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Stereoregular and Sequence-Regular Polymerization of Butadiene

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Since the discovery of the Ziegler–Natta catalysts it has been possible to make stereoregular polymers (isotactic and syndiotactic) from α-olefins. The stereostructure of the substituted carbon is controlled by the mode of coordination of the monomer on the catalyst and/or the geometrical correlation between the polymer terminal and the monomer coordinated.

There are three ways in which the familiar diolefin butadiene can be incorporated into a polymer. 1,4-Polymerization can incorporate it with either cis or trans geometry at the central double bond. 1,2-Polymerization incorporates it as an ethylene unit with a vinyl substituent. In the latter case the carbon to which the vinyl group is attached is chiral. It is therefore possible to have isotactic or syndiotactic 1,2-polybutadiene. Furthermore, these various kinds of butadiene units can in principle appear in the same polymer molecule in either regular or random sequence. With suitable catalysts one can obtain equibinary polybutadiene with 1:1 cis:trans ratio or with a 1:1 cis-(1,4):1,2 ratio.

Further possibilities for isomerism arise in the polymerization of isoprene (2-methyl-1,3-butadiene). Besides *cis*- or *trans*-1,4-polyisoprene, one can obtain syndiotactic or isotactic 1,2- or 3,4-polyisoprene.

These various polymers can all be prepared with use of suitable catalysts composed of a transition-metal compound and appropriate ligands. It is evident that sophisticated principles must govern the spectacular dependence of polymer structure on the catalyst employed, in a rather complicated reaction mechanism.

In copolymerization, regulation of the monomer sequence in the copolymer is very important. This is achieved by us by controlling the reactivity and the coordination ability of the catalyst. For example, the propylene–butadiene alternating copolymer is prepared by a catalyst prepared from VCl_4 and Et_3Al at very low temperature. The copolymer is highly alternating and capable of orientation by stretching so that when stretched it has high tensile strength.

An interesting aspect of coordinated polymerization is oligomerization to give a dimer or trimer of definite structure. With use of zerovalent nickel catalysts and protic solvents or acids, we have been able to control the mode of oligomerization.[1]

This Account offers an interpretation of such regulation in the polymerization, copolymerization, or oligomerization of diolefins, with special emphasis on reaction mechanism.

Stereoregulation in the Polymerization of Butadiene

The Ziegler–Natta type catalyst is useful not only for isotactic or syndiotactic polymerization of α-olefins but also for cis, trans, or 1,2-polymerization of diolefins. *cis*-1,4-Polyisoprene was prepared by the $TiCl_4$–Et_3Al catalyst more than two decades ago.[2] Around the same time, *cis*-1,4-polybutadiene was also prepared by use of appropriate nickel[1] or cobalt catalysts as well as the TiI_4–Et_3Al catalyst.

However, the mechanism for stereoregular polymerization is not always immediately evident. The isotactic polymerization of propylene was found to be controlled through the stereospecific coordination of propylene on the enantiomorphic catalyst surface, whereas syndiotactic propylene polymerization is governed by the effect of the polymer end on the geometry of coordination of monomer.[3] The cis polymerization of butadiene was achieved by employment of a catalyst composed of nickel chloride, whereas the corresponding trans polymerization is catalyzed by nickel iodide.[4] Teyssié et al.[5] reported interesting phenomena caused by the addition of donor reagents to a π-allylic nickel trifluoroacetate. The latter alone yields *cis*-1,4-polybutadiene, but the same catalyst system with an added strong donor, such as an alkylphosphine or phosphite, gives trans polymer, while with a weak donor, such as benzene or a benzene derivative, one obtains cis:trans 1:1 equibinary polybutadiene.

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(1) J. Kiji, K. Masui, and J. Furukawa, *Tetrahedron Lett.*, 2561 (1970); *Bull. Chem. Soc. Jpn.*, **44**, 1956 (1971); *Makromol. Chem.*, **174**, 65 (1973).

(2) S. E. Horne, F. Gibbs, and E. J. Carlson (Goodrich-Gulf Chem. Inc.), British Patent 827 365 (1954).

(3) A. Zambelli, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, 15(1), 282 (1974).

(4) T. Matsumoto and J. Furukawa, *J. Polym. Sci., Part B*, **6**, 869 (1968); **5**, 935 (1967); **7**, 541 (1969).

(5) J. P. Durand, F. Dawans, and Ph. Teyssié, *J. Polym. Sci., Part A-1*, 8, 979 (1970).

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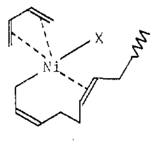
Natta et al.[6] proposed a mechanism of stereoregulation through coordination of the monomer: bidentate or cisoid coordination gives the cis polymer, whereas unidentate coordination gives the trans or 1,2-polymer.

