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Tsuyoshi Matsumoto^{ab}; Junji Furukawa^a

^a Department of Synthetic Chemistry, Kyoto University, Kyoto, Japan ^b Japan Synthetic Rubber Co., Ltd., Kyobashi, Tokyo, Japan

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A Proposed Mechanism of the Stereospecific Polymerization of Butadiene with a Transition Metal Catalyst

TSUYOSHI MATSUMOTO* and JUNJI FURUKAWA

Department of Synthetic Chemistry
Kyoto University
Kyoto, Japan

ABSTRACT

The proposed mechanism is based upon an experimental study of nickel catalysts, quantum chemical considerations, and polymerization results with various transition metal catalysts. It is concluded that polymerization proceeds through a σ -allyl metal complex, at least in cis-1,4 polymerization and the energy level of the transition metal orbital which receives the π -electrons of butadiene is a decisive factor in determining the microstructure of the polymer. According to the mechanism, the polymer of predominantly cis-1,4 structure is obtained only in the case the energy level is in the vicinity of that of the highest occupied orbital of butadiene, and, in the case where the former level is sufficiently apart from the latter, predominantly 1,2 or trans-1,4 polymer is afforded. It is found that the polymerizations resulting with various catalysts are in line with the mechanism.

*Present address: Japan Synthetic Rubber Co., Ltd., Kyobashi, Tokyo, Japan.

INTRODUCTION

The stereospecific polymerization of butadiene was not achieved until transition metal catalyst was applied to the polymerization. Many catalysts have been found for it, and the polymer of high *cis*-1,4 content has been industrially produced. Titanium, cobalt, and nickel catalyst systems have been developed in the United States, Italy, and Japan [2, 9], respectively. The authors have found several types of nickel catalyst [1-3, 5-9] and have studied the nature of the active site and the mechanism of the polymerization [1-8].

The mechanism of the stereospecific polymerization of diene is one of the interesting problems both in polymerization chemistry and in transition metal chemistry. Many considerations of the mechanism have appeared in the reports of Arlman [12], Natta et al. [13], Porri et al. [14], Furukawa [15], Van de Kamp et al. [16], Dolgoplosk et al. [17, 18], Kormer et al. [19], Otsuka [20], and Durand et al. [21]. But it seems to the authors that some of them include interpretations that conflict with experimental results of the authors, some may be applied only to the catalysts presented in their reports, and some are confined to show a condition which yields *cis*-1,4 polymer, indicating no logical relation between the condition and stereospecificity.

The present investigation is aimed at the presentation of a mechanism of stereospecific polymerization of butadiene which interprets the polymerization results obtained by various transition metal catalysts without a logical gap between theory and result. It is based on experimental results obtained by nickel catalysts and quantum chemical consideration.*

EXPERIMENTAL

Materials

π -Allyl or π -crotyl nickel halides were prepared from nickel carbonyl and allyl or crotyl halides according to the method of Fisher [22]. Benzoyl peroxide, chloranil, and tetracyanoethylene were obtained commercially and purified by ordinary method. *p*-Substituted benzoyl peroxides were prepared by the reaction

*The present mechanism has been partly reported in two meetings [10, 11].

of p-substituted benzoyl chlorides with sodium peroxide according to the procedure in Organic Synthesis [23]. Oxygen was of 99.999% purity and dried by passing through molecular sieves. Butadiene was of BR (butadiene rubber) grade provided by Japan Synthetic Rubber Co., Ltd., and dried over molecular sieves. Benzene was freed of oxygen and water by distillation over the metal ketyl from sodium and benzophenone.

Polymerization

Polymerizations were carried out in glass reaction vessels in a nitrogen atmosphere. Dry butadiene was introduced by distillation to the vessels by the use of a vacuum-nitrogen apparatus. Polymerizations were terminated by addition of methanol containing aqueous hydrochloric acid.

Reaction of π -Allyl Nickel Halide with Benzoyl Peroxide or Substituted Benzoyl Peroxide

A solution of benzoyl peroxide or substituted benzoyl peroxide was added to π -allyl nickel halide solution with shaking. The reaction mixture was aged for about 30 min at room temperature. In the case of polymerization in benzene solution, a precipitate was formed within a few minutes after the addition of benzoyl peroxide.

Reaction of π -Allyl Nickel Halide with Oxygen

A two-necked flask was connected through a cock to a gas buret which was filled up with oxygen gas. A solution of the π -allyl nickel halide was introduced into the flask in a nitrogen atmosphere. The flask was evacuated after it was cooled in a Dry Ice-methanol bath. After it was warmed to the desired temperature, a given volume of oxygen was gradually introduced with stirring by opening the cock. A precipitate formed when benzene was used as a solvent.

The reaction was usually carried out at room temperature and was stopped by cooling again to about -70°C . Unreacted oxygen was replaced with nitrogen after a check of the volume of reacted oxygen.

Separation of Benzene Insoluble Nickel Complexes

Precipitates obtained in the above reactions were nickel complexes insoluble in benzene. When the reaction mixture was used as catalyst, the above procedure was carried out in polymerization vessels. In other cases the complexes were separated from the reaction mixture by filtration in nitrogen atmosphere followed by washing several times with benzene and then drying in vacuo. They were transferred to polymerization vessels in a nitrogen box.

Infrared Spectroscopy, Magnetic Susceptibility Measurement, and Elemental Analysis of Nickel Complexes

The samples were prepared under nitrogen atmosphere by means of a dry box or other instruments for measurement. The infrared spectra were recorded on HITACHI grating spectrometer EPI-G. Magnetic susceptibility was measured by the Gouy method using a Sartorius 2514 type balance and a Nihon Komitsu 100 type electromagnet. Elemental analysis was done with independent samples for each element.

Hydrolysis of Nickel Complexes

Nickel complexes were placed in a flask equipped with two necks, one connected with a gas buret and a vacuum-nitrogen apparatus and the other closed with a rubber stopper. Aqueous hydrochloric acid was added by a syringe through the rubber stopper. The gas evolved was identified by vapor-phase chromatography with activated charcoal.

Microstructure of the Polymers

The polymers were examined in carbon disulfide solution. The method of analysis is that reported by Morero et al. [24].

Fractionation of a Polymer

One gram of the polymer was immersed in 50 ml diethyl ketone with occasional stirring for 60 hr at 10-20°C. The mixture was separated by filtration. The insoluble part was dipped in carbon disulfide for about 1 min and then filtered. The filtrate was coagulated with methanol.

RESULTS AND DISCUSSION

The terminal of polybutadiene initiated by a transition metal catalyst forms an allyl metal complex. There are two possible structures, i.e., π -allyl and σ -allyl structure. π -Allyl complex may exist in syn or anti form. If the polymer terminal is of a π -allyl metal complex, cis-1,4 polymerization should proceed through the anti form. The conformation of a π -allyl metal complex may depend upon the metal and ligands attached to the metal.

