π-allyl complex; it was speculated that the "syn" form would favor trans polymerization and the "anti" form cis polymerization, the anti form being favored by coordination to the metal of the double bond nearest the π-allylic polymer end. However, NMR data obtained in solution seem to exclude the coordination of the penultimate double bond, and to indicate that only the syn form exists as a stable complex in both substituted π-allylnickel trifluoroacetate, chloride and iodide which yield high *cis*-1,4- and high *trans*-1,4-polybutadienes, respectively (46, 133, 180, 215). These observations suggest the lack of correlation between the isomerism of the π-allylic ligand and that of the resulting polymer, although as an unstable transition state, an anti π-allyl complex that would undergo polymerization prior to rapid isomerization to the stable syn form is not necessarily ruled out.



"syn" form → trans - 1,4

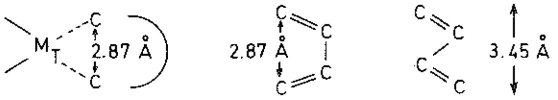


"anti" form → cis - 1,4



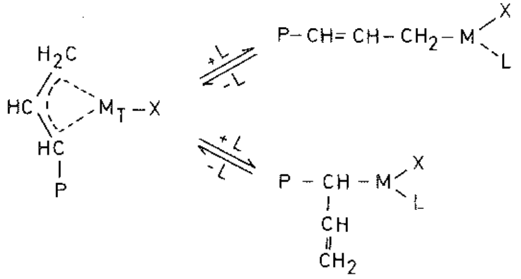
Another tentative interpretation was based on the dimeric or monomeric form of the catalytic species in solution (46, 126). At least in the case of pure cis-1,4 or trans-1,4 polymerization in the presence of π-allylnickel haloacetates, the kinetic and cryometric data exclude that a polymer chain grows on a binuclear catalytic complex, so the changes of microstructure cannot be explained on this basis.

In summary, the data currently available on the homogeneous polymerization of conjugated diolefins by π complexes, increasingly support Arlman's and Hughes and Powell's concepts that the polymerization proceeds through a σ type of transition complex; this mechanism does not exclude the coordination of the growing chain to the metal by a π-allyl bond for most of the time, but it assumes that the allylic structure passes into an alkyl one under the influence of the coordinated monomer, prior to its insertion into the chain. This mechanism implies also that the σ-π isomerization does not modify the potentially cis structure of the last incorporated monomer unit, a point that is still open to discussion. The formation of cis or trans units will be determined essentially, as in the case of propagations on α- or β-$TiCl_3$, by the capacity of a transition metal to coordinate both or only one of the two double bonds of the diene molecule. The formation of a predominantly cis structure of polybutadiene in the presence of cobalt or nickel catalysts would be rather easy, especially so since the distance between the first and fourth carbon atoms in the cis configuration of free butadiene is practically the same, i.e., 2.87 Å, as in the molecule coordinated by both double bonds:



Moreover, it seems quite probable that, as already suggested (181) the coordination of the monomer through both its double bonds occurs in fact in two consecutive steps. Chain propagation results, as indicated earlier, from a sequence of iterative events, involving formation of a π complex between the catalyst and the diene, isomerization of the π-allyl (if any) to a σ complex, and insertion of the coordinated monomer into the σ-alkyl to metal bond to give a complex similar to the initial one, with further coordination of another monomer molecule. Within the framework of this mechanism, implying six- to four-membered transition states, the structure of the initial complex between the catalyst and the diene determines the microstructure of the polymer chain.

The presence of strong electron accepting ligands (anions or organic molecules) should favor this chelation, increasing the cis-1,4 content as experimentally observed. The formation of 1,2 units might take place when monomer coordination involves only one double bond and when simultaneously the atomic distances favor the 1,2 binding, or when the type of conversion of the π-allylic complex into the σ complex determines 1,2 (instead of 1,4) stereoregulation:

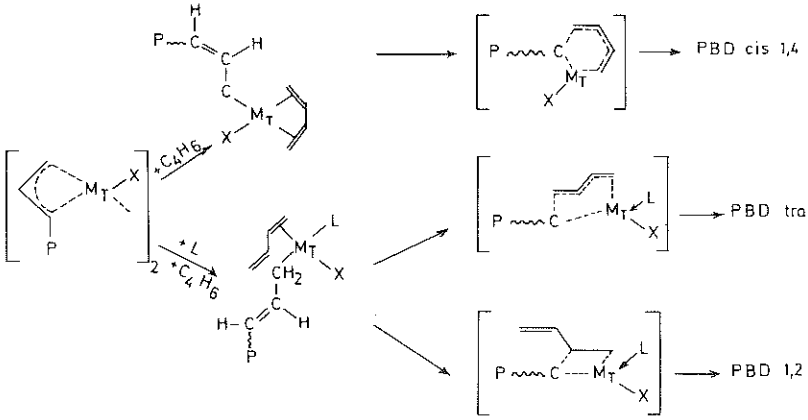


The action of electron donating additives that are capable of competing with the bidentate diene for a site in the coordination sphere of the catalyst becomes easily understandable. Only monodentate complexes

with monomer may be formed under those conditions and this leads to trans-1,4 or 1,2 polymers. The inductive influence of the counteranion on the cis-trans isomerism can also be accounted for by admitting that only the sufficiently electronegative anions are able to promote quantitatively, perhaps through a "trans" effect, the coordination of both butadiene double bonds.