Tolman pointed out the existence of two types of π-allylic structure, i.e., anti and syn forms.[7] The former seems to be a precursor of the cis polymer and the latter of the trans polymer. However, an NMR study of π-crotylnickel chloride and iodide informed us that they are both of syn structure even though they lead to different types of polymers.[4] Dolgoplosk et al.[8] proposed a modified mechanism involving the isomerization of the anti form to the syn form; the anti π-allylic end is formed from a bidentate coordinated butadiene which is unstable and transforms to the more stable syn form. This concept is based on the fact that π-allylic nickel trifluoroacetate gives the cis polymer, except that the trans polymer is produced when butadiene is present only in small amounts. However, this concept cannot account for the effect of donor reagents which promote the formation of *trans*-polybutadiene even though they stabilize the anti π-allylic structure. Moreover, it was found that the catalyst exists in a dimeric form. Consequently, there is a possibility that the trans polymer is formed by a dimeric catalyst and the cis polymer by a monomeric catalyst species.

The effect of donor reagents was attributed to the formation of different catalyst species for cis, trans, and equibinary polymerization.[9] When π-allylic nickel trifluoroacetate is quantitatively complexed with a strong or weak donor, the fraction of trans units incorporated is proportional to the amount of the catalyst–donor complex. However, the structure of the cis,trans equibinary polymer was found by NMR not to be alternating but random. It seems likely that the equibinary polymer is not formed by a simple catalyst species but by two kinds of catalyst sites existing in equilibrium.

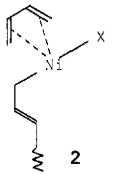
In 1975 I proposed a "back-biting coordination" hypothesis in which a second butadiene unit from the polymer end is complexed with nickel to form a ring structure facilitating cis polymerization.[10] Similar lithium[11] and palladium complexes[12] are known. X-ray analysis of the hydridocobalt methyl(heptadienyl)butadiene complex[13] revealed that the terminal double bond was located in the vicinity of the cobalt atom. A related mechanism was proposed by Hughes et al.[12] in order to explain 1,4- and 1,2-polymerizations. Back-biting coordination in the nickel catalyst was not directly established, but π-crotylnickel chloride was found by IR to be transformed into a compound mostly composed of σ-crotylnickel benzoate by the addition of benzoyl peroxide. The latter is a more reactive catalyst for cis-1,4-polymerization than is the former.[4]

It is likely that a catalyst having high coordination ability like σ-allylic nickel chloride with back-biting complexation (1) yields *cis*-polybutadiene, whereas a catalyst having a bulky ligand such as iodine (2) or a catalyst complexed with a strong donor such as phosphine or phosphite (3) produces *trans*-polybutadiene because the ligands prevent back-biting coordination.



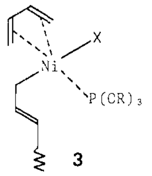
1

X: Cl, CF_3COO,



2

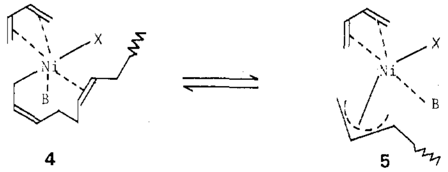
X: I,



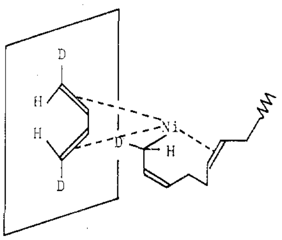
3

X: Cl, CF_3COO

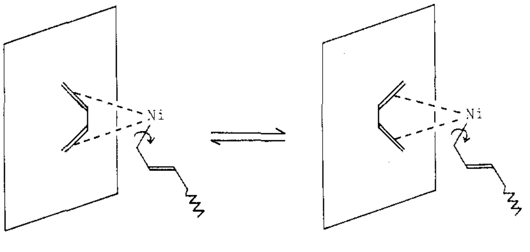
The formation of cis,trans equibinary polybutadiene with the aid of a cocatalyst such as benzene (denoted as B) is explained by a mechanism involving an intramolecular rearrangement between the back-biting coordination complex (4) and the π-allylic complex (5):



Porri[14] carried out an interesting experiment with *cis,cis*-butadiene-d_2 and established the stereochemistry by ozonolysis of the resulting polymer. The cis polymer gave racemic succinic-d_2 acid, whereas the trans polymer gave randomly deuterated succinic acid. These facts indicate that the direction of attack on the double bond in the cis polymerization is regular and alternating, but random in the trans polymerization. In other words, the cis polymerization proceeds under the steric influence of the polymer end. This fact is compatible with rigid cyclic structure 6 for the back-biting coordination in the cis polymerization but loose structure 7 for the free rotated σ-allylic polymer end in the trans polymerization.