Accordingly, the first step in the consideration of the mechanism of the stereospecific polymerization is to establish whether the mechanism of the living polymer terminal is of a π -allyl metal complex or not. As an alternative, the mechanism based on the mode of monomer coordination, bidentate or monodentate, is considered for the stereocontrol.

The Structure of the Growing Polymer Terminal

It is well known that π -allyl nickel chloride affords a cis-1,4 polymer, whereas π -allyl nickel iodide affords a trans-1,4 one [14]. For this sort of polymerization, the mechanism involving a π -allyl growing polymer terminal is proposed by Komer et al. [19], Porri et al. [14], and Dolgoplosk et al. [17, 18], although they are different from one another in some minor points.

If the growing polymer terminal in the polymerization with the catalyst is π -allyl complex and the microstructure of the polymer depends upon the syn-anti isomer ratio affected by the kind of halogen attached to nickel as typically asserted by Komer et al. [19], the syn-anti ratio of π -crotyl (1-methyl allyl) nickel halide is also considered to be affected by the kind of halogen in a similar way.

The authors investigated the structure of the π -crotyl nickel halide by IR and NMR spectroscopy [4] and found that both the chloride and iodide are exclusively in syn form, in spite of the fact that the former affords a cis-polymer and the latter a trans one. The result shows the importance of the monomer coordination mode, and Kormer's mechanism seems to be ruled out. It is rather favorable to the mechanism of σ -allyl growing terminal.

The authors reported that the benzene-insoluble but tetrahydrofuran-soluble nickel complexes were formed in the reaction of π -allyl nickel halide with oxygen [5, 6, 8]. Elemental analysis, IR spectroscopy, hydrolysis, and magnetic susceptibility measurement of the benzene-insoluble complex lead us to the conclusion that the allyl group in the complex exists in σ -allyl form, and the butadiene polymerization in benzene with the nickel complex proceeds through a σ -allyl polymer terminal complexed with the nickel atom, at least in cis-1,4, polymerization.

The polymer containing 65-70% cis-1,4, 25-30% trans-1,4, and 5% 1,2 structure was yielded by the nickel complex prepared from π -allyl nickel iodide and oxygen. In order to investigate the problem of whether or not two kinds of active center exist, one of which yields cis polymer and the other trans one, fractionation of the polymer was attempted with diethyl ketone and carbon disulfide. The solubility of cis-1,4 polymer in diethyl ketone is much larger than that of trans-1,4.

For comparison, Sample I was prepared by mixing a polymer of 90% cis-1,4 content with that of 95% trans-1,4 in solution, followed by precipitation, to form the mixture of 70% cis-1,4, 25% trans-1,4, and 5% 1,2 configuration. From this mixture, a powdered polymer of 95% trans-1,4 content was recovered in the procedure described in the experimental section with a yield of 83% with respect to trans polymer. On the other hand, the polymer obtained by the nickel complex catalyst, which was 67% cis-1,4, 28% trans-1,4, and 5% 1,2 configuration, and resembles tissue paper in appearance, was hardly soluble in diethyl ketone. The polymer recovered after the same treatment as that for Sample I was 61% cis-1,4, 34% trans-1,4, and 5% 1,2 configuration and is like tissue paper in appearance.

The results suggest that the nickel complex catalyst prepared from π -allyl nickel iodide and oxygen affords a copolymer of cis-1,4 and trans-1,4 units arising from an essentially uniform active site. Since IR analysis showed that allyl group is of the σ -allyl form and π -allyl is absent in the above nickel complex catalyst [8], trans units in the polymer obtained by the catalyst are also considered to be formed through σ -allyl polymer terminal.

The homogeneity of the polymer with respect to the composition is in contrast to the alternative case reported [12] by Natta, in which the polymer is fractionated into different compositions.

Sharaev et al. reported that the π -allyl nickel halide-chloranil system initiated the cis-1,4 polymerization [26]. The authors have studied the structure of allyl ligand in such a catalyst.

The reaction of π -allyl nickel bromide or iodide with chloranil or tetracyanoethylene in benzene formed a precipitate in each case. Polymerizations by the systems and the resulting benzene-insoluble part are listed in Table 1. The π -allyl nickel bromide-chloranil system afforded a cis-1,4 polymer with high activity. The benzene-insoluble part of this system was subjected to IR spectroscopy and Fig. 1 was obtained. The bands at 2800-3000 and 1650-1700 cm^{-1} suggest the presence of the σ -allyl group, because these bands appear in the complexes prepared from the reaction of π -allyl nickel bromide or iodide with oxygen and have been attributed to σ -allyl ligand in our previous report, although no information was obtained about the presence or absence of π -allyl ligand. A band at 1650-1700 cm^{-1} may not be assigned to the C=O group of coordinated chloranil, because the C=O band of chloranil is much sharper and stronger than that in Fig. 1 as compared with other bands. The results support the concept of the σ -allyl polymer terminal.

The mechanism of the σ -allyl growing polymer terminal may be extended to other transition metal catalysts, because it is generally accepted that the σ -allyl or σ -alkyl-metal bond is more stable in complexes of Group IV metals than in those of Group VIII metals.

Very recently Lobach et al. reported that π -allyl nickel iodide undergoes the insertion of butadiene to form a π -complex [25]. This fact is taken as a possibility of polymerization through the π -allyl polymer terminal. Therefore, there are two possibilities for the trans-1,4 polymerization: through the σ -allyl terminal by the π -allyl nickel iodide-oxide system and through the π -allyl one by the π -allyl nickel iodide itself, although the latter catalyst has less activity than the former. Based on the above-mentioned experiments and the fact that the anti-form is more unstable than the syn-form, the formation of the π -allyl terminal is not the reason for cis-polymerization rather than cis-coordination of the monomer in the transition state. However, the formation of trans-1,4 and 1,2 polymer can be derived either from the unidentate coordination of the monomer or from the isomerization of the σ -allyl

TABLE 1. Polymerization of Butadiene with Catalysts Prepared from π -Allyl Nickel Halide and Chloranil or Tetracyanoethylene^a

Catalyst component	Mixture or benzene-insoluble part	Polymerization time (hr)	Polymer yield (%)	Microstructure	
				cis (%)	trans (%)
$[\text{C}_3\text{H}_5\text{NiI}]_2$ -chloranil	Mixture	72	89	0	96
$[\text{C}_3\text{H}_5\text{NiI}]_2$ -TCNE	Mixture	72	81	0	97
$[\text{C}_3\text{H}_5\text{NiI}]_2$ -chloranil	Benzene insoluble	48	55	0	96
$[\text{C}_3\text{H}_5\text{NiI}]_2$ -TCNE	Benzene insoluble	72	46	0	96
$[\text{C}_3\text{H}_5\text{NiBr}]_2$ -chloranil	Benzene insoluble	3	32	90	6
$[\text{C}_3\text{H}_5\text{NiBr}]_2$ -TCNE	Benzene insoluble	72	6	67	28

^aConditions: $[\pi\text{-C}_3\text{H}_5\text{NiX}]_2$, 1.0 mmole; chloranil or TCNE, 1.0 mmole; butadiene, 7.2 g; benzene, 16 ml; polymerization temperature, 40°C; reaction between two components, room temperature, 15-30 min.