This propagation reaction proceeds alternatively on two different sites of the coordination complex. This is most probably the key to the interpretation of the peculiar effect of specific π ligands promoting the formation of equibinary polydienes (see Section 4.1.3). A different isomer is alternatively inserted in the chain on each side, or otherwise the whole complex switches from one geometry to the other after every insertion step.

In conclusion, and accounting for most of the experimental data currently available, the mechanism of formation of stereoregular polybutadienes in solution can be tentatively summarized as follows:



5 CURRENT PROGRESS IN RELATED AREAS

5.1 Basic Catalytic Structures

The relationships between the catalyst's structure and its activity and stereospecificity have been further elucidated by investigations of the coordination polymerization of heterocyclic monomers, such as the oxiranes and thiiranes, to high molecular weight polymers.

The first efficient catalysts were obtained either by reaction of the monomer with ferric chloride (182) followed eventually by subsequent hydrolysis or by controlled hydrolysis of organometallic derivatives (183, 184) (mostly zinc and aluminum alkyls).

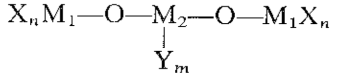
These results strengthened the idea that the responsible catalytic species were essentially composed of –M–O–M– groupings. Indeed, such species have been directly synthesized (185) by condensing a metal alcoholate with the acetate of a different metal, in a 2:1 ratio, e.g.,

$$2Al(OR)_3 + Zn(OAc)_2 \rightarrow (RO)_2Al—O—Zn—O—Al(OR)_2 + 2ROAc \uparrow$$

The new bimetallic μ-oxoalkoxides obtained are highly active for the homogeneous ring opening polymerization of oxiranes and thiiranes, which confirms that the presence of a metal to carbon bond is not essential to this type of polymerization. These results were confirmed by preparing similar species (186) with comparable activities through hydrolysis of a double metal alcoholate (Meerwein complex), e.g.,

$$[Al(OR)_3]_2 \cdot Zn(OR)_2 + 4H_2O \rightarrow (RO)_2Al—O—Zn—O—Al(OR)_2 + 4ROH\uparrow$$

Such catalysts are very active and rank among the best for preparation of polypropylene oxide elastomers (189). Both the activity and the stereospecificity of these compounds depend in a very specific manner on the nature of M_1, M_2, X, and Y in the general structure



$$X_nM_1—O—\underset{\displaystyle Y_m}{\underset{|}{M_2}}—O—M_1X_n$$

as well as on the nature of the solvent and the degree of association of the catalyst.

A comparison of the polymerization rates of different types of oxiranes, together with the competitive nature of the polymerization process, led (187) to a coordination mechanism that can be expressed as shown in Fig. 16. This scheme reveals striking similarities to the one proposed by Cossee for olefin polymerization: foreshadowing of the polymer chain by the OR group carried on the metal, and an alternating flip-flop mechanism governed by an electronic rearrangement where both chain and monomer exchange places on two different coordination positions without any important nuclear displacement. The similarity persists despite the different nature of the bonds involved, and the fact that at least two metal atoms seem necessary (188) to account for the reaction characteristics.

5.2 Catalysts with Bifunctional Behavior

A number of attempts have been made to impart to stereospecific catalyst systems a still more elaborate behavior.

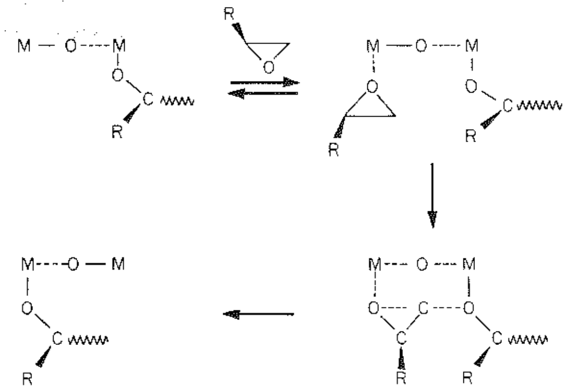


Figure 16

One of the earliest and most interesting realizations was to promote "stereoelectivity," i.e., the ability of a complex catalyst to favor the preferential incorporation in the growing chain of one of the optical isomers of a racemic monomer. This asymmetric synthesis is difficult to perform with high specificity in the polymerization of α-olefins (190), but has been more successfully achieved for oxirane and thiirane polymerization (191, 192), by substituting asymmetric groups on the catalyst, as close as possible to the determinant metal atom. A similar result has been obtained in organic synthesis, e.g., in homogeneous hydrogenation by rhodium complexes carrying an asymmetric phosphine (193).