6



7

1,2-Polymerization seems to occur by attack at the γ position in the π-allylic propagating polymer end. It is reported that the lithium-initiated polymerization of

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(6) G. Natta, L. Porri, and A. Carbonaro, *Makromol. Chem.*, 77, 126 (1964).

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(11) J. P. Oliver, J. B. Smart, and M. T. Emerson, *J. Am. Chem. Soc.*, 88, 4101 (1966); J. B. Smart, R. Hogan, P. A. Scherr, L. Ferrier, and P. Oliver, *ibid.*, **94**, 8371 (1972).

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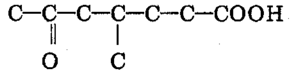
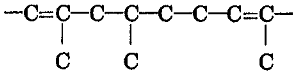
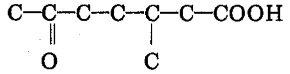
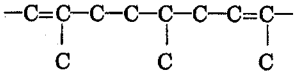
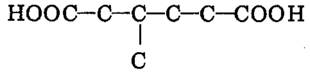
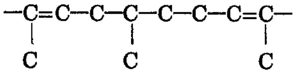
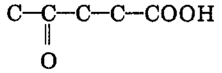
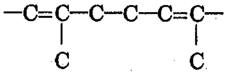
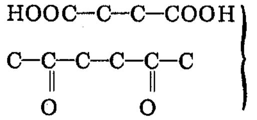
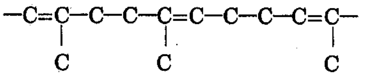
(13) G. Natta, U. Giannini, P. Pino, and A. Cassata, *Chim. Ind. (Milan)*, 47, 524 (1965).

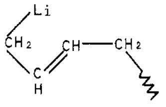
(14) L. Porri and M. Aglietto, *Makromol. Chem.*, **177**, 1456 (1976).

Table I
Ozonolysis of Alternating Copolymer of Propylene and Isoprene Prepared by $(i\text{-Bu})_3Al\text{-}VOCl_3$ (A) or $(i\text{-Bu})_3Al\text{-}TiCl_4$-Benzophenone (B) Catalyst

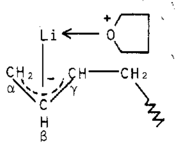
product			
	mol %[a]		
structure	A	B	possible structure for the copolymer
 $\mathrm{C{-}\underset{O}{\underset{\|}{C}}{-}C{-}\underset{C}{\underset{\mid}{C}}{-}C{-}C{-}COOH}$	40	36	 $\mathrm{{-}C{=}\underset{C}{\underset{\mid}{C}}{-}C{-}\underset{C}{\underset{\mid}{C}}{-}C{-}C{-}C{=}\underset{C}{\underset{\mid}{C}}{-}}$
 $\mathrm{C{-}\underset{O}{\underset{\|}{C}}{-}C{-}C{-}\underset{C}{\underset{\mid}{C}}{-}C{-}COOH}$	<2	8	 $\mathrm{{-}C{=}\underset{C}{\underset{\mid}{C}}{-}C{-}C{-}\underset{C}{\underset{\mid}{C}}{-}C{-}C{=}\underset{C}{\underset{\mid}{C}}{-}}$
 $\mathrm{HOOC{-}C{-}\underset{C}{\underset{\mid}{C}}{-}C{-}C{-}COOH}$	0.7	4.4	 $\mathrm{{-}\underset{C}{\underset{\mid}{C}}{=}C{-}C{-}\underset{C}{\underset{\mid}{C}}{-}C{-}C{-}C{=}\underset{C}{\underset{\mid}{C}}{-}}$
 $\mathrm{C{-}\underset{O}{\underset{\|}{C}}{-}C{-}C{-}COOH}$	0.4	2.1	 $\mathrm{{-}C{=}\underset{C}{\underset{\mid}{C}}{-}C{-}C{-}C{=}\underset{C}{\underset{\mid}{C}}{-}}$
 HOOC—C—C—COOH $\mathrm{C{-}\underset{O}{\underset{\|}{C}}{-}C{-}C{-}\underset{O}{\underset{\|}{C}}{-}C}$	0.1	0.0	 $\mathrm{{-}C{=}\underset{C}{\underset{\mid}{C}}{-}C{-}C{-}\underset{C}{\underset{\mid}{C}}{=}C{-}C{-}C{-}C{=}\underset{C}{\underset{\mid}{C}}{-}}$

[a] Based on sample.

butadiene yields 1,4-polymer (cis and trans mixture) in hydrocarbon solvents but produces 1,2-polymer in solvents containing tetrahydrofuran or an alkylamine. In the former case the polymer end is known to be of the σ-allylic structure, while in the latter case it is π-allylic according to an NMR study.[4] It is reasonable that the σ-allylic polymer end **8** gives a 1,4-polymer by



8



9

insertion of the monomer into the metal–alkyl bond, but the π-allylic polymer end **9** gives the 1,2-polymer, for in **9** the γ position seems to be more negative and reactive than the α position.