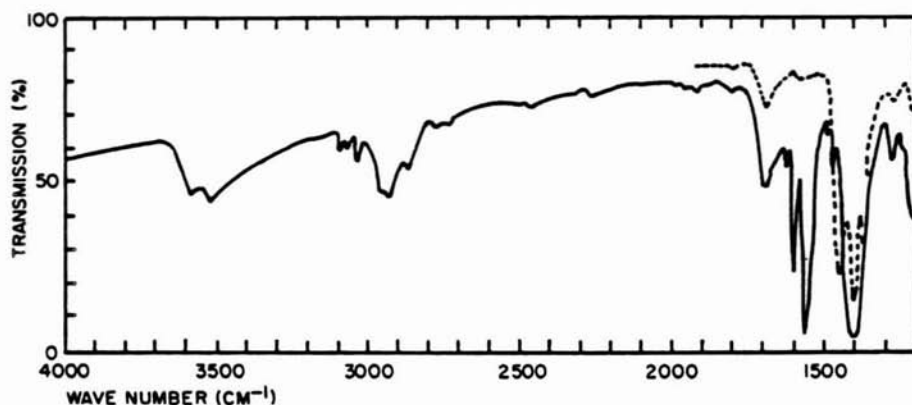


FIG. 1. Infrared spectrum of the benzene-insoluble complex prepared from π -alkyl nickel bromide and chloranil by means of hexachlorobutadiene (solid line) and nujol (broken line).

terminal to the π -allyl one after addition of the monomer. Accordingly, the π -allyl terminal is able to undergo trans-1,4 or 1,2 polymerization but not cis-1,4 polymerization.

In conclusion, the idea that the syn-anti isomer ratio of π -allyl polymer terminal as affected by other ligands is responsible for the stereospecificity of the polymerization is considered to be ruled out. The polymerization is supposed to proceed through the σ -allyl growing polymer terminal, at least in cis-1,4 polymerization, and the coordination mode of the monomer will govern the stereospecificity.

The Factor Determining the Microstructure

The authors have investigated experimentally the factor that determines the microstructure of nickel catalyts. The results are as follows:

(a) Reduced nickel on a carrier initiated cis-1,4 polymerization. In the polymerization, active catalyts were restricted to those carried on acidic carriers such as silica and silica-alumina [1, 2]. Addition of an acid (Lewis acid or organic acid) increased activity, whereas the addition of a base decreased both activity and the cis-1,4 content [1, 2].

(b) Raney nickel exhibited no activity but the Raney nickel-Lewis acid system was a catalyts for cis-1,4 polymerization [2].

(c) In the case of the system triethylaluminum-metal halide-organic salt of nickel, metal fluorides such as boron fluoride and zinc fluoride gave the polymer of the highest cis-1,4 content [3]. With regard to a catalyst of triethylaluminum-boron fluoride-organic salt of nickel, an Al/B ratio between 0.7 and 1.0 was most effective, and an increase of boron fluoride up to a mole ratio of 0.2 (i.e., B/Al = 5) hardly decreased the polymer yield and cis-1,4 content although it lowered the molecular weight of the polymer, whereas an increase of triethylaluminum up to an Al/B mole ratio of 1.5 resulted in a marked decrease of yield [3].

(d) The complex prepared from π -allyl nickel halide and oxygen yielded a polymer of 90% or more cis-1,4 content in the case of the chloride and the bromide, whereas the iodide with oxygen afforded a polymer of 70% or less cis-1,4 content in which cis and trans units were copolymerized [8, 60].

(e) It was reported that the benzene-insoluble nickel complex prepared by the reaction of π -allyl nickel halide with benzoyl peroxide was found to be an active catalyst for the stereospecific polymerization of butadiene, and that the complex was composed of nickel, benzoyloxy group, halogen, and a small amount of allyl group attached to nickel [5-7].

The effect of a substituent in the phenyl group of benzoyl peroxide has been studied, and is summarized in Table 2. The reaction of π -allyl nickel halide with p-nitro or p-methoxybenzoyl peroxide proceeded in the same manner as that with benzoyl peroxide in benzene. The precipitate formed was the active species of the catalyst system, similar to the case of benzoyl peroxide. The IR spectrum of the benzene-insoluble complex prepared by the reaction of allyl nickel iodide with p-nitrobenzoyl peroxide is shown in Fig. 2. The strong band at 723 cm^{-1} is assigned to CH deformation of the benzene ring having two substituents at the para position, one of which is the carbonyl or nitro group. The strong and sharp band at 1345 cm^{-1} is assigned to NO stretching (symmetrical) of the nitro group attached to the aromatic ring. The band at about 1515 cm^{-1} may be attributed to NO stretching (anti-symmetrical) of the nitro group. The band at $1570\text{-}1580\text{ cm}^{-1}$ seems to indicate the presence of the $\text{O}=\text{C}=\text{O}$ group by the same reason as that described in the case of benzoyl peroxide in the previous paper [7]. The band at about 1600 cm^{-1} indicates the presence of the aromatic ring. The hydrolysis of the complexes from nitrobenzoyl peroxide and methoxybenzoyl peroxide gave p-nitrobenzoic acid and p-methoxybenzoic acid, respectively. These results indicate

TABLE 2. Polymerization with Catalysts Prepared from π -Allyl Nickel Halide and Substituted Benzoyl Peroxides^a

Catalyst component	Mixture or benzene-insoluble part	Polymerization time (hr)	Polymer yield (%)	Microstructure	
				cis (%)	trans (%)
$[\text{C}_4\text{H}_7\text{NiI}]_2$ -BPO	Benzene insoluble	48	30	0	95
$[\text{C}_4\text{H}_7\text{NiI}]_2$ -p-MeOBPO	Benzene insoluble	48	36	0	96
$[\text{C}_4\text{H}_7\text{NiI}]_2$ -p-NO ₂ BPO	Benzene insoluble	8	42	84	11
$[\text{C}_3\text{H}_5\text{NiBr}]_2$ -BPO	Mixture	3	83	88	7
$[\text{C}_3\text{H}_5\text{NiBr}]_2$ -p-MeOBPO	Mixture	6	52	82	12
$[\text{C}_3\text{H}_5\text{NiBr}]_2$ -p-NO ₂ BPO	Mixture	0.3	100	89	6

^aConditions: $[\pi$ -Allyl NiX]₂, 1.0 mmole; BPO or substituted BPO, 1.0 mmole; butadiene, 10 ml; benzene, 16 ml; polymerization temperature, 40°C; reaction between two components, room temperature, 15-30 min.

