Stereospecific Polymerization of Dioelfins by h^3-Allylic Coordination Complexes

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More than fifteen years have passed since the first stereospecific polymerizations of diolefins were achieved with Ziegler-Natta catalysts. Since then more and more efficient systems have been discovered which allow greater structural control, milder reaction conditions, higher reaction rates, and smaller amounts of catalysts. Our mechanistic knowledge of these reactions has also progressed accordingly, and we begin to understand a number of the basic factors by which they are governed. However these studies have also revealed an increasingly complex picture of the behaviour of these catalysts, and we are still far from having a detailed and satisfying picture of their mode of action. In fact, it becomes evident that we have underestimated the refinement of these controls, and in particular the determinant role of rather small modifications in the overall geometry of the complexes in the reaction mixtures.

The present review, which does not intend to be exhaustive, will try to present the most significant advances made in the field as well as some of the key problems that they still raise.

1) *FUNDAMENTALS OF THE COORDINATED SPECIFIC POLYMERIZATION OF DIOLEFINS BY ZIEGLER-NATTA CATALYSTS.*

1.1) Formation of the Active Centers

The work of the past decade on Ziegler-Natta catalysts (consisting usually of a transition metal derivative and a metal alkyl or hydride, combined eventually with additional

ligands), established that the growing polymer chain is
attached to a metal atom, and the transition metal is deter-
minant in controlling the stereospecific growth reaction
(apparently this role can also be played by lithium in
coordinated-anionic polymerization). Furthermore, owing to
the monomer structure, the catalytic entity involves a metal-
allyl type of bonding with the chain. Most of the data pre-
sently available on transition metal-allyl systems indicate
that the π-electrons of the allyl group are delocalized, and
that most of the time one deals with a stabilized π- or h^3-
allylic structure (we will adopt Cotton's notation (1), which
is unambiguous and versatile). In the case of diene polymer-
ization, the active center may accordingly be represented by:
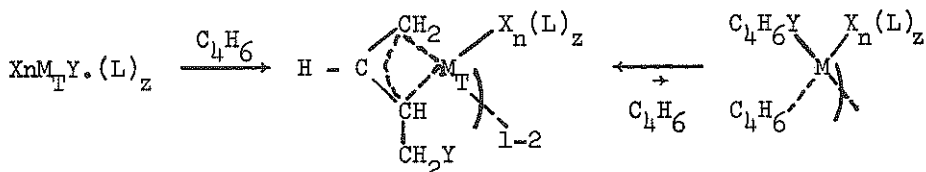
where Y = R, H, X; X = simple anion; and L = Lewis base, or
AlR_xX_{3-x} in the case of a bimetallic Ziegler catalyst (where
this aluminum derivative plays the role of a ligand able to
influence the rate and eventually the stereospecificity of
the reaction).

In support of these ideas, many h^3-allyl complexes of
transition metals have been isolated in a pure state(2,3) and
found to be reasonably active catalysts for stereospecific
diolefin addition reactions. Consequently they represent
good models in studying the corresponding polymerization as
well as open-chain- and cyclo-oligomerization catalytic
reactions(4).

Interestingly, it has been shown that the rate of the
process depends directly on the electronic density in
specific points of the coordination sphere. For instance in
a series of h^3-allylnickel complexes, all of which yield pure
cis-1,4-polybutadiene, the rate may be varied by more than a
thousand-fold simply by increasing the electron-withdrawing
character of the counter-anion(5). It is also possible to
synthesize these basic monometallic complexes which have
activities comparable(6) to the standard bimetallic Ziegler-
Natta systems (where the aluminum derivative probably plays
the role of a ligand controlling the right electronic distri-
bution).

1.2) The Propagation Mechanism

The polymerization process may now be described further in terms of two very different types of mechanisms. The first one is the *cis-rearrangement reaction* proposed by P. Cossee some 15 years ago to explain the 1,4-polymerization of butadiene by titanium chloride catalysts(7). It involves essentially a π-coordination of the monomer (mono- or bidentate depending on the number of positions available) on the σ- or h^1-allyl form of the complex, followed by an electronic rearrangement involving some migration of the h^1-bonded group to the coordinated monomer (Fig. 1). It has also been invoked in mechanistic interpretations of lithium-initiated diolefins polymerizations(7).
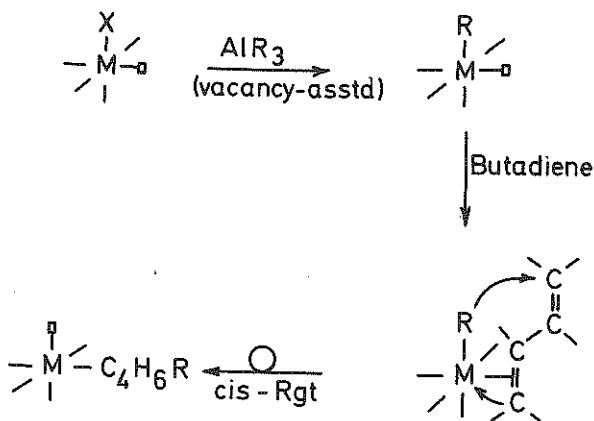
Fig. 1. *Cis-rearrangement mechanism in coordination polymerization.*