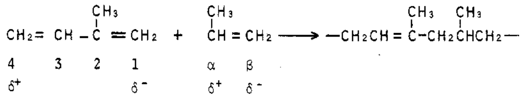
Such a concept also serves to explain 1,2-polymerization by transition-metal catalysts. There is a tendency for 1,2-polymerization to take place when the transition-metal catalyst involves a metal such as Mo or W possessing lower electronegativity, or with catalyst comprising a nickel or cobalt compound complexed with a donor reagent such as H_2O or H_2S. In other words, 1,2-polymerization occurs with the use of a catalyst which is moderately electron donating so as to form a π-allylic structure.[10]

It is interesting to note[15] that the $CoCl_2\text{–}Et_3Al$ catalyst gives 1,4-polymers but that it is transformed by a small amount of water into a catalyst giving cis-1,2 random equibinary polybutadiene and furthermore that a catalyst of $MoCl_5\text{–}3Et_3Al$ also gives the same polymer. A mechanism involving an equilibrium between π-allylic complexation and back-biting complexation is assumed.

Alternating Copolymerization of Olefin and Diolefin

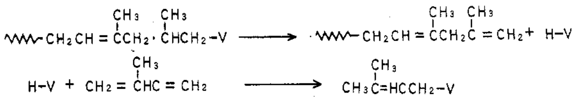
Homopolymerization of either an olefin or a diolefin can be achieved with the Ziegler–Natta catalysts, but their copolymerization is difficult because diolefins coordinate more strongly to the catalyst than olefins. However, copolymerization can be successful with the use of a modified catalyst prepared at very low temperatures.[16] Moreover, the copolymer of olefin and diolefin is shown to be highly alternating by NMR and ozonolysis studies. From the copolymer of ethylene or propylene with butadiene, no succinic acid, which would be formed from the butadiene–butadiene diad, was obtained, but acids from the alternating diads were produced. Ozonolysis of the copolymer of propylene and isoprene gave more detailed information as to the stereochemistry of the polymerization, as shown in Table I.

It was found that 90% of the ozonolysis product came from alternating diads and 10% from polyisoprene composed of head-to-tail as well as head-to-head or tail-to-tail structures. The formation of 4-methyl-6-oxoheptanoic acid as a major product indicates that the polymerization takes place predominantly at the 1-position of isoprene and the α-carbon of propylene as a result of the anionic coordinate polymerization.



$$\underset{\underset{\delta^+}{4}}{CH_2}=\underset{3}{CH}-\underset{2}{\overset{CH_3}{C}}=\underset{\underset{\delta^-}{1}}{CH_2}+\underset{\underset{\delta^+}{\alpha}}{\overset{CH_3}{CH}}=\underset{\underset{\delta^-}{\beta}}{CH_2}\longrightarrow -CH_2CH=\overset{CH_3}{C}-CH_2\overset{CH_3}{C}HCH_2-$$

The polymer obtained at elevated temperatures is of low molecular weight and its ozonolysis product contained a considerable amount of acetylacetone, which arose from the polymer terminal unit. This fact suggested that chain transfer occurred at the propylene unit as follows:



$$\sim\!\sim CH_2CH=\overset{CH_3}{C}CH_2\cdot\overset{CH_3}{C}HCH_2-V\longrightarrow \sim\!\sim CH_2CH=\overset{CH_3}{C}CH_2\overset{CH_3}{C}=CH_2+H-V$$

$$H-V+CH_2=\overset{CH_3}{C}HC=CH_2\longrightarrow CH_3\overset{CH_3}{C}=HCCH_2-V$$

In fact, the copolymer prepared from butadiene-*1,1,4,4-d_4* was found by NMR study to contain the D_2H methyl terminal group.[15]

Alternating copolymerization is much hindered by the steric hindrance of the bulky alkyl group of α-olefins

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(15) J. Furukawa, K. Haga, E. Kobayashi, Y. Iseda, T. Yoshimoto, and K. Sakamoto, *Polym. J.*, **2**, 371 (1971).

(16) J. Furukawa, *Angew. Makromol. Chem.*, **23**, 189 (1972).