Several research groups have tried to control the sequential composition of stereoregular polymers, particularly in copolymerization reactions. It would be of the utmost interest to be able to prepare block copolymers with these coordination catalysts since anionic systems, despite their outstanding efficiency in this respect, do not polymerize certain monomers (α-olefins in particular) and cannot give rise to given types of stereoregularity (e.g., pure *cis*-1,4-polybutadiene). In the case of polyolefins, although the products have not been thoroughly characterized in terms of sequential (194) molecular weight, preparation of block copolymers of ethylene and propylene has been claimed as well as an absence of termination in the syndiotactic polymerization of propylene (156). Since polar vinyl monomers are sometimes difficult to polymerize with coordination catalysts, a two-step procedure has also been devised (195–197) involving chemical transformation of the "living" polyolefin end into a reactive group (usually a peroxide) capable of initiating a radical type of formation of another (polar) sequence; this procedure usually yields mixtures of different products. Branched polymers have been prepared either by a simple "jumping" reaction (198) or by grafting techniques (207) where, for example, double bonds in a polydiene are reacted by metathesis with cyclopentene, thus promoting the formation of grafted polypentenamer side chains.

Even if the formation of block polymers by coordination catalysis with transition metals is not yet fully mastered, this is a very challenging and interesting area which could give rise to important developments in the near future, particularly in view of possible supermolecular organizations (199).

Finally, a third and exciting avenue was opened a few years ago, when it was shown that functions other than polymerization could be imparted simultaneously to the same catalytic system. For instance (200), a trimetallic catalyst, involving an aluminum alkyl, titanium chloride, and a nickel salt, has been used to polymerize internal olefins into poly-α-olefins, the nickel component ensuring a rapid isomerization of the internal olefin into the terminal α isomer which could be polymerized by the titanium moiety of the system. The polymers obtained have properties similar to those of the regular products arising from classical Ziegler type polymerization of the corresponding α-olefins.

5.3 Other Polymerization Mechanisms Involving Coordination Complexes

A long time ago, it was shown by Bier (201) that the coordination of an olefin such as ethylene to a metal salt such as silver nitrate could enhance its reactivity and allow radical type polymerization under rather mild conditions to a practically linear product. Other examples of this behavior have been described recently, such as the low activation energy polymerization of butadiene into a crystalline trans-1,4 polymer in the presence of rhodium chloride, and into a 1,4-trans-1,2 equibinary polymer in the presence of silver nitrate, in aqueous emulsion under γ-irradiation (202).

The thermal or radical induced polymerization of monomers coordinated to metal salts has also given rise to a very interesting research area. Gaylord (5, 203), among others, has attempted to rationalize several results indicating that in the presence of metal salts displaying an acceptor character, different monomers could copolymerize, either spontaneously (thermal activation) or in the presence of radicals (peroxides, radiations), to yield 1:1 alternating copolymers; this is the case for the copolymerization of butadiene and acrylonitrile in the presence of zinc chloride, as well as propylene-acrylonitrile with dichloroethylaluminum. Gaylord has claimed that the polar monomer coordinates to the Lewis acid with a resultant increase in its electron accepting ability. This complexed monomer participates in an electron transfer process with the more electron donor monomer, such as an olefin or conjugated diene, to form a charge transfer complex that could be considered a diradical species. Chain growth involves spontaneous or radical initiated homopolymerization of this Lewis acid activated diradical charge transfer complex, as illustrated in Fig. 17.

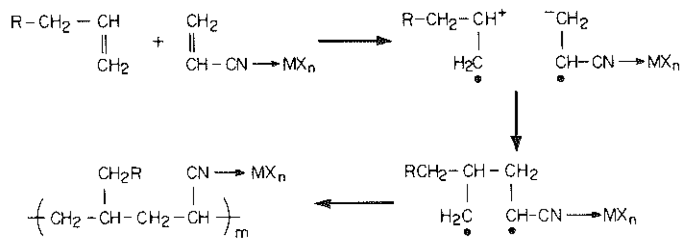


Figure 17

The intermediate complex explains the constancy of the polymeric composition irrespective of the monomeric ratio, mode of initiation, and reaction conditions, when the metal salt is present. (The metal is no longer required when the two monomers have sufficiently different donor-acceptor properties, for instance, the styrene-maleic anhydride pair). This reaction mechanism, which may have some formal similarities to the Diels-Alder reaction, has not been convincingly substantiated. In a more detailed analysis of these reactions, Zubov (218) has concluded that they can be described in terms of common kinetic schemes of addition radical polymerization, despite "anomalous" features for radical processes. Complex formation simply changes the relative reactivities by modifying resonance and polar characteristics of the monomers and radicals, or by changing the structure of the transition complex.

This type of structural control opens the way to preparing a broad class of new products, whose properties can be evaluated in terms of a regular arrangement of the two different monomeric units. Some of them, e.g., the alternating equimolar butadiene-acrylonitrile and butadiene-propylene copolymers, have been studied as specialty rubbers in view of their good overall set of properties (204, 222). The fact that under certain experimental conditions, the chains might grow without termination is still an additional attractive feature of these reactions.

6 CONCLUSION: TRENDS AND DIRECTIONS OF RESEARCH

We now have a much clearer view of the active center structure and the stereospecific propagation mechanism in coordination polymerization.