On the other hand, several authors(8,9,10,11) have considered a completely different type of electronic rearrangement, closely to the *allylic transposition* invoked i.e., in the addition of metal-allyl derivatives to ketones(12). In the case of palladium-catalyzed 1,2-addition reactions(10), the new carbon-carbon bond has been shown indeed to be formed outside the coordination sphere. It implies first (Fig. 2) the reversible coordination of monomer with simultaneous conversion of the complex into the h^1-form, involving a σ-bond between the metal and the *least substituted* carbon atom of the allyl group. Furthermore, the bonding of the h^1-allyl group (C^3 atom) to the free C^4-carbon of the coordinated diene proceeds probably through a concerted process.
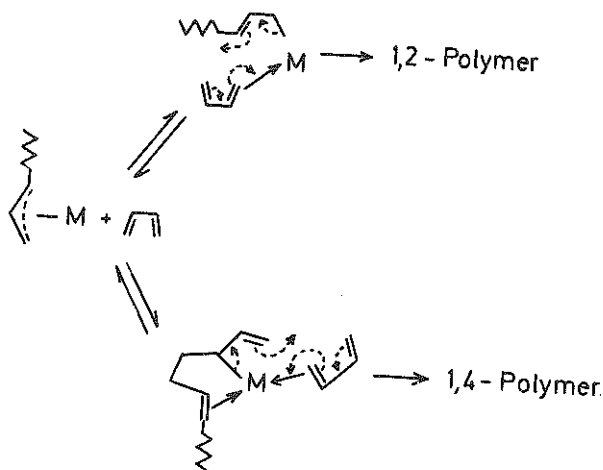
Fig. 2. Allylic transposition mechanism (outer sphere pericyclic rearrangement) in coordination polymerization. Courtesy of J. Amer. Chem. Soc., 94, 7731 (1972).

This mechanism has been tentatively extended to 1,4-polymerization by other transition metals, like nickel, even though the stereochemistry involved is completely different(12). However, the application of this scheme to 1,4-polymerization raises several difficulties. It gives no interpretation of the *cis-trans* controls discussed below; on the other hand, it would imply(10) several unlikely situations, such as coordination of the diene by the most substituted double bond (13), and σ-bonding of the h^1-allyl group to the metal by the carbon atom carrying the growing chain. Anyhow, both mechanisms imply a transitory h^1-allyl complex carrying a π-coordinated monomer molecule; this model will be adopted for further discussion as it is well-substantiated by the general chemistry of the allyl complexes.

Further investigations should determine if *cis*-rearrangement predominates in 1,4-addition (butadiene 1,4-polymerization by Ti, Ni, and Li catalysts), while allylic transposition is the main process in the formation of branched addition products (butadiene 1,2-polymerization by Pd or Li-OR catalysts, addition of allyl-Grignard reagents to ketones, piperylene cyclodimerization by nickel complexes).

2) *THE STEREOREGULATION OF THE PROPAGATION PROCESSES IN TRANSITION-METALS CATALYZED POLYMERIZATION.*

2.1) Control of Structural Isomerism (1,2/1,4)

It is by now well established that the structural isomerism of the polydienes obtained by coordination catalysis on transition metal complexes depends essentially on the nature of the metal involved, although in some cases specific ligands can influence it to some extent. For example, 1,2-polybutadiene can be obtained in the presence of palladium, chromium and molybdenum derivatives, while 1,4-polymers are obtained in the presence of titanium, cobalt, nickel, and rhodium complexes (see i.e., (4)). In both cases steric purities higher than 95% are easily obtained, reaching often 98 to 99%.

The lack of experimental methods allowing a progressive variation of this structural isomerism (from pure 1,2 to pure 1,4) by a systematic modification of the catalyst structure, prevented up to now a thorough investigation of this change in microstructures. A combination of electronic and geometrical factors is probably involved. Till now however, the only simple mechanistic proposal remains that of Arlman(18), based on the respective distances between the C_2 or C_4 atoms of the coordinated diolefin and the α-CH_2 group of the h^1-allyl-metal undergoing the rearrangement. This distinction might eventually be coupled with a change in mechanism from *cis*-rearrangement to allylic transposition, or alternatively to a change in the geometry of the complex undergoing this allylic transposition(10). Obviously, more experiments, i.e., with dienes substituted in specific positions, are required to solve these problems.

2.2) Control of the Geometrical Isomerism (cis 1,4/trans 1,4).