Table II
Effect of Polymerization Temperature on Rate Constants and Concentrations of Active Species in the $TiCl_4$-$(i\text{-}Bu)_3Al$-Benzoic Acid Catalyst System

polym temp, °C	k, min^{-1}	$[P^*]$,[a] M	k_{tr}/k_p	k_p, M^{-1} min^{-1}	k_{tr}, M^{-1} min^{-1}
−30	26.4×10^{-4}	1.56×10^{-4}	2.57×10^{-3}	16.9	4.34×10^{-2}
−40	12.5×10^{-4}	1.32×10^{-4}	2.04×10^{-3}	9.45	1.93×10^{-2}
−50	3.64×10^{-4}	1.03×10^{-4}	1.58×10^{-3}	3.53	0.54×10^{-2}

[a] $[P^*]$ = concentration of the active species, [propylene] = 3.71 M, [butadiene] = 3.71 M, $TiCl_4$ = [benzoic acid] = 6.69×10^{-3} M, $[(i\text{-}Bu)_3Al] = 15.7 \times 10^{-3}$ M; toluene as solvent.

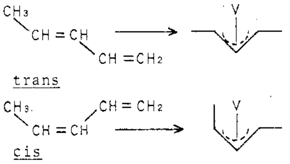
Table III
Effect of Polymerization Temperature on Rate Constants and Concentrations of Active Species in the $VOCl_3$-$(i\text{-}Bu)_3Al$-$(i\text{-}PrO)_3Al$ Catalyst System

polym temp, °C	k, min^{-1}	$[P^*]$,[a] M	k_{tr}/k_p	k_p, M^{-1} min^{-1}	k_{tr}, M^{-1} min^{-1}
−70	9.55×10^{-4}	1.56×10^{-4}	2.64×10^{-3}	6.12	1.62×10^{-2}
−74	6.61×10^{-4}	1.56×10^{-4}	2.12×10^{-3}	4.24	0.899×10^{-2}
−78	3.74×10^{-4}	1.50×10^{-4}	1.88×10^{-3}	2.49	0.468×10^{-2}

[a] [Propylene] = 2.76 M, [butadiene] = 2.76 M, $[VOCl_3] = 3.89 \times 10^{-3}$ M, $[(i\text{-}Bu)_3Al] = 19.5 \times 10^{-3}$ M, $[(i\text{-}PrO)_3Al] = 4.67 \times 10^{-3}$ M; toluene as solvent.

and substituted butadienes. The copolymerization of butadiene or isoprene with 3-methylbutene or 4-methylpentene gave copolymers having a deficiency of the α-olefin unit, while 2,3-dimethylbutadiene did not give an alternating copolymer.

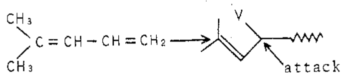
Interesting is the case of the copolymerization of pentadiene and an olefin.[17] *trans*-Pentadiene gave an alternating copolymer but the cis monomer did not. This fact is explained by the concept that polymerization occurs at the π-allylic polymer terminal; the π-allylic terminal formed from *trans*-pentadiene exists in a stable syn form, **10**, whereas that from *cis*-pentadiene does not exist due to the instability of anti-form **11**.



10
syn – syn

11
anti – syn

Moreover, the pentadiene unit in the former copolymer was found to be a 1:1 mixture of 1,4-trans and 1,2 structures. This is attributed to equivalent reactivity of the α and γ positions of the syn π-allylic terminal unit. In fact, in the alternating copolymerization of 4-methylpentadiene with olefin the diolefin unit was found to be incorporated in the 1,2 manner, presumably as suggested by the following scheme.



A kinetic study revealed that polymerization proceeded through step-growth propagation and chain transfer, because the molecular weight of the resulting polymer increased with increasing polymerization time and leveled off only at the final stage. The overall rate of polymerization was first order with respect to total monomer.[18] The rate constants of monomer consumption, propagation, and chain transfer and the concentrations of the active species (k, k_p, k_{tr}, and $[P^*]$) were evaluated for $VOCl_3$ and $TiCl_4$ catalysts and listed in Tables II and III.

