

# MECHANISM OF DIENE POLYMERIZATION

JUNJI FURUKAWA

*Department of Synthetic Chemistry, Faculty of Engineering,  
Kyoto University, Kyoto 606, Japan*

## ABSTRACT

An industrial catalyst comprised of nickel carboxylate, boron fluoride, tri-alkylaluminum and butadiene was developed in Japan. Kinetic study suggested that catalyst structure to be  $\pi$ -allylic nickel borate. In order to elucidate the mechanism for *cis*-polymerization, the structure of  $\pi$ -crotyl nickel halides were analysed by nuclear magnetic resonance. All kinds of halides were found to possess a *syn*- $\pi$ -allylic structure irrespective of their different modes of polymerization, chloride, bromide and iodide yielding *cis*-, *cis-trans*-, and *trans*-polymer, respectively.

For the *cis*-polymerization a mechanism involving a  $\pi$ -allylic polymer terminal with an intramolecular coordination of the double bond of the penultimate unit (called 'back-biting coordination') is proposed in which a *cis*-double bond is formed not only from *anti*- $\pi$ -allylic but also from the *syn*- $\pi$ -allylic polymer terminal, because the resulting *cis*-double bond has little hindrance whereas the *trans*-one has large hindrance.

Effects of additives to the catalyst were discussed. An electron donor may coordinate to the catalyst to hinder the back-biting coordination and has a tendency to give *trans*-polymer. On the contrary, an electron acceptor releases ligand anion to remove its steric hindrance. As a result *cis-trans* (1:1) polybutadiene is formed.

Various phenomena such as the incorporation of a *trans*-unit in polymerization at a low concentration of butadiene and in the copolymerization with styrene are accounted for. 1,2-Polymerization is explained as an attack on the  $\gamma$ -position of the  $\pi$ -allylic terminal. The selection of  $\alpha$ - and  $\gamma$ -positions is controlled by the nature of the anion ligand. The polymerization of substituted dienes is also discussed, in which a large steric hindrance is considered only for  $\beta,\gamma$ -disubstituted monomer.

## INTRODUCTION

*cis*-1,4-Polymers of butadiene and isoprene are now important synthetic rubbers. *cis*-Polyisoprene is prepared with the use of alkyllithium or a Ziegler catalyst, i.e.  $\text{TiCl}_4\text{—R}_3\text{Al}$ , whereas *cis*-polybutadiene is prepared not by the above catalyst but by  $\text{TiI}_4\text{—R}_3\text{Al}$ ,  $\text{CoX}_2\text{—R}_2\text{AlCl—pyridine}$  or  $\text{NiX}_2\text{—Et}_3\text{Al—BF}_3$ , X being chlorine or carboxylate anion (Table I).

The last catalyst was developed by the research group of Bridgestone Tire Company under the guidance of the author. The chemistry of *cis*-, *trans*- or vinyl-polymerization has been investigated by several authors, but

its mechanism was not completely elucidated in spite of several postulates. In principle, the mechanism is divided into two categories. One is based on the mode of monomer coordination, *cisoid* bidentate coordination favouring the *cis*-structure whereas the unidentate one favours the *trans*-structure.

Table 1. Catalysts for *cis*-polymerization

Isoprene	Butadiene
RLi TiCl <sub>4</sub> —R <sub>3</sub> Al	RLi in h/c 1.4 ( <i>cis-trans</i> ) TiI <sub>4</sub> —R <sub>3</sub> Al CoX <sub>2</sub> —R <sub>3</sub> AlCl NiX <sub>2</sub> —Et <sub>3</sub> Al—BF <sub>3</sub>

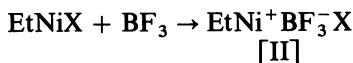
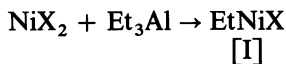
The other depends on the structure of the growing allylic polymer terminal, the *anti*-form being converted to the *cis*-double bond, whereas the *syn*-form is changed to the *trans*-one.

In this paper the author criticizes the above theories based on several experiments published by the author and other workers. A hypothesis is proposed in which the coordination of the penultimate unit on the catalyst facilitates the formation of the *cis*-configuration.

## I. INDUSTRIAL NICKEL CATALYSTS

The nickel catalyst composed of nickel carboxylate, boron fluoride and triethylaluminium was developed by the research groups of Bridgestone Tire Co., Japan Synthetic Rubber Co. and the author. The catalyst comprises nickel salt (industrially naphthenate used), boron trifluoride etherate and triethylaluminium.