Very plausible reaction mechanisms have been elaborated which involve complexes of definite structure, and which are able to explain in detail at the atomic level the stereospecific insertion of the monomer into the growing chain. All these descriptions, often based on direct experimental evidence indicating not only the structure of the complex but also its behavior in the polymerization medium, stress the same conclusion: The active center is a metal complex, carrying different ligands and the growing polymer chain (attached on two coordination positions) and offering to the monomer to be incorporated, one or more suitable free coordination positions. Both the activity and the stereospecificity of this complex are determined by its geometry and by the electronic distribution dictated by the presence of different ligands, such as another monomer and/or a second metallic entity.

Despite the tremendous variety of catalytic ingredients used in these reactions, all of them apparently proceed through the common general type of structure outlined above. This means that the responsible species may be formed in situ by numerous and very different reaction paths. In other words, the coordination polymerization of very different monomers by very different catalysts may proceed through the same basic mechanism, which in fact explains a much broader class of catalytic processes involving much of organic chemistry. We have here a rewardingly unifying concept which is of great help in interpreting and forecasting catalytic behavior. This is the case, for example, for the epoxide/oxoalkoxide as well as the diolefin/π-allyl-metal-X systems. Some unity between the behavior of transition metal complexes and lithium derived catalysts might also be expected (3, 4).

New directions include the exploratory search for catalysts able to polymerize new monomers stereospecifically or known monomers into polymers of yet unknown stereoregular structure such as 1,3 polymerization of propene, controlled ring opening polymerization, new alternating copolymers, and equibinary polydienes. There is no doubt that unexpected and interesting results will be obtained.

The use of already known coordination catalysts to perform more involved polymerization reactions, in particular to produce di- or multisequential block copolymers, will certainly yield new products of great interest, in particular for the study of materials organized on a supermolecular scale, access to which has been restricted until now to the use of anionic catalysts. Other related interesting fields in rapid development are the studies of the mechanism by which heterogeneous Ziegler-Natta catalysts control the direct growth of fibrillar structures, and also by which some inorganic or polymer-supported coordination catalysts are able to increase both the activity (parts per million range) or lifetime of the catalytic species, and its specificity or electivity (219).

The last step in the elucidation of polymerization control by catalytic structure has yet to be accomplished in many cases. We have a rather good "chemical" picture of the situation, in terms of the well-defined composition of the active complexes as well as of the gross electronic influence of the ligands and metal involved. However, it appears that a significant part of this control is due to the stereogeometry and/or the fine electronic balance in the complex *in the polymerizing mixture.* It is highly probable that this knowledge will be gained only through the simultaneous application of several elaborate physical methods.

REFERENCES

1. K. Ziegler, in H. Zeiss, ed., *Organometallic Chemistry*, Reinhold, New York, 1960.
2. P. Teyssié, *Rev. Gén. Caoutch. Plast.*, **46,** 851 (1969).
3. M. Morton and A. D. Sanderson, Symposium on Stereoregular Polymerization, CIC/ACS Meeting, Toronto, May 1970.
4. S. Bywater, Symposium on Stereoregular Polymerization, CIC/ACS Meeting, Toronto, May 1970.
5. N. G. Gaylord and A. Takahashi, *J. Polymer. Sci.*, **B6,** 749 (1968).
6. D. Ketley, *Stereochemistry of Macromolecules*, Vols. I and II, Dekker, New York, 1969, and references cited therein.
7. V. A. Zakharov, et al., *Makromol. Chem.*, **175,** 3035 (1974).
8. K. Vesely et al., *J. Polym. Sci.*, **C16,** 417 (1967).
9. E. S. D'yachkovskii et al., *Polym. Sci., USSR*, **8,** 336 (1966).
10. E. S. D'yachkovskii et al., *J. Polym. Sci.*, **C16,** 2333 (1967).
11. A. K. Shilova et al., *Polym. Sci., USSR*, **9,** 903 (1967).
12. E. A. Grigoryan et al., *Polym. Sci. USSR*, **9,** 1372 (1967).
13. I. Pasquon et al., *J. Polym. Sci.*, **C16,** 2501 (1967).
14. G. Henrici-Olivé and S. Olivé, *Adv. Polym. Sci.*, **6,** 421 (1969).
15. G. Henrici-Olivé and S. Olivé, *Angew. Chem., Int. Ed.*, **7,** 821 (1968).
16. G. Henrici-Olivé and S. Olivé, *Makromol. Chem.*, **121,** 70 (1969).
17. G. Henrici-Olivé and S. Olivé, *J. Polym. Sci.*, **C22,** 965 (1969).
18. A. Zambelli et al., *Chim. Ind. (Milan)*, **46,** 1464 (1964).
19. F. Dawans and P. Teyssié, *Eur. Poly. J.*, **5,** 541 (1969).
20. W. Cooper and G. Vaughan, *Progress in Polymer Science*, Vol. I, Pergamon Press, Oxford, 1967.
21. J. Boor, Jr., *Ind. Eng. Chem., Res. Dev.*, **9,** 437 (1970).
22. J. P. Kennedy and E. G. M. Tornqvist, *Polymer Chemistry of Synthetic Elastomers*, Wiley-Interscience, New York, 1969.
23. A. Rawe, *Organic Chemistry of Macromolecules*, Dekker, New York, 1967, p. 111.
24. R. E. Rinehart et al., *J. Am. Chem. Soc.*, **83,** 4864 (1961).
25. R. E. Rinehart et al., *J. Am. Chem. Soc.*, **84,** 4145 (1962).
26. A. J. Canale et al., *Chem. Ind.*, **1962,** 1054.