There are two propagation steps, one from the propylene (PP) end to butadiene (BD) and the other from the butadiene end to propylene. The kinetic expression (eq 1, where R_P is the rate of polymerization, k_{PB} (k_{BP})

$$R_P = k_{PB}K_B[P_P^*][BD] + k_{BP}K_P[P_B^*][PP] \quad (1)$$

is the rate constant of propagation to butadiene (propylene), and K_B (K_P) is the coordination constant of butadiene (propylene), respectively) therefore contains two terms. For equibinary polymerization the condition of eq 2 obtains. Since the concentration of total active

$$k_{PB}K_B[P_P^*][BD] = k_{BP}K_P[P_B^*][PP] \quad (2)$$

sites, $[P^*] = [P_B^*] + [P_P^*]$, may be assumed to be constant during polymerization, eq 3 is derived. A

$$2[P^*]/R_P = 1/(k_{PB}K_B[BD]) + 1/(k_{BP}K_P[PP]) \quad (3)$$

linear relation was found between $1/R_P$ and $1/[BP]$ or $1/[PP]$, from which $k_{PB}K_B$ and $k_{BP}K_P$ for a titanium catalyst were evaluated as 67.4 and 9.6 M^{-1} min^{-1}, respectively. Thus the overall rate constant for the propagation from the propylene end to the butadiene monomer is larger than that from the butadiene end to the propylene one due to the higher reactivity of the propylene end than that of the butadiene end and/or the higher coordination tendency of butadiene than of propylene.

The vanadium catalyst system was investigated by means of potentiometric titration and ESR measurement.[16] In the binary system of VCl_4 and Et_3Al in various compositions, the valency of vanadium decreases from four to two with increasing amount of Et_3Al. On the other hand, the content of propylene in the resulting copolymer increases with increasing amount of Et_3Al and attains 50 mol % at a Al/V ratio of 3.

The binary system of oxyvanadium acetylacetonate ($VO(acac)_2$) and Et_3Al yields mainly 1,2-polybutadiene, whereas that of $VO(acac)_2$ and Et_2AlCl yields *trans*-1,4-polybutadiene. The alternating copolymer is obtained by the ternary system of $VO(acac)_2$, Et_3Al, and Et_2AlCl as illustrated in Figure 1.

The ESR study showed that the binary system of $VO(acac)_2$ and Et_2AlCl gives an eight-line signal char-

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(17) I. Maruyama, Dissertation, Kyoto University, 1976.
(18) M. Taniguchi, Dissertation, Kyoto University, 1976.

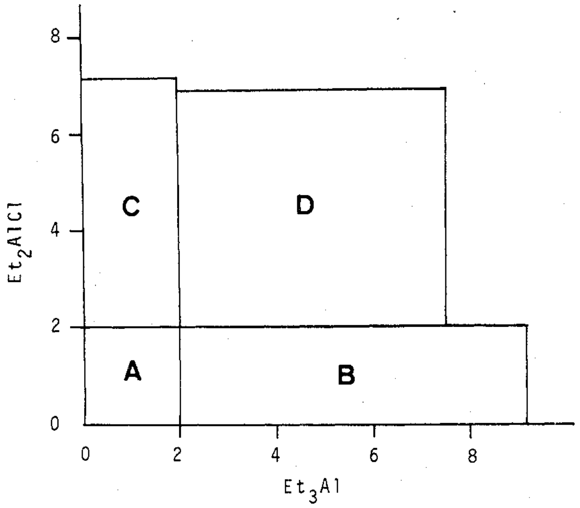
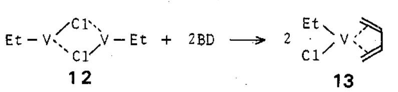


Figure 1. Mode of polymerization affected by the composition of the catalyst consisting of VO(Acac)$_2$, Et$_3$Al, and Et$_2$AlCl. A: Vanadium exists as V^{4+}, giving no polymer. B: Vanadium exists as V^{2+}, giving 1,2-polybutadiene. C: Vanadium exists as a mixture V^{2+} and V^{3+}, giving *trans*-polybutadiene. D: Vanadium exists as associated V^{2+}, giving alternating copolymer.

Table IV
Usual Catalysts for the Alternating Copolymerization of Propylene and Butadiene

catalyst	cocatalyst
AlR_nX_{3-n}-VX_4	$Al(OPr)_3$ $Zn(O\text{-}i\text{-}Pr)_3$ $Ca(CH_3COO)_2$
AlR_nX_{3-n}-$VO(OR)_{3-n}X_n$ AlR_nX_{3-n}-$VO(OR)_3$	t-BuCl, I_2, $SOCl_2$, $EtAlCl_2$, $SnCl_4$, CrO_2Cl_2, $TiBr_4$

acteristic of divalent vanadium, whereas the ternary system of VO(acac)$_2$, Et$_2$AlCl, and Et$_3$Al loses the eight-line signal probably due to association of divalent vanadium through a chlorine bridge. From these observations, divalent vanadium stabilized by loose association (**12**) is deduced to be the precursor of the catalyst. It undergoes dissociation in the presence of butadiene to form the actual catalyst **13** having a controlled coordination number, as follows:



12 13

The catalyst linked with the propylene end enables the bidentate coordination of butadiene, whereas that linked with the butadiene end forms a π-allylic complex with lower coordination number. The latter does not allow the further bidentate coordination of butadiene but does allow the unidentate coordination of propylene. In this way, alternating coordination of butadiene and propylene occurs.