2.2.1) *Influence of the Ligands.* As already mentioned, bis-(h^3-allylnickel trifluoroacetate), or $(ANiTFA)_2$, promotes the rapid formation of a very high *cis*-1,4-polybutadiene(5). However, in the presence of different additional ligands, the geometrical isomerism of the polymer obtained changes drastically as indicated in Table 1., while the structural isomerism remains unchanged (99% 1,4). This change from *cis* to *trans* isomerism, common to several catalysts, has been tentatively interpretated by different theories.

TABLE 1.

Control of geometrical isomerism by additional ligands in the 1,4-butadiene polymerization by (ANiTFA)$_2$.

L	[L] / [Ni]	% cis	% trans
----	----	98	1
P(OR)$_3$	1	----	99
C$_2$H$_5$OH	1	----	99
CF$_3$COOH	1	50	49
C$_6$H$_{6-n}$X$_n$	< 500	48	50

The first one, proposed by Otsuka in 1965(14), is based on the existence of two different isomers of the h^3-allyl bonded chain: the *anti* intermediate, promoting the formation of a *cis* double bond in the chain upon insertion of the next monomeric unit and reformation of a new h^3-allyl group; and the *syn* intermediate promoting the formation of a *trans* unit (see Fig. 3). This interpretation has two strong drawbacks. First, several NMR studies(15,16,17) have shown that various h^3-allyl catalysts, giving *cis* or *trans* or mixed polybutadienes, are always in the most probable *syn* form. This result cannot exclude of course the possibility that a transient *anti* form might lead to *cis* polymerization. There is, however, no reason to believe that the *anti* form has much higher activity than the *syn* one. Furthermore, such a control might imply a reaction between two π-bonded entities (h^3-allyl chain and π-butadiene), which is not too likely in the chemistry of allyl-metal complexes.

Another interpretation(7,18), proposed by Cossee is simply based on a monodentate-*trans* or bidentate-*cis* coordination of the diolefin which leads respectively to the formation of *trans* or *cis* configurations in the polymer (see Fig. 4). This hypothesis is strongly supported by the fact that α-TiCl$_3$, which offers only one coordination vacancy at the active center, promotes the formation of *trans*-1,4-polymerization, whereas β-TiCl$_3$ which offers more vacancies favours the formation of a mixture of homo-*cis* and homo-*trans* polymers.
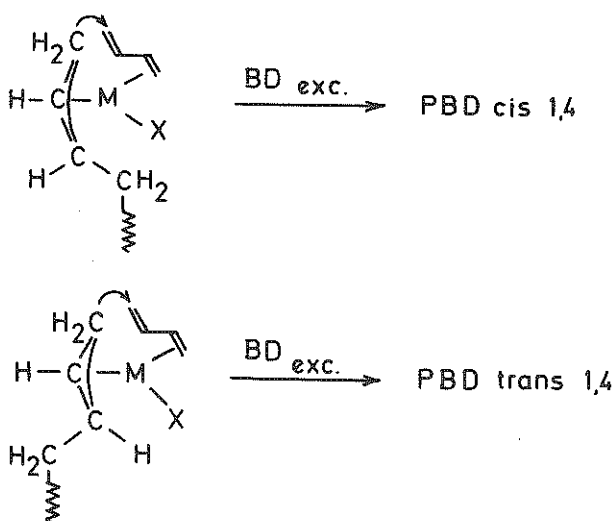
Fig. 3. *Control of the cis or trans config-uration of the h^3-allyl group isomerism in 1,4-diolefins polymerizations.*
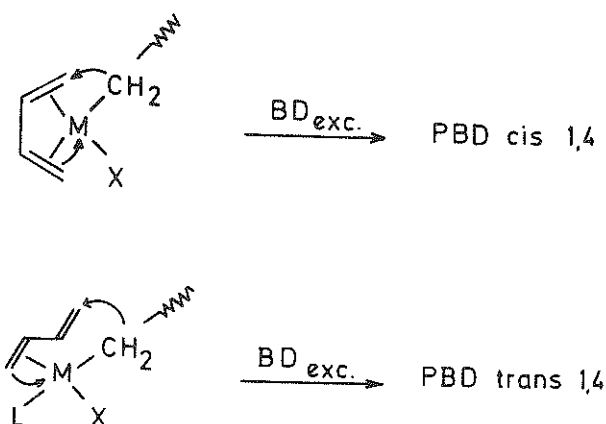

Fig. 4. *Control of the cis or trans config-urations by the coordinated monomer conforma-tion in 1,4-diolefins polymerizations.*

This mechanism also can explain the influence of strong basic ligands (phosphites, alcohols) which converts the *cis*-catalyst into a *trans*-catalyst. These ligands are known to dissociate the binuclear complex and to occupy one coordination position on the mononuclear form. In this way, they prevent the bidentate coordination of the monomer on the mononuclear complex(19), which is necessary to generate the 1,4-*cis* polymer(20).