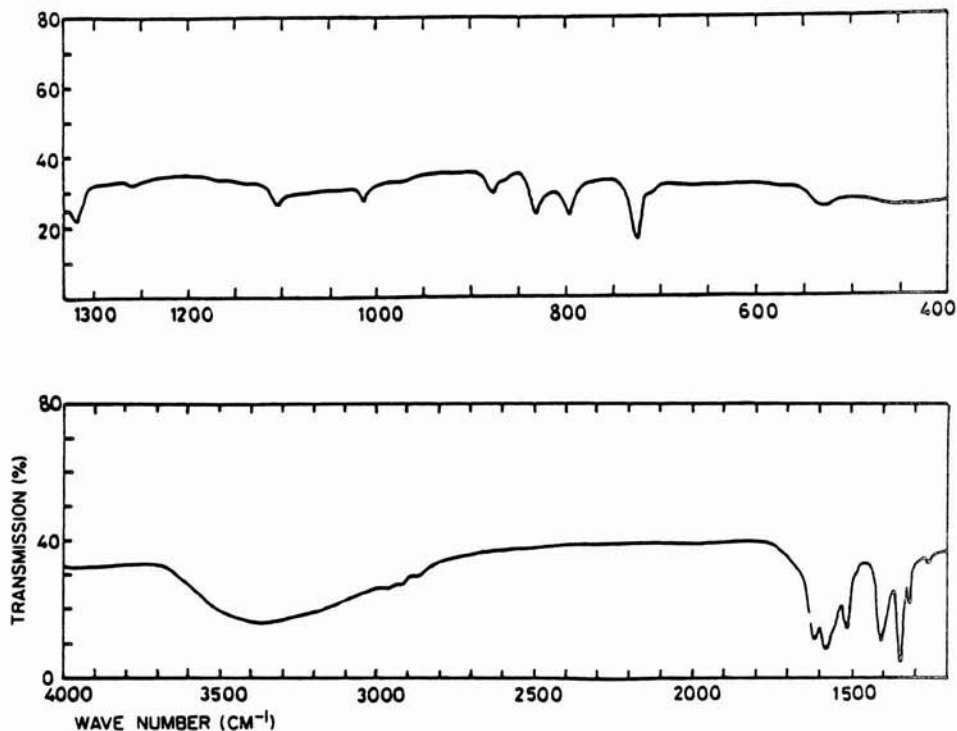


FIG. 2. Infrared spectrum of the benzene-insoluble complex prepared from π -allyl nickel iodide and *p*-nitrobenzoyl peroxide (KBr disk).

the presence of the substituted benzyloxy group of conjugated structure in the benzene-insoluble complex.

It is to be noted that the introduction of the nitro group to the benzyloxy group has the same effect on stereospecificity as the change in halogen attached to nickel from iodine to bromine. The steric effect seems to be negligible, because the methoxy group is ineffective. Complexes prepared from π -allyl nickel chloride or bromide and *p*-nitrobenzoyl peroxide exhibited much higher activity than those from benzoyl peroxide.

(f) The activities of the above-mentioned catalysts to vinyl monomers were studied. The catalysts for *cis*-1,4 polymerization, such as reduced nickel on diatomaceous earth [1], triethylaluminum-boron

fluoride-organic salt of nickel system [3], π -allyl nickel halide-oxygen system (or reaction product) [8], and π -allyl nickel chloride or bromide-benzoyl peroxide system (or reaction product) [7], initiated cationic polymerization of vinyl ether with high activity and were not active for the polymerization of methyl methacrylate and acrylonitrile. The benzene-insoluble complex prepared from π -allyl nickel iodide and benzoyl peroxide, which was the catalyst for trans-1,4 polymerization, could also initiate vinyl ether polymerization but was much less active than cis-1,4 catalysts, as shown in Table 3.

TABLE 3. Polymerization Activity for Isobutyl Vinyl Ether^a

Catalyst ^b component	Charged component mole ratio	Polymer yield (%)	Cis content in butadiene polymerization (%)
$[\text{C}_3\text{H}_5\text{NiBr}]_2\text{-BPO}$	1:1	78	90
$[\text{C}_3\text{H}_5\text{NiBr}]_2\text{-O}_2$	1:0.5	77	91
$[\text{C}_4\text{H}_7\text{NiI}]_2\text{-BPO}$	1:1	3	0
$[\text{C}_4\text{H}_7\text{NiI}]_2\text{-O}_2$	1:0.5	81	70

^aConditions: Ni in the catalyst, 0.21 mg atom; vinyl ether, 7.6 g; benzene, 16 ml; polymerization temperature, 40°C; time, 15 hr.

^bIn all runs the benzene-insoluble part was used as catalyst.

(g) Copolymerization of styrene and p-methylstyrene by cis-1,4 catalysts also indicated that the cis-1,4 catalysts are capable of initiating a cationic polymerization of styrene monomers, as shown in Table 4. On the other hand, the catalyst for trans-1,4 polymerization did not polymerize both monomers.

The above experimental results lead to the following conclusions:

- (1) No specific atom or group is required for stereospecificity.
- (2) The relatively small electron density on the nickel atom is necessary for cis-1,4 polymerization.

TABLE 4. Copolymerization of Styrene (m_1) and *p*-Methylstyrene (m_2)^a

Catalyst ^b component	Content of m_2 in monomer feed (%)	Polymer yield (%)	Content of m_2 in polymer (%)	Cis content in butadiene polymerization (%)
$[C_3H_5NiBr]_2$ -BPO	35	4.6	69	90
$[C_3H_5NiBr]_2$ -O ₂	35	5.5	63	91
$[C_4H_7NiI]_2$ -BPO	35	0	-	-

^aConditions: $[C_3H_5NiBr]_2$, 0.5 mmole; styrene, 3.5 g; benzene, 4 ml; polymerization temperature, 40°C; time, 6 hr.

^bIn all runs the benzene-insoluble part was used as catalyst.

- (3) The number of vacant sites in the central metal of the catalyst is not necessarily an essential factor in determining the microstructure of the polymer.

Mechanism of Microstructure Control

The following two points are the summary of our above study: The mode of monomer coordination is responsible for the microstructure of the polymer, and the microstructure is much affected by the electron density of the metal atom.

Accordingly, the relationship between the electron density of the metal atom and the butadiene coordination mode to the metal seems to be a very important point in the mechanism for the determination of the microstructure.

In order to investigate the relationship, the authors have studied the molecular and atomic orbitals of butadiene and transition metal, because generally a coordination mode is realized through the molecular orbitals peculiar to the mode.

The following consideration of the coordination mode will be by means of quantum chemical and coordination chemical principles. The conclusion will be associated with the polymerization on the

assumption that unidentate coordination effectuate 1,2 or trans-1,4 polymerization and bidentate coordination cis-1,4 polymerization. Polymerization results with various transition metal catalysts will be interpreted by the proposed mechanism.