Chain transfer takes place at the propylene end. In order to reduce the incidence of chain transfer, one must perform the polymerization at low temperatures. However, various improved catalysts available at elevated temperatures were developed and are listed in Table IV.

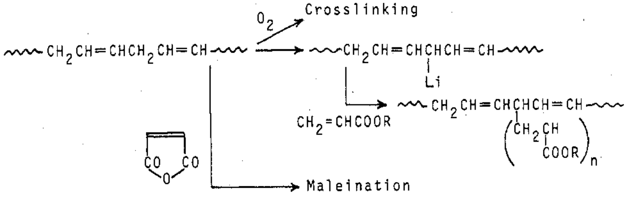
The alternating copolymer of propylene and butadiene seems to be versatile as an industrial rubber. It has high strength and is capable of high orientation by stretching. The stress–strain curve is very similar to that of natural rubber, showing a steep increase in stress at high elongation. The raw rubber has also good processability, showing high strength and elongation at break.

Table V
Formation of Cyclic and Linear Dimers of Butadiene Catalyzed by Nickel Salt and Reducing Agent Systems

	NaBH$_4$ in ethanol[a]		CH$_3$ONa in 2-propanol[a]	
Ni salt	A, %[b,c]	B, %[b,d]	A, %[b]	B, %[b]
$NiBr_2(n\text{-}Bu_3P)_2$	80–82	7	58	28
$NiCl_2(n\text{-}Bu_3P)_2$	30	11	43	19
$Ni(NO_3)_2(n\text{-}Bu_3P)_2$	26	18	25	16

[a] Reducing agent. [b] Dimer yield. [c] A, 2-methylenevinylcyclopentane. [d] B, mixture of isomeric n-octatrienes. Reaction conditions: 80 °C for 24 h, nickel salt 0.3–0.5 mmol, reducing agent 0.3–1.0 mmol, butadiene 24–25 mmol.

Ordinary Ziegler catalyst polymerizes acetylene and diolefin to homopolyacetylene only, but a nickel catalyst composed of nickel naphthenate and diethylaluminum chloride gave a copolymer of varying acetylene content depending on the feed monomer composition.[19] NMR study showed the copolymer to have a random structure and the double bonds of either monomer to be of the cis structure. The polymer may have applications for the coating industry, because it is readily air-dried and can function as substrate for graft polymerization by virtue of its reactive methylene group adjacent to two double bonds.



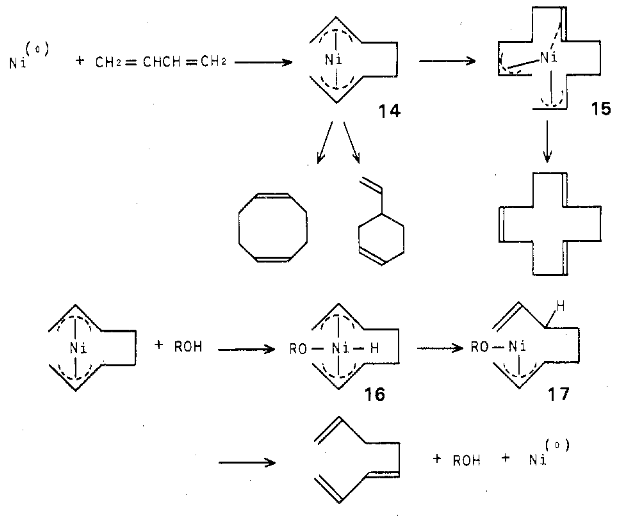
Oligomerization of Butadiene

Cyclic dimers and trimers of butadiene were prepared by Wilke et al.[20] using a zerovalent nickel catalyst, and linear oligomers or vinylcyclohexene were prepared by various investigators with iron or cobalt catalysts. We found that the zerovalent nickel produced cyclic, linear, and new oligomers, selectively, by adjusting the catalyst activity; the catalyst gives cyclooctadiene or cyclododecatriene in an aprotic solvent, whereas it gave linear oligomer in a protic solvent such as an alcohol.[1] Zerovalent nickel with an alcohol and a strong acid afforded 2-methylenevinylcyclopentane in good yield. As shown in Table V, the strength and amount of the protic acid were essential factors controlling the mode of oligomerization.