27. R. S. Berger and E. A. Youngman, *J. Polym. Sci.*, **A2,** 357 (1964).
28. P. Teyssié, *C. R. Acad. Sci. (Paris)*, **256,** 2846 (1963).
29. P. Teyssie and R. Dauby. *Bull. Soc. Chim. France*, **1965,** 2842.
30. M. Morton et al., *Rubber Plast. Age*, **46,** 404 (1965).
31. R. Dauby et al., *J. Polym. Sci.*, **C16,** 1989 (1967).
32. M. Morton and B. Das, *J. Polym. Sci.*, **C27,** 1 (1969), and references cited therein.
33. R. Cramer, *J. Am. Chem. Soc.*, **89,** 1633 (1967), and references cited therein.
34. K. Hiraki and H. Hiroi, *J. Polym. Sci.*, **B7,** 449 (1969).
35. G. Natta et al., *J. Polym. Sci.*, **B2,** 349 (1964).
36. G. Natta et al., *Makromol. Chem.*, **81,** 253 (1965).
37. F. W. Michelotti and W. P. Keaveney, *J. Polym. Sci.*, **A3,** 895 (1965).
38. R. E. Rinehart and H. P. Smith, *J. Polym. Sci.*, **B3,** 1045 (1965).
39. R. E. Rinehart, *J. Polym. Sci.*, **C27,** 7 (1969).
40. A. D. Ketley and J. A. Broatz, *J. Polym. Sci.*, **B6,** 341 (1968).
41. P. Pino, *Adv. Polym. Sci.*, **4,** 393 (1966), and references cited therein.
42. G. Allegra et al., *Makromol. Chem.*, **90,** 60 (1966).
43. F. X. Werber et al., *J. Polym. Sci.*, **A6,** 743, 755 (1968).
44. G. Mazzanti, *Chem. Ind. (London)*, **1969,** 1204, and references cited therein.
45. W. S. Anderson, *J. Polym. Sci.*, **A1,** 5, 429 (1967).
46. B. A. Dolgoplosk and E. I. Tinyakova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, 344, and references cited therein.
47. V. A. Yakovlev et al., *Vysokomol. Soedin.* **A11,** 1645 (1969), and references cited therein.
48. K. I. Ueda et al., *Kogyo Kagaku Zasshi*, **66,** 1103 (1963).
49. T. Otsu et al., *J. Polym. Sci.*, **B5,** 835 (1967).
50. T. Otsu and M. Yamaguchi, *J. Polym. Sci., A-1*, **7,** 387 (1969).
51. U.S. Pat. 3,739,003 (to Institut Français du Pétrole, 1973).
52. F. Dawans et al., *J. Polym. Sci.*, **B10,** 493 (1972).
53. S. Kunichika et al., *Kogyo Kagaku Zasshi*, **72,** 1814 (1969).
54. J. Boor, Jr., *J. Polym. Sci.*, **3,** 995 (1965).
55. French Pat. 1,361,677 (to United States Rubber Co., 1964).
56. U.S. Pat. 3,414,555 (to Int. Synthetic Rubber Co., 1964).
57. U. A. Kormer et al., Neth. Appl. Pat. 69, 13 450 (1969).
58. U.S. Pat. 3,021,319 (to Hercules Powder Co., 1962).
59. Belgian Pat. 595,685 (to Union Carbide Corp., 1961).
60. K. Kuhlein and K. Clauss, *Makromol. Kolloq.*, Freiburg, 1969.
61. Canadian Pat. 620,209 (to Farbwerke Hoechst, A. G., 1961).
62. U.S. Pat. 3,037, 971 (to Hercules Powder Co., 1962).
63. C. Beerman and H. Bestian, *Angew. Chem.*, **71,** 618 (1959).
64. G. L. Karapinka et al., *J. Polym. Sci.*, **50,** 143 (1961).
65. British Pat. 856,434 (to National Lead Co., 1960).
66. U.S. Pat. 2,951,796 (to Union Carbide Corp., 1960).
67. U.S. Pat. 3,000,870 (to Montecatini, 1960).