This very straightforward and appealing mechanism, which is also invoked in several interpretations of lithium-induced anionic polymerizations, presents, however, one serious problem: indeed if inbetween every insertion step the h^1-allyl chain returns to the *syn* h^3-allyl form (which is the thermodynamically favoured one for transition metals), the *cis*-configuration formed in the h^1-allyl chain will be lost, and the *syn* h^3-allyl bond will most probably regenerate a *trans* configuration after insertion of the next monomer. Consequently one is forced to postulate that the h^1-allyl chain must have a very high reactivity and is able to insert many monomeric units in this form before returning to the h^3-allyl form, and that the latter is the "dormant" state of the active complex.

With this mechanism, one has a plausible explanation for the control of *cis* or *trans* isomerism, as well as of the di-isomeric specificities discussed in the next section (3.3).

Finally, an elegant alternative explanation has been proposed more recently by Furukawa(21) suggesting a control of the *cis* isomerism by the coordination (or "backbiting") of the first free double-bond in the chain to the nickel atom, whatever the *syn* or *anti* structure of the h^3-allyl group. However, this interesting proposal, which will have to be ascertained by experimental data, raises also several serious problems in terms of intromolecular movements and electronic charge displacements.

2.2.2) *Influence of the Counter-anions.* Using a series of bis-(h^3-allylnickel-X)complexes, one can also obtain pure (99%) 1,4-polybutadienes, whose geometrical isomerism ranges from 98% *cis* (X = CF_3COO) to 99% *trans* (X = I), with a monotonic variation through Cl and Br (6). This control seems to depend more on the electronegativity of the counter-anion than on its bulkiness, as indicated by the formation of very high *cis*-1,4-polybutadiene from h^3-allylnickel-1,3,5-trinitrophenate(5) (picrate salt). This kind of dependence might of course imply a more or less easy dissociation of the initially binuclear h^3-allyl complexes, leading or not to a mononuclear complex capable of accomodating the monomer in a bidentate coordination (i.e., able to give the *cis*-1,4-isomer, see 2.2.1).

However, several kinetics and structural studies have shown that the formation of both pure *cis* (20) and pure *trans* (22, 23) polybutadienes imply most probably a transient mononuclear species; accordingly it seems more likely that it is the electron withdrawing character of the counter-anion which influences the geometry of the active complex and favours the coordination of the double bond of the second monomer. It could also change the M-X distance and consequently the effective steric hindrance of the anion to this bidentate coordination.

Anyhow, the profound influence of the anion electronegativity on the overall structure of the complex, and in particular of the h^3-allyl group, has been confirmed by NMR spectroscopy(17). More electronegative anions induce a higher dissymmetry of the allyl group (higher bond order for C_2-C_3 than for C_1-C_2, although the group remains h^3-bonded), promoting a resultant twisting of the first methylene group of the chain.

In conclusion, this important question of the *cis/trans* isomerism control is still far from being settled, although the mode of the monomer coordination in a *cis*-rearrangement mechanism seems to offer an attractive straightforward explanation of the results obtained. Again, more experimental results are needed to further our understanding of this specificity.

2.3) Control of Specific Binary Isomerisms: the Case of Equibinary Polydienes

2.3.1) *Overall characteristics of equibinary polymerizations.* In the course of a study of butadiene polymerization by the very active complex, bis(h^3-allylnickel-trifluoroacetate), it was discovered a few years ago(29) that the addition of specific ligands could lead to the formation of a polymer containing exactly equal amounts of *cis* and *trans* isomers. It was later shown that this type of behaviour is quite general in coordination polymerization, and the name "equibinary polydienes" has been coined for these polymers containing equal amounts of two different isomeric units. Typical examples in addition to the equibinary (*cis* 1,4-*trans* 1,4) polybutadiene described above are the equibinary (1,4-1,2) polybutadiene(25), (*cis* 1,4-3,4) polyisoprene(26), and (1,2-3,4) polyisoprene(26), obtained in the presence of various metals like nickel, molybdenum and cobalt. It soon became evident that this phenomenon exhibited all the characteristic features of a specific coordination competitive reaction, as summarized in Fig. 5.
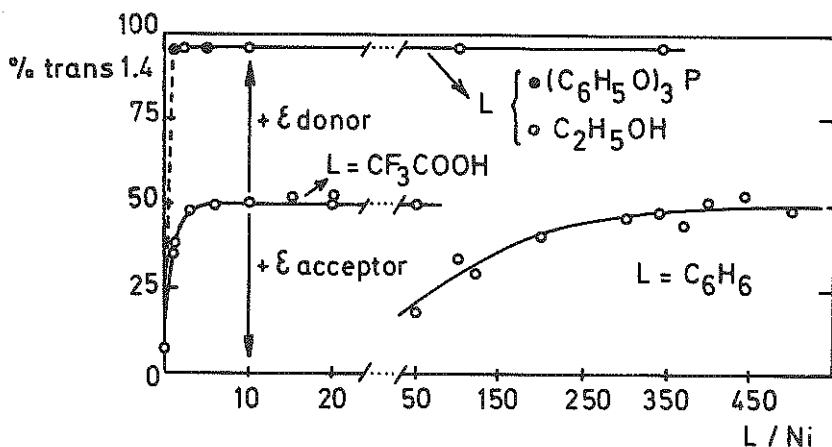
Fig. 5. Coordination equilibria in equibinary 1,4-polybutadiene formation. (Courtesy of J. Polymer Sci. A1, 987 (1970)).