The Number of Coordination Site

By "titled" site is meant a vacant site or a site capable of being replaced by butadiene around the central atom of the catalyst. If the steric environment permits only a single titled site, butadiene coordination is carried out monodentately. However, this case does not seem to be general because, with regard to soluble catalysts such as tris- π -allyl titanium and tris- π -allyl chromium, π -allyl ligand is considered to be capable of being replaced by butadiene as indicated by Wilke in oligomerization and, with regard to insoluble catalyst, the authors showed in the previous section that cis and trans structures are obtained from one active site or from sites of similar steric environment. Generally speaking, it is difficult to assume in all the 1,2 or trans-1,4 polymerization catalysts listed below that the steric environment restricts such coordination sites to only one.

Accordingly, in a general consideration of the mechanism, it is assumed that there are two such coordination sites around the central metal of a catalyst; in other words, there is little steric hindrance for bidentate coordination in an active catalyst center.

Molecular Orbitals and Conformations for Mono- and Bidentate-Coordinations

Butadiene complexes of transition metals have been isolated for both uni- and bidentate coordinations. They are listed in Table 5. It is a reasonable assumption that butadiene coordination to the polymerization site takes place in the same conformation as that in the above complexes. Data in Table 5 indicate that, both for uni- and bidentate coordination, the mode of butadiene-metal bonding is substantially the same regardless of the kind of metal and other ligands. With regard to the bidentate coordination, butadiene coordinated is in the cis form and completely planar with C-C-C bond angles of about 120° and π -electrons with carbon atoms of sp^2 hybrid as shown in Fig. 3 [27].

TABLE 5. Examples of Butadiene Complex of Transition Metal

Bidentate coordination			
	NMR, τ value and (intensity)	IR (cm^{-1})	Refs.
$\text{C}_3\text{H}_5\text{VC}_4\text{H}_6(\text{CO})_2$	5.6 (2), 7.8 (2),	10.2 (2) 1483	} 27, 28, 63
$\text{C}_5\text{H}_2\text{MnC}_4\text{H}_6(\text{CO})$	5.3 (2), 8.2 (2),	11.6 (2) 1466	
$(\text{C}_4\text{H}_6)_2\text{Mo}(\text{CO})_2$	5.8 (2), 8.6 (2),	9.8 (2) 1466	
$[\text{C}_4\text{H}_6\text{Co}(\text{CO})_2]_2$	5.0 (2), 8.3 (2),	9.3 (2) 1477	
$(\text{C}_4\text{H}_6)_2\text{Fe}(\text{CO})_3$	4.7 (2), 8.3 (2),	9.8 (2) 1464	
Assignment of absorption band	$\text{H}_{3,4}$ $\text{H}_{2,5}$ $\text{H}_{1,6}$	Coordinated double bond	29, 30
Unidentate coordination			
	IR	Refs.	
$[\text{C}_5\text{H}_5\text{Fe}(\text{C}_4\text{H}_6)(\text{CO})_2]^+$	1626	31	
$\text{C}_4\text{H}_6\text{Fe}(\text{CO})_4$	1620	32	
$\text{C}_4\text{H}_6\text{Mo}(\text{CO})_5$	~1620	33	
$(\text{C}_4\text{H}_6)_2\text{W}(\text{CO})_4$	~1620	33	
Assignment	Noncoordinated double bond		

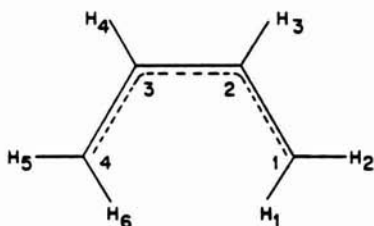


FIG. 3. Conformation of bidentately coordinated butadiene.

The position of proton signals in NMR of H_1 and H_6 indicates a fairly short metal-hydrogen bond. This picture has been confirmed by x-ray analysis of $(C_4H_6)Fe(CO)_3$ [34]. All C—C distances are 1.45 to 1.46 Å and equal. The C—C—C bond angle is 118° and the iron atom is nearly equidistant from all the C-atoms of the diene (2.1 Å).

On the other hand, the unidentate complexes are characterized by the IR absorption spectrum showing the presence of a free double bond, as shown in Table 5. The bond corresponding to the free double bond appears in the vicinity of 1623 cm^{-1} of C=C stretching in ethylene (Raman effect), suggesting that the free double bond is scarcely conjugated with the one bonded to metal. In other words, butadiene coordinates with localized (i.e., ethylenic) π -electrons, leaving one double bond uncoordinated.

Figure 4 shows the active sites assumed to be octahedral complexes, where $M-C\sim$ indicates a living polymer terminal of σ -allyl structure, and L_1 , L_2 , and L_3 are other ligands. In the case of the bidentate complex, C_1 and C_4 are placed near X and Y axes, respectively, C—metal and C—C distances being taken to be equal to those in $Fe(CO)_3(C_4H_6)$.

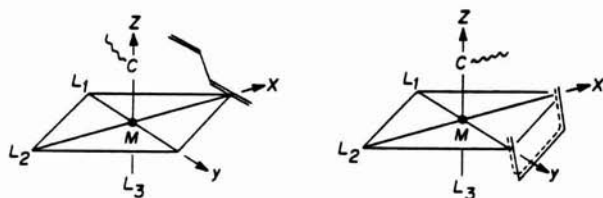


FIG. 4. The active site of the polymerization catalyst assumed for mono- or bidentate coordination of monomer.

Consider the octahedral configuration of a transition metal entering into bonding with ligands through the d^2sp^3 hybrid (dx_y , dy_z , and dz_x orbitals) as shown in Fig. 4. The d^2sp^3 hybrid orbitals are:

$$\psi_1 = \frac{1}{\sqrt{6}} s + \frac{1}{\sqrt{3}} d_{z^2} + \frac{1}{\sqrt{2}} p_z$$

$$\psi_2 = \frac{1}{\sqrt{6}} s - \frac{1}{\sqrt{3}} d_{z^2} + \frac{1}{\sqrt{2}} p_z$$

$$\psi_3 = \frac{1}{\sqrt{6}} s + \frac{1}{\sqrt{12}} d_{z^2} + \frac{1}{2} d_{x^2-y^2} + \frac{1}{\sqrt{2}} p_x$$

$$\psi_4 = \frac{1}{\sqrt{6}} s + \frac{1}{\sqrt{12}} d_{z^2} + \frac{1}{2} d_{x^2-y^2} - \frac{1}{\sqrt{2}} p_x$$

$$\psi_5 = \frac{1}{\sqrt{6}} s + \frac{1}{\sqrt{12}} d_{z^2} - \frac{1}{2} d_{x^2-y^2} + \frac{1}{\sqrt{2}} p_y$$

$$\psi_6 = \frac{1}{\sqrt{6}} s + \frac{1}{\sqrt{12}} d_{z^2} - \frac{1}{2} d_{x^2-y^2} - \frac{1}{\sqrt{2}} p_y$$