The catalyst activity is much enhanced by the addition of boron fluoride without any change of *cis*-selection. The role of boron fluoride was investigated. It reacts with triethylaluminium to form diethylaluminium fluoride and ethylaluminium difluoride, the former being active but the latter not as cocatalyst. However, diethylaluminium fluoride is not an essential cocatalyst since it still requires some amount of boron fluoride to exhibit catalytic activity. Boron fluoride, as a Lewis acid, reacts with alkylnickel [I] to give a stable complex [II] which may be an active species.

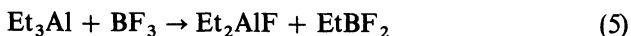
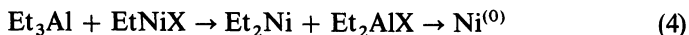
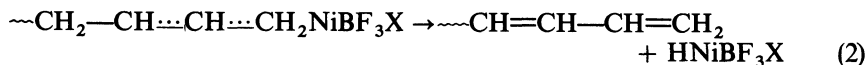


Kinetic study reveals that the polymerization is a stepwise addition of monomer accompanied by a transfer reaction<sup>1</sup> and the rate of polymerization,  $R_p$ , is expressed by equation 1<sup>2</sup>.

$$R_p = \frac{k_p[\text{Ni}][\text{Al}][\text{B}]}{k'[\text{Ni}][\text{Al}]^n + k''[\text{Al}][\text{B}]} \quad (1)$$

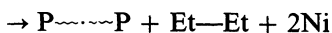
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where  $[Ni]$ ,  $[Al]$ ,  $[B]$  and  $BD$  are concentrations of  $NiX_2$ ,  $Et_3Al$ ,  $BF_3 \cdot OEt_2$ , and butadiene, respectively. Some side reactions may occur as follows:

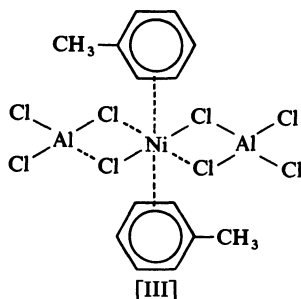


Equations 2, 3, 4 and 5 imply a hydrogen transfer, a re-initiation, a reduction of nickel to zero-valent, and a reaction between alkylaluminium and boron fluoride, respectively.

The polymerization proceeds through successive insertion of butadiene into the nickel-carbon bonds. It was found that the addition of an excess amount of triethylaluminium at the end of polymerization results in increase of the molecular weight of the polymer<sup>3</sup>. This type of molecular weight jump is different from that proposed by Ring *et al.*<sup>4</sup>. In the latter case alkyl halide is used instead of alkylaluminium and a considerable amount of branching reaction also takes place, whereas in the former case triethylaluminium added may cause a coupling reaction for molecular weight jumping.



The reaction product of nickel oxide, aluminium chloride and butadiene was also found to be an active catalyst without metalalkyl<sup>5</sup>. The catalyst was found to be of the following structure in toluene from chemical analysis, u.v. and magnetic measurement. A divalent nickel forms an octahedral complex with a coordination number of six.



## II. $\pi$ -CROTYLNICKELS AS A MODEL FOR THE GROWING POLYMER TERMINAL

$\pi$ -Crotylnickel halides were investigated as a model for a growing polymer terminal<sup>6</sup>. These halides possess some catalytic activity by themselves toward the polymerization of butadiene, chloride, bromide and iodide yielding *cis*-, *cis-trans*-, and *trans*-polymer, respectively.

These halides are obtained in crystalline dimeric forms and their structure can be analysed by n.m.r. It was found that all crotyl groups are in *syn- $\pi$* -allylic structure in spite of their different *cis,trans*-selectivity in the polymerization. This fact seems to be unfavourable for the concept based on the structure of  $\pi$ -allylic polymer terminal. It is also found that the reaction products of  $\pi$ -crotylnickel halides with benzoyl peroxide exhibit enhanced catalytic activity and *cis*-selectivity and that they have a rather  $\sigma$ -allylic crotyl group from i.r. observation. The product is found to be crotyl nickel benzoate of an association number of 6–10.

Durand *et al.*<sup>7</sup> reported that  $\pi$ -allylic nickel trifluoroacetate is also a similar *cis*-polymerization catalyst. It forms a crystalline dimeric complex but it is dissociated to a monomeric one in the presence of butadiene or a strong basic ligand such as triphenylphosphite. The catalyst is *cis*-selective, but is transformed to *trans*-selective by the addition of basic ligand. They<sup>8</sup> also found an interesting phenomenon that the addition of an excess amount of trifluoroacetic acid to  $\pi$ -allylic nickel trifluoroacetate alters the catalyst from *cis*-polymerization-selective to *cis-trans*(1:1)-selective. This fact suggests that there are several kinds of active species: *trans*, *cis* and a *trans-cis*(1:1)-selective one depending upon the kind of additives.