(1) This equibinary composition is reached asymptotically when adding increasing amounts of ligand (i.e., olefinic, aromatic or chlorinated hydrocarbons, or trifluoroacetic acid). Furthermore, the 50/50 composition is obtained with more or less important proportions of ligand, depending on the nature of this ligand; in other words, a greater curvature of the plots in Fig. 5 might reflect a higher relative stability (K_f) of the new active entity L-Allyl Ni (-BD).

(2) The phenomenon is reversible as expected for a simple coordination control: elimination of the ligand (i.e., by evaporation) or addition of stronger ligands either donor or acceptor), affects the stereospecificity.

(3) Finally, it should be stressed that the complex is highly specific. The amount of a third isomer remains very low; i.e., in the case of (1,4 *cis*-1,4 *trans*) polybutadiene, the content of 1,2 units is usually lower than 1%. On the other hand, the equibinary composition can be obtained in a very broad range of concentrations and temperatures (from –10 to +70°).

These data suggest that the formation of the equibinary polymers depends on a new, different, and specific catalytic center, as shown by the fractionation of a 1,4-polybutadiene having an intermediate geometric composition (Table 2). (This sample was obtained by adding a limited amount of aromatic ligands to the complex generating the *cis*-polymer).

TABLE 2.

Fractionation of a 1,4 polybutadiene of intermediate composition.

Product	% weight	% *cis* 1,4
Total crude	100	66
Insol. in C_6H_6/CH_3OH	70	75
Sol. in C_6H_6/CH_3OH	30	48

The results show clearly that there are two different catalytic centers in equilibrium, the first one yielding a high *cis*, and the other one the equibinary polybutadiene. The same fractionation of an equibinary 1,4–polybutadiene does not change its 50/50 composition(27).

It should be emphasized that these *cis/trans* isomerisms are directly and irreversibly controlled by the catalyst during the polymerization reactions. In other words, a pre–formed polybutadiene polymer cannot be isomerized by the catalyst.

2.3.2) *Structure of the active center.* NMR studies have revealed that the complex carrying the growing chain in the equibinary 1,4–butadiene polymerization $((ANiTFA)_2$ in benzene) is predominently in the form of a binuclear *syn*–h^3–allylnickel complex. Obviously, these results do not prove the actual structure of the complexes in the active state, and could well represent a "dormant" situation. (That could be corro–borated by a definite increase of resolution in the spectra when the reaction is stopped(17), by lowering the temperature of exhausting the monomer). In particular, it is most pro–bable that the reaction proceeds through a h^1–allyl type of bonding of the polymer chain in the insertion step.

The binuclear structure of the active catalytic center is supported by the results gathered in Fig. 6. Comparison with Fig. 5 showed that under conditions specific for equi–binary polymerization, a decrease in catalyst concentration causes a return to the specificity characteristic of the com–plex before addition of the solvent–ligand (this being event–ually the monomer itself), although the same amounts of this
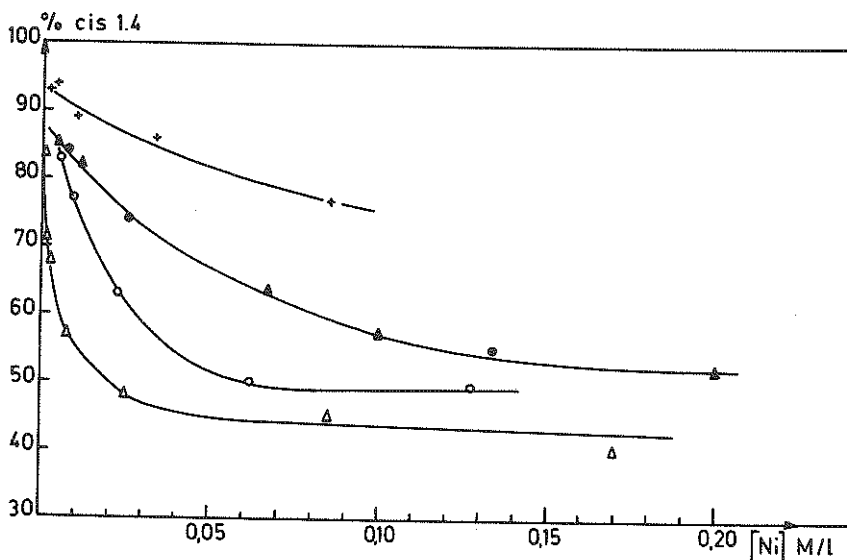
Fig. 6. Competition between cis 1,4- and equibinary 1,4-orientations in function of catalyst concentration, in butadiene polymerizations by (ANiTFA)$_2$. + Polymerization in heptane, 40°C; ● Bulk polymerization, 5°C; ▲ Bulk polymerization, 40°C; O Polymerization in benzene, 5°C; △ Polymerization in benzene, 40°C; [BD] = 2.5 M when polymerized in solution.