68. British Pat. 881,004 (to Montecatini, 1958).
69. G. Natta et al., *Chim. Ind. (Milan)*, **39,** 1032 (1957).
70. U.S. Pat. 2,992,212 (to Hercules Powder Co., 1961).
71. K. Yomo et al., *Kogyo Zasshi*, **68,** 352 (1965).
72. French Pat. 1,437,892 (to Farbwerke Hoechst, A. G., 1965).
73. French Pat. 1,540,898 (to Idemitsu Kosan Co., 1968).
74. U. Giannini and U. Zucchini, *Chem. Commun.*, **1968,** 940.
75. U. Zucchini et al., *Chem. Commun.*, **1969,** 1174.
76. S.A. Pat. 59/2269 (to Montecatini, 1959).
77. French Pat. 1,249,666 (to National Lead Co., 1961).
78. Belgian Pat. 608,604 (to Montecatini, 1962).
79. British Pat. 889,591 (to Montecatini, 1962).
80. D. F. Herman and W. K. Nelson, *J. Am. Chem. Soc.*, **75,** 3877, 3882 (1953).
81. A. Yamamoto and S. Ikeda, *J. Am. Chem. Soc.*, **89,** 5989 (1967).
82. U.S. Pat 3,405,112 (to Japan Synthetic Rubber Co., Ltd., 1968).
83. S. Otsuka et al., *J. Am. Chem. Soc.*, **87,** 3017 (1965).
84. S. Otsuka et al., *Eur. Polym. J.*, **3,** 73 (1967).
85. F. Dawans and P. Teyssié, *C. R. Acad. Sci. (Paris)*, **261,** 4097 (1965).
86. F. Dawans and P. Teyssié, *J. Polym. Sci.*, **B3,** 1045 (1965).
87. F. Dawans and P. Teyssié, *C. R. Acad. Sci. (Paris)*, **263C,** 1512 (1966).
88. U.S. Pat. 3,400,115 (to Institut Français du Pétrole, 1968).
89. L. Porri et al., *J. Polym. Sci.*, **B5,** 629 (1967).
90. T. Arakawa, *Kogyo Kagaku Zasshi*, **70,** 1738 (1967).
91. T. G. Golenko et al., *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1968,** 2271.
92. B. D. Babitskii et al., *Dokl. Akad. Nauk SSSR*, **161,** 836 (1965).
93. Jap. Pat. 25,007 (1965) and 19,833 (1966) (to Japan Synthetic Rubber Co., Ltd.)
94. J. P. Durand et al., *J. Polym. Sci.*, **B6,** 757 (1968).
95. G. Wilke et al., *Angew. Chem., Int. Ed.*, **5,** 151 (1966), and references cited therein.
96. S. Otsuka and M. Kawakami, *Angew. Chem.* **75,** 858 (1963).
97. B. D. Babitskii et al., *Dokl. Akad. Nauk SSSR*, **165,** 95 (1965).
98. German Pat. 1,209,752 (to Badische Anilin und Soda Fabrik A. G., 1966).
99. German Pat. 1,269,811 (to Badische Anilin und Soda Fabrik A. G., 1968).
100. British Pat. 1,138,817 (to Stamicarbon N. V., 1969).
101. Jap. Pat. 17,687 (to Bridgestone Tire Co., Ltd., 1962).
102. S. Otsuka and M. Kawakami, *Kogyo Kagaku Zasshi*, **68,** 874 (1965).
103. U.S. Pat. 3,255,170 (to United States Rubber Co., 1966).
104. French Pat. 1,416,412 (to Badische Anilin und Soda Fabrik A. G., 1964).
105. British Pat. 1,027,867 (to Badische Anilin und Soda Fabrik A. G., 1966).
106. Jap. Pat. 6960 (to Japan Synthetic Rubber Co., Ltd., 1968).
107. W. Strohmeier and P. Hartmann, *Z. Naturforsch.*, **21b,** 1119 (1966).
108. W. Strohmeier and P. Hartmann, *Z. Naturforsch.*, **24b,** 777 (1969).
109. F. Dawans and P. Teyssié, *Ind. Eng. Chem. Res. Dev.*, **10,** 261 (1971).
110. French Pat 1,410,430 (to Studiengesellschaft Kohle, 1964).