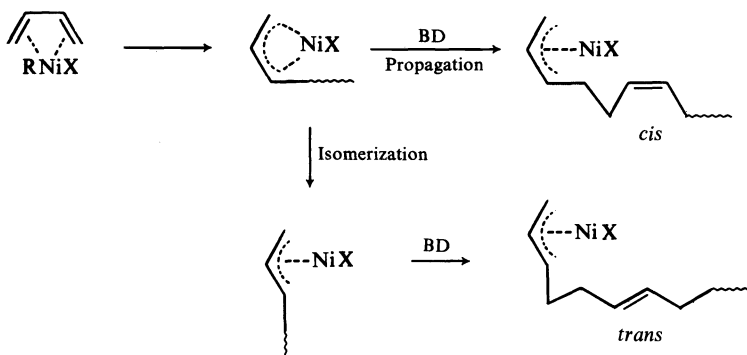
### III. STRUCTURE OF THE GROWING POLYMER TERMINAL

The actual structure of the polymer terminal in the course of polymerization was investigated by n.m.r. with the use of deuterated butadiene monomer in the lithium-initiated polymerization by Morton *et al.*<sup>9</sup> and in the nickel-initiated one by Kormer *et al.*<sup>10</sup>. In the case of  $\pi$ -crotyl nickel iodide the growing terminal forms also a  $\pi$ -allylic nickel complex in each propagation step. Recently, a similar result was obtained by Teyssié<sup>11</sup> even in *cis*-polymerization catalysed by  $\pi$ -allylic nickel trifluoroacetate. It is surprising that in all cases the growing terminal is of *syn- $\pi$* -allylic structure irrespective of *cis*- or *trans*-polymerization. This fact seems to be unfavourable for the concept explaining the *cis*-, *trans*-selectivity in view of the structure of  $\pi$ -allylic polymer terminal. Also the concept based on the mode of monomer coordination loses its support since the effect of monomer coordination, unidentate or bidentate, if any, disappears in the stage of formation of the *syn- $\pi$* -allylic growing terminal.

To eliminate the above discrepancy Dolgoplosk *et al.*<sup>12</sup> proposed a mechanism which involves the formation of *anti- $\pi$* -allyl at first and its slow isomerization from *anti*-form to the *syn*-one during the propagation step. This assumption is based on the fact that even in the *cis*-polymerization by  $\pi$ -allylnickel chloride,  $\pi$ -allylnickel trifluoroacetate or  $\text{TiCl}_2\text{I}_2$  a considerable amount of *trans*-polymer was formed when the monomer concentration was very low. At low concentrations of monomer the propagation is slow and accompanied by an isomerization of *anti*-form to the *syn*-one.

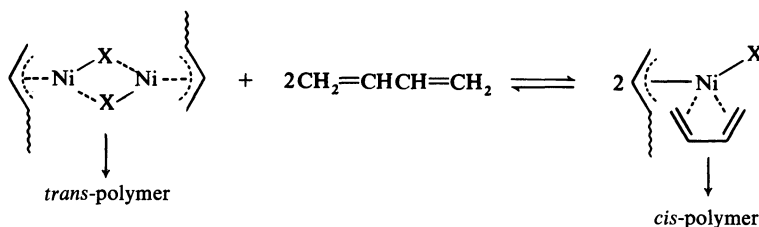
However, a system of  $\pi$ -allylic nickel trifluoroacetate with an excess amount of trifluoroacetic acid is known to yield a *cis-trans* (1:1) polybutadiene in a wide range of butadiene concentration. The concept of  $\pi$ -allylic structure modified by isomerization does not give a reasonable explanation for the fact that the *cis-trans* composition attains an extreme

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value of 1 : 1. It is rather likely to assume different active species more than two for *cis*-, *trans*-, or *cis-trans*-polymerization.

The butadiene concentration employed in their experiment was very low and there may possibly be an equilibrium between a dimeric form of  $\pi$ -allylic nickel and its monomeric one according to Teyssi's experiment<sup>13</sup>.



The author found that the degree of association estimated from cryoscopic measurement shows the transformation from a dimeric form to a monomeric one in a range of 0 to 2 moles of butadiene per unit mole of nickel. In this case the dimeric form yields *trans*-polymer whereas the monomeric one gives *cis*-polymer. The formation of 1 : 1 polymer will be discussed later.