solvent–ligand is still present. Even in *n*–heptane, where the catalyst gives a high *cis*–content, an increase of this catalyst concentration leads to a definite increase in the *trans* content.

These key–experimental results can be easily explained (20) if one assumes that the equibinary polymer is formed on a binuclear complex, which dissociates upon dilution to give a mononuclear species; the latter is responsible for the formation of pure *cis*–polybutadiene because this complex is capable of accomodating the monomer in the bidentate conformation. Alternatively, the formation of the *cis*–isomer in the equibinary polymer might imply a temporary rupture of one of the bridging bond of the binuclear complexes, to liberate the necessary additional coordination position; the severed bridging bond being restored after monomer insertion to the binuclear structure. The role of the ligand–solvent is probably to stabilize the binuclear form (i.e., by coordination in an apical position), against the different competing coordination equilibria (monomer, spontaneous dissociation, ...).

2.3.3) *Distribution of the equibinary isomeric units in the chain: a new type of control of the polymer structure.* To account for this 50/50 specific composition, several hypotheses can be considered a priori(27).

(1) The formation of equal weights of *cis*-1,4- and *trans*-1,4-polymeric chains, either independent (homopolymers) or linked together in a stereoblock polymer. These two possibilities have no precedence in coordination polymerization, and can be ruled out (at least for the case of long stereosequences) by the fact that the polymer cannot be separated into fractions rich in *cis* or *trans* units. The polymer also has none of the physical properties characteristic of the pure *cis*- or *trans*-polybutadiene.

(2) Either a perfectly random or a perfectly alternating distribution of the *cis* and *trans* isomeric units along the chain. This problem has been approached by two different methods. Equibinary polymers of structural isomers such as equibinary poly(1,2-1,4)butadiene can be ozonolyzed, and analysis of the ozonolysis products permits a determination of the distribution. This method is however not applicable to equibinary polymers involving two geometrical isomers. For these polymers, one can determine the distribution with high resolution ^{1}H NMR with spin decoupling(28).

The results obtained are quite astonishing, and demonstrate again that structural controls by the coordination complexes are extremely sensitive to the reaction conditions. Poly (*cis*-1,4-1,2) butadiene(29) prepared in the conventional manner has a random distribution of the isomer units in the chain as shown by ozonolysis and NMR. The equibinary poly (*cis*-1,4-3,4) isoprene has also been studied; the ozonolysis products indicate that this polymer contains large blocks of head-tail, head-head, and tail-tail 1,4-polyisoprene units (30).

A detailed study of poly (*cis* 1,4-*trans* 1,4) butadiene formation in the presence of (ANiTFA)$_2$, revealed a still much more complex behaviour(31). Polymerization in hydrocarbon solvents (heptane + CF$_3$COOH, benzene) gave a product which is perfectly random in its distribution of the *cis* and *trans* isomers according to NMR. This distribution fits a Bernoullian type statistics, and is similar to that obtained by isomerizing a pure *cis*-1,4-polybutadiene to a 50/50 composition by usual chemical techniques(32) (Fig. 7A). In other solvents like dichloromethane, the equibinary polybutadiene obtained displays a distinct preference (∿65%) for alternating placement of *cis* and *trans* units (Fig. 7B) following a first-order Markov statistics.
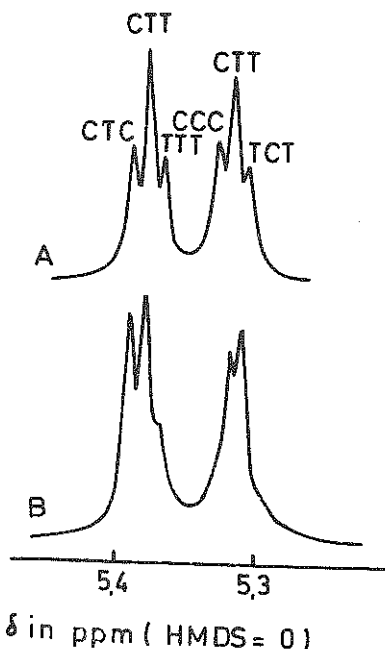
Fig. 7. High-resolution ^1H NMR spectra (olefinic protons) of random (A), and highly alternating (B) equibinary 1-4-polybutadienes.