According to a simple Hückel method, the delocalized orbital of butadiene is as follows, where x_n is a $2p$ orbital of carbon, ϕ_n is a molecular orbital, ϵ_n is the energy of ϕ_n , α is the Coulomb integral of x_n , and β is the resonance integral between x_n and x_{n+1} :

$$\epsilon_n = \alpha + \lambda_n \beta$$

$$\lambda_1 = 1.62 \quad \phi_1 = 0.372x_1 + 0.602x_2 + 0.602x_3 + 0.372x_4$$

$$\lambda_2 = 0.62 \quad \phi_2 = 0.602x_1 + 0.372x_2 - 0.372x_3 - 0.602x_4$$

$$\lambda_3 = -0.62 \quad \phi_3 = 0.602x_1 - 0.372x_2 - 0.372x_3 + 0.602x_4$$

$$\lambda_4 = -1.62 \quad \phi_4 = 0.372x_1 - 0.602x_2 + 0.602x_3 - 0.372x_4$$

In relation to the unidentate coordination, it is assumed on the basis of the above-mentioned data that butadiene coordinates by means of ethylenic π -electrons whose π -orbitals are:

$$\lambda_1 = 1.0 \quad \phi_1 = \frac{1}{\sqrt{2}} x_1 + \frac{1}{\sqrt{2}} x_2$$

$$\lambda_2 = -1.0 \quad \phi_2 = \frac{1}{\sqrt{2}} x_1 - \frac{1}{\sqrt{2}} x_2$$

On the basis of orbital symmetry, the overlap of orbitals is considered to take place between the following orbitals, as illustrated in Fig. 5.

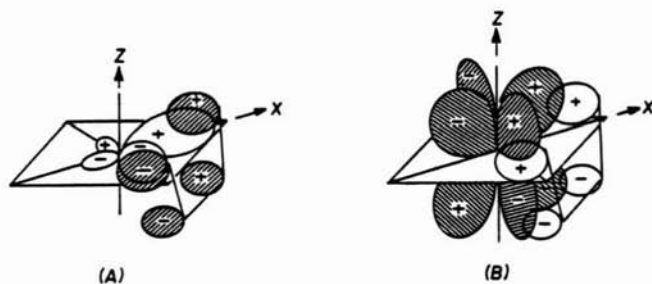


FIG. 5. Overlap of orbitals in bidentate coordination. (A) Donation: $\phi_2 \sim (1/\sqrt{2})(\psi_3 - \psi_5)$. (B) Back donation: $\phi_3 \sim (1/\sqrt{2})(d_{xz} + d_{yz})$.

Bidentate coordination:

$$\text{Donation, } \phi_1(\text{BD}) \sim \frac{1}{\sqrt{2}} (\psi_3 + \psi_5) \text{ (metal)}$$

$$\phi_2(\text{BD}) \sim \frac{1}{\sqrt{2}} (\psi_3 - \psi_5) \text{ (metal)}$$

$$\text{Back donation, } \phi_3(\text{BD}) \sim \frac{1}{\sqrt{2}} (d_{xz} + d_{yz}) (\text{metal})$$

$$\phi_4(\text{BD}) \sim \frac{1}{\sqrt{2}} (d_{xz} - d_{yz}) (\text{metal})$$

Unidentate coordination:

Donation, ϕ_1 (ethylene) $\sim \psi_3$ (metal)

Back donation, ϕ_2 (ethylene) $\sim d_{xy}$ (metal)

Energy Levels of Orbitals Available to the Coordination of Butadiene

The following levels are estimated from the ionization potentials and the electronic spectra of butadiene and ethylene [35]:

Butadiene:	Highest occupied orbital (ϕ_2)	9.1 eV
	Lowest vacant orbital (ϕ_3)	3.4 eV
Ethylene:	Occupied orbital (ϕ_1)	10.5 eV
	Vacant orbital (ϕ_2)	3.0 eV

It is to be noted that the difference between ϕ_2 of BD and ϕ_1 of ethylene is 1.4 eV, whereas that between ϕ_3 of BD and ϕ_2 of ethylene is 0.4 eV.

Discussion regarding the energy level of the transition metal orbital to receive the donation of π -electron from butadiene (hereafter ϕ metal and ϵ metal refer to the orbital and the energy level in question) is one of the important points of the present investigation. Here, the authors assume that the metal is electronically neutral as the result of σ and π interactions between the metal and ligands.

The ionization potential of the metal itself is taken to be a measure of the ϵ metal in the above case, since the ϕ metal (ψ_3 and ψ_5 in an octahedral complex) before the coordination of butadiene is essentially a nonbonding orbital. The ionization potential ranges from 6.5 to 8.0 eV for Ti, V, Cr, Mo, Mn, Fe, Co, and Ni. The ϵ metal may be somewhat higher than the ionization potential of the metal itself, according to the calculation of Nyholm et al., i.e., the ionization potential of $3d^{10} \rightarrow 3d^9$ in Ni 5.8 eV ($3d^8 4s^2 \rightarrow 3d^9$: 7.63 eV) [36] and the ϕ metal is d^2sp^3 hybrid in an octahedral complex. The above energy levels are summarized in Fig. 6, where the metal orbital means the ϕ metal defined above.

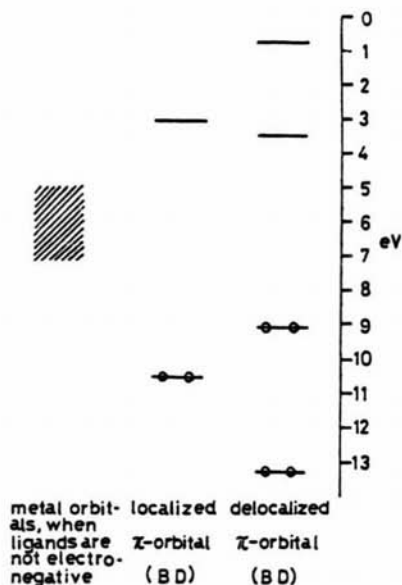


FIG. 6. Energy levels of butadiene orbitals and transition metal orbitals to receive π -electrons of butadiene.

It is essential to the present investigation that the ϵ metal in the above situation lies higher than the energy level of the highest occupied orbital (ϕ_2) of butadiene and lower than that of the lowest vacant one (ϕ_3).

The Change in Energy of a Metal Coordination Orbital Caused by Electronegative Ligands

The ϕ metal is essentially a nonbonding orbital before the coordination of butadiene. Generally speaking, electrons in a nonbonding orbital have an energy depending on the potential energy given by the atomic core composed of the nucleus and the other electrons, and the electronic repulsion between electrons. Therefore, the energy of a nonbonding orbital is affected by the shielding effect of other electrons belonging to the same atom.