## IV. GEOMETRICAL CONSIDERATION OF *cis*-POLYMERIZATION

The phenomena mentioned above require the re-investigation of the postulate that the *anti*- $\pi$ -allylic terminal always yields *cis*-double bonds and the *syn*-one *trans*-double bonds.

In a simple model the *anti*- $\pi$ -allylic terminal might give a *cis*-double bond whereas the *syn*-one could give a *trans*-double bond. However, in the insertion reaction of butadiene into  $\pi$ -allylic nickel, the  $\gamma$ -carbon of  $\pi$ -allyl is coordinated with nickel atom before insertion and may hold its coordination site even after the insertion of new butadiene monomer as illustrated in Figure 1.

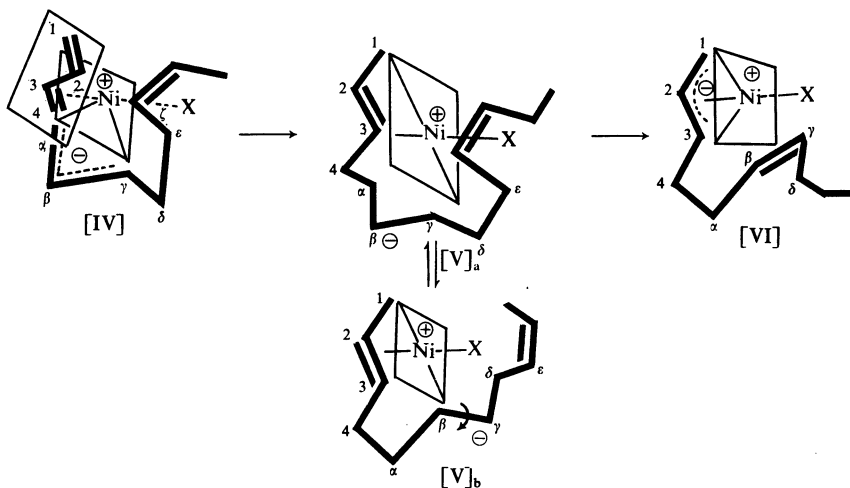


Figure 1. Geometry of complex during the addition of butadiene to *syn*- $\pi$ -allylic nickel salt.

Actually, such a type of intramolecular heptahapto-coordination is observed in a stable form in the case of hydridocobalt methylheptatrienyl<sup>14</sup> or  $\pi$ -allylic palladium<sup>15</sup>. If this type of coordination, so-called 'back-biting coordination' by the author, occurs, the mode of polymerization is somewhat complicated. Hughes *et al.*<sup>15</sup> assumed that such a type of coordination facilitates the dissociation of the dimeric nickel complex and enhances the 1,4-polymerization much more than the 1,2-one. The author points out rather the enhancement of the *cis*-polymerization by the back-biting coordination.

The *anti*- $\pi$ -allylic terminal favours the formation of the *cis*-double bond, but the formation of *cis*-double bond is also possible from the *syn*- $\pi$ -allylic terminal. In this scheme the reaction takes place between the 4-position of butadiene monomer and the  $\alpha$ -position of *syn*- $\pi$ -allylic terminal in a complex (IV) to give an intermediate [V]<sub>a</sub>. In the second stage the  $\beta$ - $\gamma$  bond transforms to the double bond, which coordinates again to the metal in a mode of back-biting. Since this transformation proceeds under the influence of the previous back-biting coordination of the  $\zeta$ -*i* double bond, the  $\beta$ - $\gamma$  bond forms favourably rather *cis*-double bond. Moreover, in the final stage [VI] the back-biting coordination of the  $\beta$ - $\gamma$  double bond allows the bidentate coordination of a new butadiene monomer only when the  $\beta$ - $\gamma$  double bond is of *cis*-structure, because the *trans*-double bond, if formed, hinders the successive coordination of the next monomer. In this scheme the rotation of the  $\beta$ - $\gamma$  bond is necessary and this may be possible through the intermediate [V]<sub>b</sub>, since [V]<sub>b</sub> includes a five-membered ring with Ni-atom and 3-, 4-,  $\alpha$ -, and  $\beta$ -carbon and is more stable than [V]<sub>a</sub>.

From the consideration of orbital symmetry anionic polymerization is assumed, where electrons move from the highest occupied orbital of  $\pi$ -allyl to the lowest vacant orbital of butadiene. Figures 2 and 3 illustrate both orbitals and their symmetry.