111. G. Wilke, *Angew. Chem., Int. Ed.*, **2,** 105 (1963).

112. G. Wilke, 8th International Conference on Coordination Chemistry, Vienna, September 1964.

113. E. I. Tinyakova et al., International Symposium on Macromolecular Chemistry, Budapest, 1969.

114. French Pat. 1,470,794 (to Farbwerke Hoechst A. G., 1966).

115. V. A. Yakovlev et al., *Dokl. Akad. Nauk SSSR,* **187,** 354 (1969).

116. S. V. Lebedev, French Pat. 1,550,097 (to All-Union Scientific Research Institute of Synthetic Rubber, 1967).

117. U.S. Pat. 3,497,488 (to Institut Français du Pétrole, 1970).

118. J. P. Durand et al., *J. Polym. Sci.*, **B5,** 785 (1967).

119. French Pat. 1,551,887 (to SNAM Progetti S.p.a., 1967).

120. G. Lugli et al., *Inorg. Chim. Acta,* **3,** 151 (1969).

121. J. P. Durand and P. Teyssié, *J. Polym. Sci.*, **B6,** 299 (1968).

122. French Pat. 1,590,083 (to Institut Français du Pétrole, 1970).

123. U.S. Pat. 3,542,695 (to Institut Français du Pétrole, 1970).

124. F. Dawans and P. Teyssié, *J. Polym. Sci.*, **B7,** 111 (1969).

125. L. Porri et al., *Chim. Ind. (Milan)*, **46,** 426 (1964).

126. L. Porri et al., *J. Polym. Sci.*, **C16,** 2525 (1967).

127. T. Matsumoto et al., *J. Polym. Sci.*, **B6,** 869 (1968).

128. French Pat. 1,556,962 (to Institut Français du Pétrole, 1969).

129. V. I. Skoblikova at al., *Vysokomol. Soedin.*, **B10,** 590 (1968).

130. J. C. Maréchal et al., *J. Polym. Sci.*, **A8,** 1993 (1970).

131. V. A. Kormer et al., *Dokl. Akad. Nauk SSSR,* **180,** 665 (1968).

132. T. Matsumoto et al., *J. Polym. Sci.*, **B7,** 541 (1969).

133. J. P. Durand et al., *J. Polym. Sci.*, **A8,** 979 (1970).

134. E. V. Kristalnyi et al., *Vysokomol. Soedin.*, **A12,** 836 (1970).

135. J. P. Durand and F. Dawans, *J. Polym. Sci.*, **B8,** 743 (1970).

136. French Pat. 1,561,515 (to Imperial Chemical Industries, Ltd., 1969).

137. Jap. Pat. 13,091 (to Idemitsu Kosan Co, Ltd., 1967).

138. British Pat. 1,091,296 (to Imperial Chemical Industries, Ltd., 1968).

139. British Pat. 1,184,592 and 3 (to Idemitsu Kosan Co. Ltd., 1970).

140. Jap. Pat. 9925 (to Nippon Gosei Gomu K.K., 1970).

141. L. I. Redkina et al., *Dokl. Akad. Nauk SSSR,* **186,** 397 (1969).

142. L. I. Redkina et al., International Symposium on Macromolecular Chemistry, Budapest, 1969.

143. D. G. H. Ballard et al., *J. Chem. Soc. (B)*, **1968,** 1168.

144. V. A. Kormer et al., *Dokl. Akad. Nauk SSSR,* **185,** 873 (1969).

145. P. Cossee, *J. Catal.*, **3,** 80 (1964).

146. E. J. Arlman, *J. Catal.*, **3,** 89 (1964).

147. E. J. Arlman and P. Cossee, *J. Catal.*, **3,** 99 (1964).

148. P. Cossee, in D. Ketley, ed., *Stereochemistry of Macromolecules,* Dekker, New York, 1967, p. 145.

149. L. A. M. Rodriguez and H. M. Van Looy, *J. Polym. Sci.*, **4,** 1971 (1966).

150. P. Cossee, *Tetrahedron Lett.*, **17,** 12 (1960).

151. L. A. M. Rodriguez, et al., *J. Polym. Sci.*, **4,** 1905 (1966).

152. J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, **1953,** 2939.

153. P. Cossee et al., 4th International Congress on Catalysis, Moscow, 1968.

154. D. Hoeg, in A. Ketley, ed., *Stereochemistry of Macromolecules,* Dekker, New York, 1967, p. 95.

155. J. Boor, Jr., and E. A. Youngman, *J. Polym. Sci., A-1,* **4,** 1861 (1966).

156. A. Zambelli et al., *Makromol. Chem.*, **112,** 160 (1968).

157. B. Hessett and P. G. Perkins, *Chem. Ind. (London)*, **1970,** 747.

158. C. G. Overberger and G. W. Halek, *J. Polym. Sci., A-1,* **8,** 359 (1970).

159. V. Desreux, personal communication.

160. H. Yuki et al., *J. Polym. Sci., A-1,* **7,** 1933 (1969).

161. T. G. Fox et al., *J. Am. Chem. Soc.*, **80,** 1768 (1958).

162. R. St John Manley, *J. Macromol. Sci.-Phys.*, **B2,** 501 (1968), and references cited therein; Symposium on Stereoregular Polymerization, CIC/ACS Meeting, Toronto, May 1970.

163. J. Y. Gutman and J. E. Gillet, Symposium on Stereoregular Polymerization, CIC/ACS Meeting, Toronto, May 1970.

164. R. H. Marchessault et al., Symposium on Stereoregular Polymerization, CIC/ACS Meeting, Toronto, May 1970.

165. J. L. Herisson and Y. Chauvin, *Makromol. Chem.*, **141,** 161 (1971).

166. K. Matsuzaki and T. Yosukawa, *J. Polym. Sci.*, **A1,** 511 (1967).

167. F. Dawans and P. Teyssié, *Makromol. Chem.*, **109,** 68 (1967).

168. P. Teyssié et al., *J. Polym. Sci.*, **C22,** 221 (1968).

169. S. S. Medvedev, *Russ. Chem. Rev.*, **37,** 842 (1968).

170. B. P. Bourdauducq and F. Dawans, *J. Polym. Sci., A-1,* **10,** 2527 (1972).

171. O. P. Parenago et al., *Kinet. Katal.* **10,** 273 (1969).

172. I. V. Ostrovskaya et al., *Dokl. Akad. Nauk SSSR,* **181,** 892 (1968).

173. J. F. Harrod and L. R. Wallace, *Macromolecules,* **2,** 449 (1969); Symposium on Stereoregular Polymerization, CIC/ACS Meeting, Toronto, May 1970.