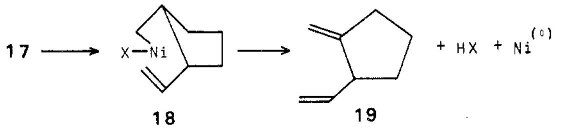
A mechanism involving a bis-π-allylic nickel and its hydrido complex as intermediates was proposed. The bis-π-allylic complex **14** or **15** was proposed by Wilke for cyclooligomerization.[20] In the presence of a weak protic compound such as an alcohol, the bis-π-allylic nickel may be protonated to form an unstable intermediate **16** which induces the protonation toward bis-π-allylic group to form an intermediate **17**. If a more

(19) J. Furukawa, E. Kobayashi, and T. Kawagoe, *J. Polym. Sci., Part B*, 11, 573 (1973).

(20) B. Bogdanovic, P. Heimbach, M. Kröner, and G. Wilke, *Justus Liebigs Ann. Chem.*, **727**, 143 (1969).

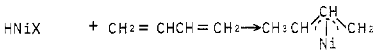


acidic compound is used, the intermediate **17** is more stable, which allows the insertion of a double bond to the nickel–carbon bond, i.e., **17** to **18**, before deprotonation. In this way, 2-methylenevinylcyclopentane (**19**) is produced.[1] In support of this mechanism, 2-methylenevinylcyclopentane-*3-d* was formed when a deuterated acid was employed.



It was reported by Tolman[21] that zerovalent nickel can be protonated with a very strong acid such as sulfuric acid or trifluoroacetic acid and that (π-crotyl)nickel is formed from butadiene. (π-Crotyl)nickel thus formed is able to induce the further insertion of butadiene to yield polybutadiene. In fact, Teyssié et al.[5] found that reactivity in the polymerization of butadiene by the zerovalent nickel complex promoted by various acids increases with increasing acid strength. It is inferred that the zerovalent nickel can induce the coupling of coordinated butadiene, whereas it forms a hydridonickel in the presence of a strong acid which is converted to crotylnickel. With use of an acid of controlled acid strength, the protonation occurs after the coupling reaction and also induces the isomerization or the double bond insertion.

$$\mathrm{Ni^{(0)} + HX \longrightarrow HNiX}$$



$$\mathrm{HNiX + CH_2{=}CHCH{=}CH_2 \longrightarrow CH_3CH\overset{CH}{\cdots}CH_2} \;(\mathrm{Ni})$$

Actually a protonated nickel catalyst was prepared from nickel bromide and sodium alkoxide. It was found that the composition of various kinds of oligomers is affected by the ratio of NaOR to $NiBr_2$ or that of added HBr to Ni. This fact is associated with the formation of HNiBr and Ni^0 from $NiBr_2$ or from zerovalent nickel as intermediates.

$$\mathrm{NiBr_2 \underset{HBr}{\overset{NaOR}{\rightleftharpoons}} HNiBr \underset{HBr}{\overset{NaOR}{\rightleftharpoons}} Ni^{(0)}}$$

In relation to conjugated diolefins norbornadiene is to be cited. We investigated the effect of phosphine ligands on the mode of the dimerization of norbornadiene (the 4 + 4 reaction) and the addition of norbornadiene to acrylonitrile (the 4 + 2 addition). There are exo and endo isomers in the reaction products. It was found that the dimerization of norbornadiene is governed by the steric hindrance of the bulky group on the phosphine ligands, whereas the addition to acrylonitrile is governed by the electronic effect of the polar group on the phosphine ligands.[22]

Various types of dimerizations or additions of norbornadiene were performed with modified nickel catalysts.[23]

Concluding Remarks

In the products of polymerization of 1,3-diolefins there is isomerism among cis, trans, and 1,2 structures. They are much affected by ligands governing backbiting coordination of the second unit from the propagating polymer end. In copolymerization of butadiene with α-olefins, the π-allylic structure derived from the diolefin end does not permit the further coordination of the diolefin but does permit the incorporation of only an α-olefin, leading to alternating copolymers.

In oligomerization of butadiene aprotic solvents afford hydrido complexes giving isomerized oligomers through a hydrogen transfer. Such controlled polymerizations or oligomerizations as these are achieved by adjusting the coordination ability of transition-metal catalysts.

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(21) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 6768 (1970).

(22) S. Yoshikawa, K. Aoki, J. Kiji, and J. Furukawa, *Bull. Chem. Soc. Jpn.*, **48**, 3239 (1975); **49**, 1093 (1976).

(23) J. Kiji, S. Nishimura, S. Yoshikawa, E. Sasakawa, and J. Furukawa, *Bull. Chem. Soc. Jpn.*, **47**, 2523 (1974).