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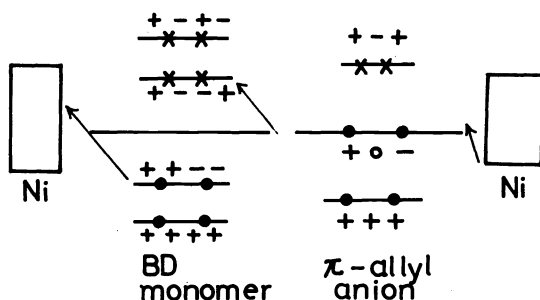


Figure 2. Molecular orbitals of butadiene,  $\pi$ -allyl anion and nickel with the symmetry symbol.

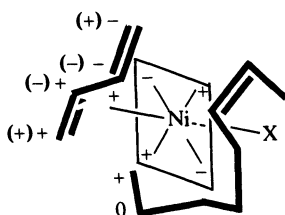
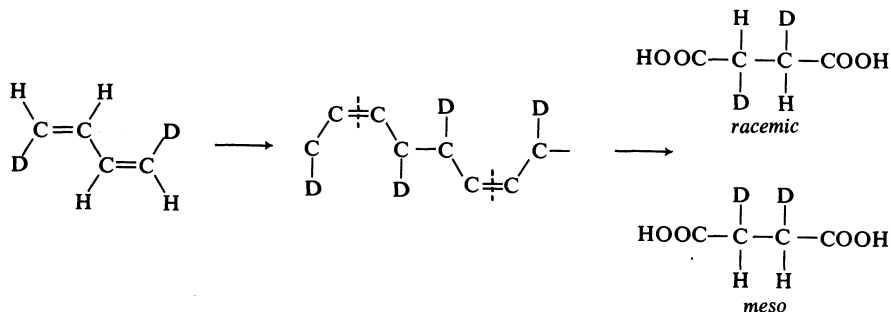


Figure 3. An arrangement of butadiene, *syn*- $\pi$ -allyl anion and *cis*-double bond on nickel allowed by the symmetry rule.

In the actual case, both *anti*- and *syn*- $\pi$ -allylic metal complexes were known. Natta reported that hydridocobalt methylheptatrienyl with butadiene forms a complex having an *anti*- $\pi$ -allylic structure, whereas  $\pi$ -allylic nickel complexes were found to exist in a *syn*- $\pi$ -allylic form both in  $\pi$ -crotyl complex and in the polymer terminal. The structure of the polymer terminal during the polymerization catalysed by cobalt catalysts was not known and therefore it is not clear whether the *cis*-polymerization proceeds through *anti*- $\pi$ -allylic polymer terminal or through a *syn*- $\pi$ -allylic one. In the case of the nickel catalyst the polymer terminal was known to be a *syn*- $\pi$ -allylic complex even in the case of *cis*-polymerization. At least the latter case can be explained by the isomerization with the help of back-biting coordination.

On the other hand, the geometry of polymerization of butadiene was investigated by Porri *et al.*<sup>16</sup> with use of *cis,cis*- $d_2$ -butadiene as a monomer.



Oxidation of the polymers was found to give racemic succinic acid from the *cis*-polymer prepared with nickel catalyst whereas that with titanium iodide catalyst was the *racemic-meso* (1 : 1) product.

This experiment provides information about the mode of opening of the double bond and attacking of the anion.

Figure 4 illustrates modes of polymerization according to the back-biting mechanism. In order to fit the result that the *cis*-polymer obtained by nickel catalysts yields racemic products, the monomer is required to coordinate in a *transoid* form.

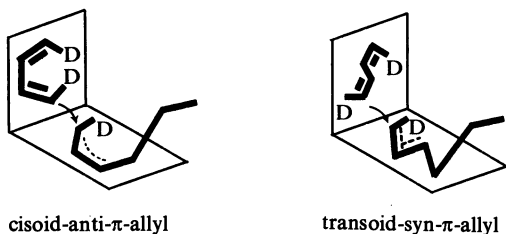


Figure 4. Opening mode of double bond and direction of anion attack to  $\pi$ -allylic polymer terminal compatible with Porri's experiment.

In these respects, the mechanism of the *cis*-polymerization by a nickel catalyst can be explained in terms of the back-biting and *syn*- $\pi$ -allylic coordination. In other cases with cobalt or titanium as catalyst, the structure of the polymer terminal was not known and accordingly the possibility of *anti*- $\pi$ -allylic mechanism has still to be discussed as well as the *syn*- $\pi$ -allylic one. It is emphasized at least in the case of the nickel catalyst that the *cis*-polymerization can occur irrespective of *anti*- or *syn*- $\pi$ -allylic terminal when a back-biting coordination is considered.