δ in ppm (HMDS = 0)

In conclusion, the catalyst system described here appears capable of exerting certain degree of controlling the distribution of the isomeric units along the chain, without affecting the equibinary (50/50) composition(33). This control depends essentially on the temperature and the nature of the solvents, as may be expected for a coordination equilibrium between metal and solvent (ligand). This represents a new type of specific catalytic control in the coordination polymerization of diolefins.

Investigation of intermediate compositions, i.e. 75% cis-1,4/25%-trans-1,4, have indicated distributions of the Coleman-Fox type suggesting again the presence of two independent centers in equilibrium, one promoting the formation of equibinary polymer and the other one that of a stereoblock polybutadiene (predominantly cis-1,4), in agreement with the fractionation experiments reported above.

The differences found in the isomeric units distribution for polymers having the same 50% cis - 50% trans composition, raise an interesting mechanistic problem. Assuming that this type of control arises from a binuclear catalytic center, stabilized by different ligands or solvents, a random placement of pure equibinary 1,4 structure over a broad range of conditions implies probably a mutual control between two growing centers bound in the same specific complex. This

Fig. 8. Tentative scheme of the different structural controls involved in specific 1,4-butadiene polymerisations.

hypothesis fits with the fact that there is indeed one growing chain per nickel atom (see below).

A very tentative interpretation of the alternating distribution control is a modification of the relative kinetics of the monomer insertion by reaction temperature and solvent (versus some geometrical rearrangement in the binuclear complex). In other words, there would be a thermodynamic control of the equibinary phenomenon (binuclear complex stabilization), and a kinetic control of the degree of alternation (relative rate of exchange of the *cis-* and *trans-*controlling positions versus the rate of monomer insertion).

In summary, although it is still too early to propose a detailed mechanism for these controls, one could suggest tentatively the following scheme (Fig. 8) for the 1,4-polymerization of butadiene by bis(h^3-allylnickel-trifluoroacetate). It might be also worthwhile to stress that equibinary polymerization may be a general phenomenon in coordination catalysis as suggested by several recent results in copolymerization of olefins(34), in catalytic cyclopropanation of olefins(35,36) and in coordination isomerization of allylamido derivatives (37,38) (yielding in both cases 50/50 mixtures of *cis* and *trans* isomers in limiting conditions).

3) *COURSE OF THE DIOLEFINS COORDINATION POLYMERIZATION: THE DIFFERENT REACTION STEPS.*

It may be useful to conclude this review by a summary of the most characteristic kinetic features of these polymerization reactions initiated by transition metal complexes, based on the results obtained in detailed studies on the behaviour of two representative catalysts: bis(h^3-allylnickel iodide) or (ANiI)$_2$, and bis(h^3-allylnickel trifluoroacetate), or (ANi-TFA)$_2$.

3.1) Initiation Step.

Two important points emerge from the different studies already published.

(1) The allyl group initiates the polymeric chain and becomes the terminus of this chain, formed by successive insertions of monomer molecules. The reaction scheme given below has been ascertained by g.l.c.(39), infrared spectrometry(39), and NMR measurements(17). The structure of the products obtained by using a h^3-crotyl complex(17) suggests that a *cis*-rearrangement mechanism is preferred over an outer-sphere electrocyclic rearrangement of the Powell's type (this latter mechanism would require the unlikely pre-

sence of the chain on the carbon atom directly σ-bonded to the metal in the reactive h^1-allyl form).