In the case where ligands are more electronegative, the shielding effect of bonding electrons may decrease and as a result the

nonbonding orbital may have a lower energy. The formal valency state of a metal and a lone electron pair coordinated to the metal also influence the density of the electrons which shield the interaction between the ϕ metal and the nucleus. The π -interaction between the metal and ligands are also to be taken into account as a factor affecting the electron density at the metal atom.

The Determination of Coordination Mode in Terms of the Energy Level

According to Fukui et al. [37] the interaction between the conjugated system and the other atom is given by

$$-\Delta E = \left(z \sum_i^{\text{occ}} - \mu \sum_i^{\text{all}} \right) \frac{(C_i)^2}{\lambda_i - k} \gamma^2 \beta$$

where the Coulomb integral of the atomic orbital is $\alpha + k\beta$, energies of orbitals of the conjugated system are $\alpha + \lambda_i\beta$, and $\gamma\beta$ is the resonance integral.

It is to be noted in general that ΔE is very large when $\lambda_i - k$ is small. Therefore, in the case of two conjugated systems reacting with an atomic orbital, the conjugate system having the energy level closer to the atomic energy level is more reactive.

In a similar way the interaction is compared in both cases, i.e., ϕ metal with delocalized butadiene and localized one. When ligands are very low in electronegativity, the ϕ metal has considerably higher energy than the highest occupied level of delocalized butadiene.* In such a case, the above principle of energy level difference plays no important role in selectivity.

On the contrary, when ligands are so electronegative that the ϕ metal has energy close to the highest occupied level of delocalized butadiene, the metal will react with delocalized butadiene selectively. Delocalized butadiene is much more overlapped with metal orbitals in the cis form than in the trans form, provided that the butadiene coordinates to one metal. In fact, transoid butadiene coordination

*The difference of ionization potential between cis and trans butadiene was estimated to be less than 0.1 eV [38].

to one metal atom by means of delocalized orbitals has not been found, and cisoid coordination is realized with delocalized orbitals in the actual butadiene complexes, as shown in the previous section. Polymerization will give the polymer of cis-1,4 configuration in such cases.

The ligand of exceedingly high electronegativity will lower the energy level of ϕ metal to the vicinity of that of the occupied orbital of ethylenic π -electrons. In such a case the metal will react with butadiene of the localized form because of the large amount of energy obtained by resonance. In other words, butadiene will coordinate monodentately. Polymerization will give a polymer of trans-1,4 or 1,2 configuration.

The Effect of Overlap between Orbitals

In the case of ligands of very low electronegativity, the energy level difference is not decisive in determining the coordination mode of monomer. In such a case, the degree of overlap between the metal and butadiene orbitals is to be considered. It is noted that ethylene coordinates to a transition metal of low vacant level with considerable stability by a large back donation from the metal to the ethylene.

The overlap integral (S) between metal and coordinated butadiene was calculated according to the method applied by Orgel et al. to ferrocene [39]. In calculating, the equation of $\alpha_{sd} = \alpha_{ds} = \alpha_c = 1.60$ was assumed according to Craig et al. [40]. The conformation adopted for the bidentate coordination is shown in Fig. 7, where atomic distances are assumed to be same as those of $\text{Fe}(\text{C}_4\text{H}_6)(\text{CO})_3$. AB/BC is assumed to be 1/2.

The results with respect to one molecule of butadiene are as follows:

Back donation:

$$S \text{ (bidentate), } 1/\sqrt{2}(d_{xz} + d_{yz}) \sim \phi_3(\text{BD}) \quad 0.042$$

$$1/\sqrt{2}(d_{xz} - d_{yz}) \sim \phi_4(\text{BD}) \quad 0.074$$

$$S \text{ (unidentate), } d_{xy} \sim \phi_2 \text{ (ethylene)} \quad 0.276$$

Donation:

$$S \text{ (bidentate), } 1/\sqrt{2}(\psi_3 - \psi_5) \sim \phi_2(\text{BD}) \quad 0.339$$

$$1/\sqrt{2}(\psi_3 + \psi_5) \sim \phi_1(\text{BD}) \quad 0.289$$

$$S \text{ (unidentate), } \psi_3 \sim \phi_1 \text{ (ethylene)} \quad 0.574$$

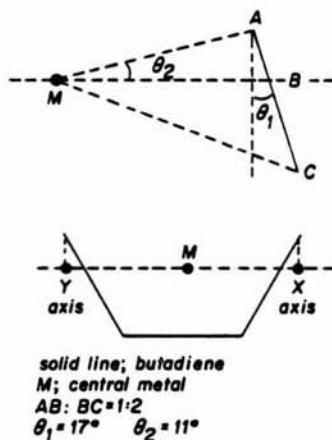


FIG. 7. Assumed conformation of bidentate coordination of butadiene.

The following points should be taken into account. The energy level of ϕ_3 of butadiene is only 0.4 eV lower than that of ϕ_2 of ethylene according to the estimate made from ionization potentials and spectral data. ϕ_1 and ϕ_4 do not contribute significantly to the bond between metal and butadiene. The above figures are with respect to one butadiene molecule. In the case of the unidentate coordination, ψ_3 and d_{yz} remain unoccupied in the above calculation but will be occupied by another butadiene molecule or a solvent in the presence of excess butadiene and solvent.

In conclusion, unidentate coordination is much more advantageous than bidentate coordination with reference to the overlap of orbitals especially in back donation. In other words, unidentate coordination will take place, giving rise to the 1,2 or trans-1,4 polymerization.

Summary of the Theory

The energy level of the transition metal orbital receiving π -electrons of butadiene is a decisive factor in determining the microstructure of the polymer. According to the author's mechanism, stereospecific catalysts are classified into three groups A, B, and C, where ϵ_{metal} means the energy level defined previously in this report, $\epsilon_{\text{BD-deloc}}$

means the energy level of the highest occupied orbital of delocalized butadienic π -electrons (ca. 9.1 eV), and ϵ_{ET} means the energy level of the occupied orbital of ethylenic π -electrons (ca. 10.5 eV).

- A. ϵ_{metal} is much higher than $\epsilon_{\text{BD-deloc}}$
Predominantly the 1,2 or trans-1,4 polymer is yielded.
- B. ϵ_{metal} is in the vicinity of $\epsilon_{\text{BD-deloc}}$
Predominantly the cis-1,4 polymer is yielded.
- C. ϵ_{metal} is in the vicinity of ϵ_{ET}
Predominantly the trans-1,4 or 1,2 polymer is yielded.

The level of ϵ_{metal} is influenced by the interaction between the metal and ligands; e.g., electronegativity of ligands and valency of the metal.