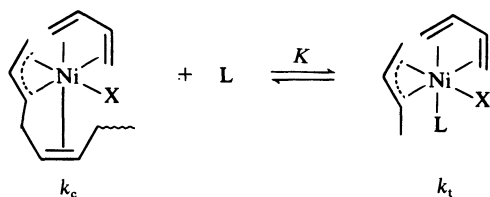
## V. EFFECT OF ELECTRON-DONOR AND ACCEPTOR

It was known that the *cis*-content of the polybutadiene can be varied by the addition of electron-donor substances such as ether or amine. Durand *et al.*<sup>17</sup> reported a quantitative change of *cis*-content induced by the addition of various kinds of donor-substances such as phosphite or alcohol and of acceptors such as trifluoroacetic acid or dichlorobenzene to  $\pi$ -allylic nickel trifluoroacetate. Interestingly, the former increases *trans*-content up to 100 per cent, whereas the latter up to 50 per cent, yielding a *cis-trans* (1 : 1) polybutadiene. Such a saturation phenomenon suggests the existence of a specific active site for the *trans*-polymerization and the *cis-trans* (1 : 1) polymerization in addition to that for the *cis*-polymerization.

According to the back-biting coordination mechanism the effect of donor-substances is explained in terms of the coordination of donor, which prohibits the back-biting coordination and thus the *cis*-polymerization, while it promotes the *trans*-polymerization. According to the following equilibrium,



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the fraction of *trans*-double bond formed is expressed by equation 6,

$$\frac{\text{trans}}{\text{trans} + \text{cis}} = \frac{k_t K [\text{L}]}{k_c + k_t K [\text{L}]} \quad (6)$$

where  $[\text{L}]$  is the concentration of donor-substance.  $K$  is an equilibrium constant and  $k_t$  and  $k_c$  are the rate constant of *trans*-polymerization caused by donor-coordinated species and that of *cis*-polymerization by non-coordinated species, respectively.

In contrast, electron acceptors may act on the ligand  $X$  so as to release it and as a result, the steric effect of the ligand  $X$  is decreased. Not only *cis*-double bond but also the *trans*- one can undergo the back-biting coordination as illustrated in Figure 5.

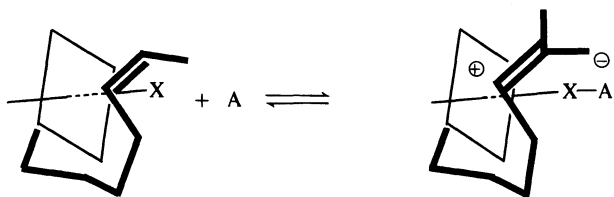
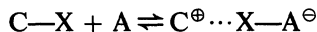


Figure 5. Effect of electron-acceptor: released ligand  $X$  allowing both *cis*- and *trans*-double bond in a back-biting coordination.

In the following equilibrium,



two kinds of catalyst species are assumed,  $\text{C}-\text{X}$  being responsible for *cis*-polymerization with a rate constant of  $k_c$  and  $\text{C}^{\oplus} \cdots \text{X}-\text{A}^{\ominus}$  for *cis*- and *trans*-one with rate constants of  $k'_c$  and  $k'_t$ , respectively. In the latter species a steric hindrance of ligand  $X$  is diminished and as a result the back-biting coordination becomes possible not only for the *cis*-double bond but also for the *trans*-one. In other words,  $k'_t$  is almost equal to  $k'_c$  and it follows that

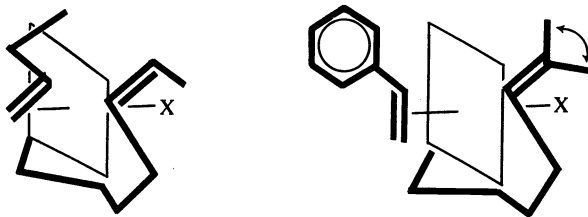
$$\frac{\text{cis}}{\text{trans}} = \frac{k_c + k'_c K [\text{A}]^n}{k'_t K [\text{A}]^n} = 1 + \frac{k_c}{k'_t K [\text{A}]^n} \quad (7)$$

Equation 7 was found to fit Durand's<sup>17</sup> data, giving the following values:

Acceptor	$n$	$k_c/k'_t K [\text{A}]^n$
$\text{CF}_3\text{COOH}$	0.38	0.9
<i>o</i> -Dichlorobenzene	1.8	900

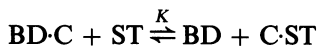
A similar phenomenon was reported by Teyssié *et al.*<sup>18</sup> in a copolymerization of butadiene and styrene, in which the *cis*-configuration of the butadiene unit in the copolymer is decreased from 100 per cent to 50 per cent with increasing amounts of styrene monomer in the feed.