Initiation

$$\downarrow \quad 1 \ C_4H_2D_4$$

Propagation

$$\downarrow \quad n \ C_4H_2D_4$$
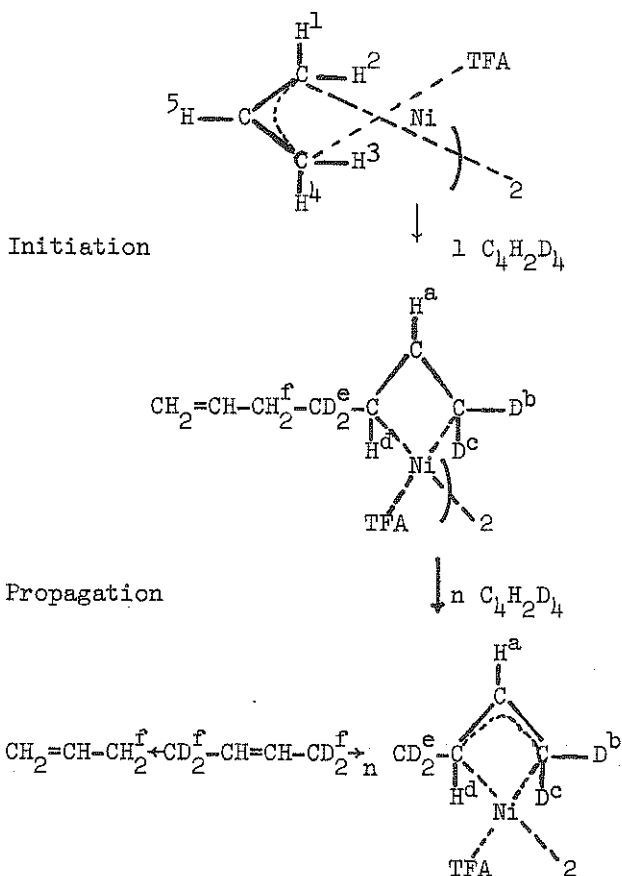
(2) The initiating complex is rather rapidly consumed even at low monomer/catalyst (M/C) ratios(39,40). This implies that every metal atom can be active even if the catalytic centers remain under the form of a binuclear complex. In fact the propagating center differs from the original complex only in the substitution of the C^3 in the allyl group by the polymer chain. With substituted dienes, the initiation rate may be higher while the propagation rate is lower(41,42) than with butadiene.

3.2) Propagation Step.

Relative initiation and propagation rates have been determined by NMR measurements on the polymerizing mixture

(39,40). From the ratios of the CH_2^e and CH_2^f resonance peaks, one finds that k_p is certainly greater than k_i, but both have the same order of magnitude. This is expected from complexes having very similar structures. The reaction rate is usually first order in monomer concentration, in agreement with the above coordination scheme for a binuclear complex. The order in catalyst concentration depends on several factors. With $(ANiI)_2$, it varies from 0.5 to 1 (43,22,23,44) with decreasing catalyst concentration suggesting that under these conditions *trans*-1,4 polymerization takes place on a mononuclear species formed in a rate-determining dissociation step. With $(ANiTFA)_2$ under conditions yielding the equibinary polymer, i.e., aromatic solvents, the kinetics is first order in catalyst concentration(45); this corresponds to two chains growing on a binuclear catalytic complex and every nickel atom being active.

$\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ have the usual values for this type of polymerization, i.e. around −20 e.u. (23) and 10 to 15 Kcal/Mole(23,43,45), respectively. It has also been shown in several cases that the overall rate of these processes usually increase with the polarity of the solvents(22,46).

3.3) Transfer Reactions.

The fact that every nickel atom is active and initiates one growing chain by these catalysts suggests a living system. Behaviors characteristic of a living polymerization have been indeed observed; one such example is shown by seeding-resumption experiments(39). However, at higher M/C ratios, the molecular weights do not increase anymore, indicating the interference of transfer reactions(22,39). Depending on the catalyst structure, they are more or less influenced by solvent; for example o-dichlorobenzene can greatly decrease these chain transfers(39).

A mechanistic proposal based on a hydride shift(47) has been confirmed by NMR spectra, indicating(39) the presence of crotyl complexes at the end of polymerizations initiated by $(ANiTFA)_2$. Transfer reactions have also been observed when the structure of the active site is altered during the course of a polymerization to synthesize block-copolymers or -stereoisomers(46).

In particular, the addition of styrene to living equi-binary polybutadiene resulted in the formation of two different homopolymers easily separated by fractionation. Similarly the addition of butadiene containing $P(OR)_3$ to the same living polymer in order to make a stereoblock containing one poly*cis* and one poly*trans* sequence resulted in the formation of the two independent pure polymeric isomers.

4) *CONCLUSIONS*

Our understanding of the diolefin coordination polymerization has clearly improved during the past decade. The basic structure of the catalyst has been elucidated by studies on well-defined allyl-complexes, and a detailed determination of the polymers microstructure has lead to a better knowledge of the mechanistic pathways.

There is no doubt however that much remains to be done in two particular directions. From a preparative point of view, the synthesis of equibinary polymers with a perfectly alternating isomers distribution is a worthwhile goal. So is the preparation of living high molecular weight polybutadienes and their block copolymers. From a mechanistical point of view, it would be most interesting on the one hand to clarify the nature of the electronic rearrangements involved (specially in terms of the rules governing the concerted reactions). On the other hand, it is becoming obvious that these elaborated stereocontrols depend on the overall geometry of the active complexes in the reaction medium. It would be most helpful to accumulate experimental informations about this actual structure in order to devise still better control of the polymers stereoregularities. It is highly probable that this knowledge can be obtained only through the simultaneous application of several physical methods such as magnetic measurements (susceptibility, EPR, NMR) and optical spectroscopy.

Even without taking into account possible unexpected new breakthroughs in the field, there are still a lot of exciting challenges in this fascinating area of research where, by very different routes, the chemists have attained a degree of activity and specificity nearly comparable to those encountered in biological systems.

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