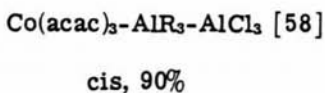
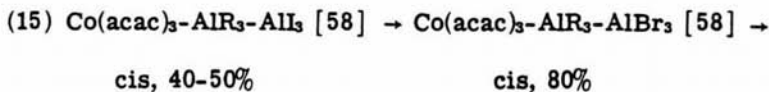
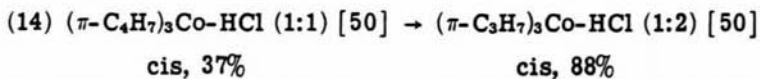
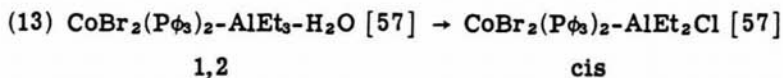
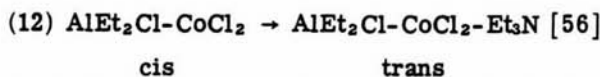
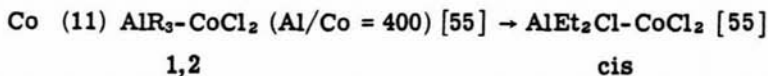
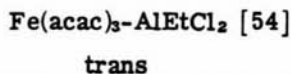
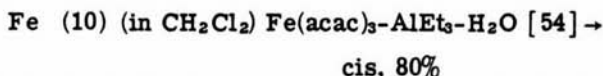
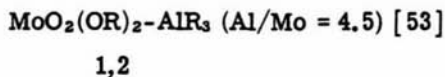
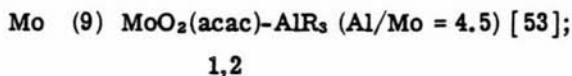
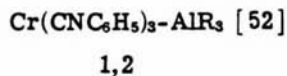
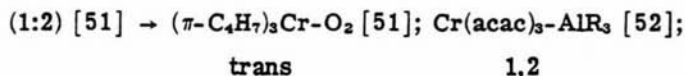
Application of the Theory to Actual Catalysts

With reference to actual catalysts, ϵ_{metal} can be estimated only very roughly. Therefore, it is difficult for the mechanism proposed here to predict precisely the microstructure of a polymer yielded by an actual catalyst. It can, however, predict the correlation between the change of the microstructure and the change in the factor affecting the energy level of ϵ_{metal} , e.g.,

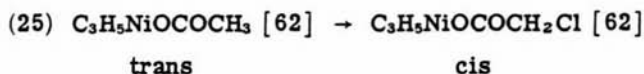
(1) Relative to catalysts with the same central metal, as the electronegativity of ligands changes from small to large and/or the valency state of the metal changes from low to high, the microstructure changes from 1,2 or trans-1,4 to cis-1,4 and then again to 1,2 or trans-1,4.

(2) Relative to catalysts with different central metals, a catalyst of the more electronegative metal needs more electronegative ligands for cis-1,4 polymerization.

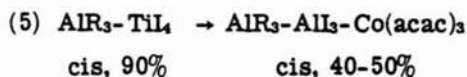
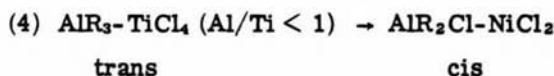
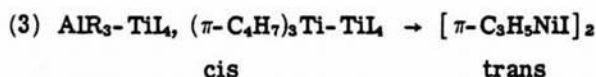
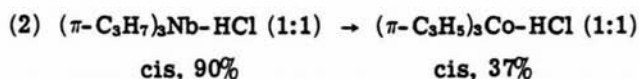
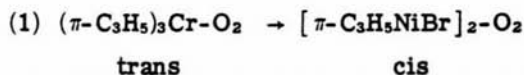
Many different kinds of transition metal catalysts have been found for the stereospecific polymerization of butadiene. The classification of catalysts according to Rule (1) leads to the following conclusion: 1,2 and trans-1,4 polymerization catalysts are distributed systematically. According to the change in electronegativity of ligands from small to large and/or the valency state of the metal from low



- (16) $\text{Co}(\text{C}_3\text{H}_5)_2\text{I}$ [59] \longrightarrow $\text{Co}(\text{C}_3\text{H}_5)_2\text{I}-\text{AlBr}_3$ [59]
 mainly cis, partly pure cis: much more active
 1,2: poorly active
- Ni (17) Catalysts for cis-1,4 initiate cationic polymerization
 [1, 3, 5-7, 60].
- (18) $[\pi\text{-C}_3\text{H}_5\text{NiI}]_2$ [14] \rightarrow $[\pi\text{-C}_3\text{H}_5\text{NiCl}]_2$ [14]
 trans cis
- (19) $[\pi\text{-C}_3\text{H}_5\text{NiI}]_2\text{-O}_2$ [6, 8] \rightarrow $[\pi\text{-C}_3\text{H}_5\text{NiBr}]_2\text{-O}_2$ [6, 8]
 cis, 60-70% cis, 90%
- (20) $[\pi\text{-C}_3\text{H}_5\text{NiI}]_2\text{-BPO}$ or MeOBPO [6, 60] \rightarrow
 trans
 $[\pi\text{-C}_3\text{H}_5\text{NiI}]_2\text{-O}_2\text{NBPO}$ [6, 60]
 cis, 80%
- (21) $\text{Ni}(\text{COOR})_2\text{-AlEt}_3\text{-BCl}_3$ [3] \rightarrow $\text{Ni}(\text{COOR})_2\text{-AlEt}_3\text{-BF}_3$ [3]
 cis, 80% cis, 98%
- (22) $\text{Ni}(\text{COOR})_2\text{-AlEt}_3\text{-TiCl}_4$ [3] \rightarrow
 cis, 85%
 $\text{Ni}(\text{COOR})_2\text{-AlEt}_2\text{F-TiCl}_4$ [3] \rightarrow
 cis, 92%
 $\text{Ni}(\text{COOR})_2\text{-AlEt}_3\text{-ZnF}_2$ [3]
 cis, 98%
- (23) $[\pi\text{-C}_3\text{H}_5\text{NiBr}]_2$ \rightarrow $[\pi\text{-C}_3\text{H}_5\text{NiBr}]_2\text{-O}_2$ [6], AlBr_3 [14],
 trans cis
 or chloranil [26]
- (24) $[\pi\text{-C}_4\text{H}_7]_2\text{Ni}$, etc.- MI_n [61] \rightarrow $[\pi\text{-C}_4\text{H}_7]_2\text{Ni}$, etc.- MCl_n [61]
 trans cis



Regarding kinds of metal:



As shown above, transition metal catalysts of metals of Groups IV to VIII are classified according to the mechanism proposed in this report.

The authors have also studied polymerization by catalysts other than those listed above in the same manner. No series or set of catalysts that conflict with the present mechanism has been found.

In conclusion, the mechanism presented in this report covers most of the transition metal catalysts in the stereospecific polymerization of butadiene, although catalysts having a high steric factor are excluded.

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