According to the back-biting coordination mechanism styrene monomer coordinated to the catalyst unidentately leaving another vacant coordination site. In other words styrene monomer exhibits less hindrance to the back-biting coordination than butadiene monomer and consequently, a polymer of *cis-trans* (1:1) composition is afforded as illustrated in *Figure 6*.



*Figure 6*. Bidentate coordination of butadiene and the unidentate one of styrene effecting the mode of back-biting coordination.

In the following equilibrium among styrene (ST), butadiene (BD) and catalyst (C),

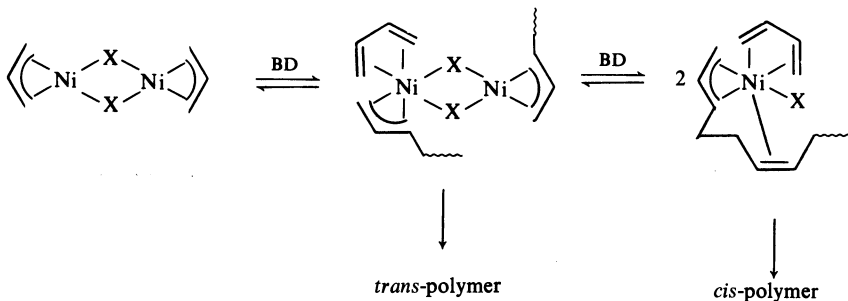


it is likely to be assumed from the similar nature of styrene and butadiene that  $k'_c = k'_t = k_c$  and  $K = 1$ , and it follows that,

$$\begin{aligned} \text{cis/trans} &= 1 + \frac{[\text{BD}]}{[\text{ST}]} \\ (\text{cis} + \text{trans})/\text{cis} &= 2 - \frac{[\text{BD}]}{[\text{BD}] + [\text{ST}]} \end{aligned} \quad (8)$$

Teyssié's data seem to agree with equation 8.

The dimeric nickel complex occurring at low butadiene concentration seems to give *trans*-polymer. This may be explained by the assumption that the available vacant site is so limited by bridged ligand that the back-biting coordination is hindered as shown in *Figure 7*.

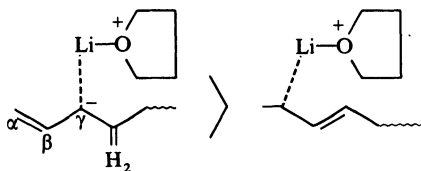


*Figure 7*. Mode of coordination of dimeric and monomeric complexes.

## VI. 1,2-POLYMERIZATION

1,2-Polybutadiene is prepared by lithium or alkyl lithium in the presence of a donor substance such as tetrahydrofuran or tetramethylethylenediamine. Under these conditions the growing polymer terminal exists in a  $\pi$ -allylic anion according to Morton *et al.*<sup>9</sup> In a hydrocarbon solvent, on the contrary, the terminal exists in a  $\sigma$ -allylic form and 1,4-polymer composed of *cis*- and *trans*-units is formed. The reason for the formation of the latter polymer is explained in terms of the back-biting coordination mechanism. In fact, such a type of coordination is observed by Oliver<sup>19</sup> in the case of butenyl-lithium by n.m.r. *cis-trans*-Selection in lithium-initiated polymerization is not conducted and this fact may be ascribed to the absence of anion ligand controlling *cis-trans* structure unlike the case of the nickel catalyst.

The formation of 1,2-polybutadiene in donor solvent is associated with high reactivity of  $\gamma$ -carbon of a  $\pi$ -allylic anion, because the  $\gamma$ -position is much more activated than the  $\alpha$ -position due to the hyperconjugation with the neighbouring methylene group.



1,2-Polybutadiene is also prepared by catalysts<sup>20</sup> of titanium alkoxide or vanadium acetylacetonate with trialkylaluminium. One explanation for the formation of 1,2-polybutadiene by these catalysts is given by the lower electronegativity of these transition metals than nickel and the lower electron-attractive nature of alkoxide or acetylacetonate than chloride. These catalysts yield  $\pi$ -allylic anions similarly to the allylic lithium.