174. G. M. Khvostik et al., *Dokl. Akad. Nauk SSSR,* **186,** 894 (1969).

175. N. I. Pakaro et al., *Dokl. Akad. Nauk SSSR,* **185,** 1323 (1969).

176. F. Dawans et al., *J. Organomet. Chem.*, **21,** 259 (1970).

177. B. D. Babitskii et al., *Dokl. Akad. Nauk SSSR,* **180,** 420 (1968).

178. E. J. Arlman, *J. Catal.*, **5,** 178 (1966).

179. B. A. Dolgoplosk et al., *J. Polym. Sci.*, **C16,** 3685 (1968).

180. T. Matsumoto and J. Furukawa, *J. Polym. Sci.*, **B5,** 935 (1967).

181. L. Porri et al., *Eur. Polym. J.*, **5,** 1 (1969).

182. M. E. Pruitt and J. M. Baggett, U.S. Pat. 2,706,189 (to Dow Chem. Co., 1955).

183. E. J. Vandenberg, U.S. Pat. 3,135,706 (to Hercules Powder Co., 1964); *J. Polym. Sci.*, **47,** 149 (1960).

184. H. Tani et al., *J. Am. Chem. Soc.*, **89,** 173 (1967).

185. M. Osgan and P. Teyssié, *J. Polym. Sci.*, **B5,** 789 (1967).

186. J. P. Pasero, Thesis, University of Paris, 1971.
187. N. Kohler et al., *J. Polym. Sci.*, **B6,** 559 (1968).
188. E. J. Vandenberg, *J. Polym. Sci., A-1,* **7,** 525 (1969).
189. M. Osgan et al., ACS 157th Symposium Division of Petroleum Chemistry, A89, 1968.
190. P. Pino, *Adv. Polym. Sci.*, **4,** 393 (1965).
191. S. Inone et al., *Makromol. Chem.*, **90,** 131 (1966).
192. P. Sigwalt and N. Spassky, personal communication.
193. W. S. Knowles et al., *Chem. Tech.*, **1972,** 590.
194. I. Pasquon et al., in A. Ketley, ed., *Stereochemistry of Macromolecules,* Dekker, New York, 1967, p. 220.
195. French Pat. 1,531,409 (to Avisun Corp., 1967).
196. French Pat. 1,563,716 (to Rexall Drug and Chem. Co., 1967).
197. Neth. Appl. Pat. 69, 12354 (to Société Nationale des Pétroles d'Aquitaine, 1969).
198. W. Ring and H. J. Cantow, *Makromol. Chem.*, **89,** 138 (1965).
199. C. Sadron, *Chim. Ind.*, **96,** 507 (1966).
200. Y. Chauvin et al., *Bull. Soc. Chim. France,* **1966,** 3223.
201. Belgian Pat. 602,153 (to Farbwerke Hoechst, A. G., 1961).
202. J. Duchemin et al., French Pat. 1,603,773 (1971).
203. A. Takahashi and N. G. Gaylord, *J. Macromol. Sci.*, **A4,** 127 (1970).
204. J. Furukawa et al., *J. Polym. Sci.*, **B7,** 561 (1969).
205. T. Koshiwagi et al., *J. Polym. Sci.*, **B8,** 173 (1970).
206. M. Tsutsui et al.,. *Angew. Chem., Int. Ed.*, **8,** 410 (1969).
207. F. Dawans, *Inf. Chim.*, No. 122, 105 (1973).
208. V. M. Frolov et al., *Kinet. Katal.*, **15,** 1475 (1974).
209. Y. I. Yermakov et al., *Kinet. Katal.*, **13,** 1422 (1972).
210. F. I. Karol et al., *J. Polym. Sci., A-1,* **10,** 2621 (1972).
211. B. G. H. Ballard, *Adv. Catal.*, **23,** 263 (1973).
212. Y. Chauvin, private communication.
213. M. Julemont et al., Ziegler Symposium on Coordination Polymerization, 167th ACS Meeting, Los Angeles, 1974.
214. M. Julemont et al., *Makromol. Chem.*, **175,** 1673 (1974).
215. R. Warin et al., *J. Polym. Sci.*, **B11,** 177 (1973).
216. F. Dawans, *Tetrahedron Lett.*, No. 22, 1943 (1971).
217. R. P. Hughes and J. Powell, *J. Am. Chem. Soc.*, **94,** 7723 (1972).
218. V. P. Zubov, 23rd International Congress of Pure and Applied Chemistry, Boston, *Special Lectures,* **8,** 69 (1971).
219. N. Kohler and F. Dawans, *Rev. IFP*, **27,** 105 (1972).
220. W. A. Hewett, private communication.
221. C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **96,** 7808 (1974).
222. J. Furukawa, *Angew. Makromol. Chem.*, **23,** 189 (1972); *J. Polym. Sci.*, **C48,** 19 (1974).

E. W. Duck and J. M. Locke

International Synthetic Rubber Co., Ltd.
Southampton, England

Chapter 4 Polydienes by Anionic Catalysts

1 INTRODUCTION

Synthetic rubbers produced by anionic catalysts such as alkali metals were the first to become commercially important. It is only within the last 15 years, however, that significant quantities of widely used general purpose synthetic rubbers have been manufactured by anionic processes. Today, lithium alkyls and their complexes are among the most favored of the anionic initiators for polydienes because they offer several advantages, and it is with these catalysts that commercial growth has been so rapid. Compared with the other alkali metal compounds the lithium alkyls show