It is interesting to note that a 1:1-polybutadiene with respect to *cis*-1,4- and 1,2-structure is prepared by catalysts of cobalt acetylacetonate-triethylaluminium with water<sup>21</sup> and molybdenum alkoxyhalide with excess amount of triethylaluminium<sup>22</sup>. In the latter case the addition of three moles of  $\text{Et}_3\text{Al}$  affords a catalyst for the 1,2-polymerization and that of ten moles a catalyst for the 1,2-*cis* (1:1) polymerization. The role of water or an excess amount of triethylaluminium is not clear but it seems likely that

Table 2. Catalysts for equibinary polybutadiene

<i>cis-trans</i>	$\pi$ -allyl Ni-OCCF <sub>3</sub> + CF <sub>3</sub> COOH	
	1 : 10	
	(Teyszié)	
<i>cis-vinyl</i>	$\text{CoX}_2 + \text{Et}_3\text{Al} + \text{H}_2\text{O}$	1,2- <i>cis</i>
	$\text{R}_m\text{MoX}_n + 3\text{R}_3\text{Al}$	1,2
	$\text{R}_m\text{MoX}_n + 10\text{R}_3\text{Al}$	1,2- <i>cis</i>
		(Furukawa)

other active species are formed by the reaction with water to give a metal oxide or with triethylaluminium to give a lower-valent metal complex. As summarized in *Table 2* it seems that the more electron-attracting ligands such as halogen favour the 1,4-addition whereas the less electron-attracting ones such as alkoxide or acetylacetonate favour the 1,2-addition. The removal of ligands by an excess amount of alkylaluminium brings about an equivalent balance between the 1,4- and 1,2-additions.

The *cis*-1,4-1,2-equibinary polybutadienes formed by the above catalysts were subjected to ozonolysis or  $^{13}\text{C}$ -n.m.r. They were found to be of random structure with respect to the 1,4- and 1,2-units. Therefore there seems to be no penultimate unit effect.

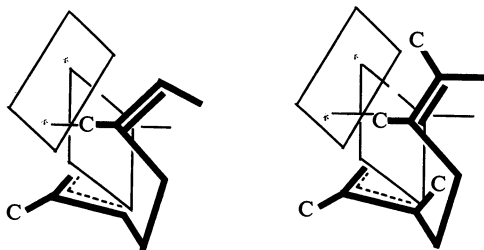
## VII. SUBSTITUTED DIENES

In the back-biting coordination mechanism a substituent at the 2-position of butadiene has a slight steric hindrance whereas that in the 3-position has a large one. For example, isoprene or cyclohexadiene gives a *cis*-rich polymer, but 2,3-dimethylbutadiene yields a *trans*-polymer with  $\pi$ -crotyl nickel chloride. A similar result was obtained in the copolymerization of diolefins with acetylene by a catalyst of Ni-naphthenate- $\text{Et}_2\text{AlCl}$ <sup>23</sup> as listed in *Table 3*.

*Table 3.* *cis*-1,4- and 1,2-polymerization catalysts of various transition metal complexes with additives

	Ti	V	Mo	Co	Ni
X	1,4		1,2	1,4- <i>cis</i>	1,4
Acac		1,2			
RO	1,2				
H <sub>2</sub> O				1,2- <i>cis</i>	
R <sub>3</sub> Al excess			1,2- <i>cis</i>		Oligomer

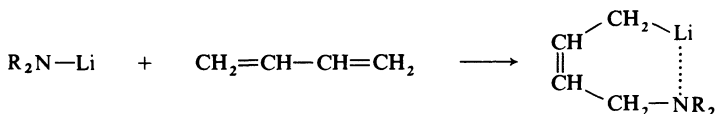
In the alternating copolymerization of butadiene with propylene by a catalyst of  $\text{VO}(\text{acac})_2\text{-Et}_3\text{Al-Et}_2\text{AlCl}$ , the structure of the butadiene unit in the copolymer was found to be all-*trans* in contrast to the copolymerization of butadiene with acetylene<sup>24</sup>. In the former case the propylene unit does not perform the back-biting coordination whereas in the latter case the acetylene unit does, as illustrated in *Figure 8*.



*Figure 8.* Difficulty of back-biting coordination of poly-2,3-dimethylbutadiene as compared with polyisoprene.

## MECHANISM OF DIENE POLYMERIZATION

An idea of back-biting coordination seems to be useful for the explanation of the oligomerization of butadiene and other related reactions. For instance, the formation of *cis*-adduct of butadiene with amines catalysed by butyllithium was reported by Tsuruta<sup>2,5</sup>, which may be accounted for by an assumption of the back-biting coordination of the amino group in the intermediate.



## CONCLUDING REMARKS

The back-biting coordination mechanism is merely one of the working hypotheses for the explanation of *cis*-polymerization. Direct investigation of back-biting coordination is scheduled but it seems to be very difficult at present, because additives such as ether or alkyl phosphine are necessary for stabilizing a nickel catalyst and they may disturb the measurement of back-biting coordination.

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