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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 nickel¹ 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 enantiomorphous 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.

(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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Table I
Ozonolysis of Alternating Copolymer of Propylene and Isoprene Prepared by $(i\text{-Bu})_3\text{Al-VOC}_3$ (A) or $(i\text{-Bu})_3\text{Al-TiCl}_4$ -Benzophenone (B) Catalyst

product structure	mol % ^a		possible structure for the copolymer
	A	B	
	40	36	
	<2	8	
	0.7	4.4	
	0.4	2.1	
	0.1	0.0	

^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



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

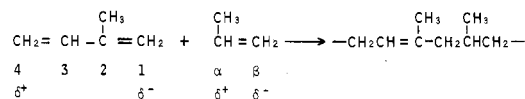
It is interesting to note¹⁵ that the $\text{CoCl}_2\text{-Et}_3\text{Al}$ catalyst gives 1,4-polymers but that it is transformed by a small amount of water into a catalyst giving cis-1,2 random equibinary polybutadiene and furthermore that a catalyst of $\text{MoCl}_5\text{-3Et}_3\text{Al}$ also gives the same polymer. A mechanism involving an equilibrium between π -allylic complexation and back-biting complexation is assumed.

Alternating Copolymerization of Olefin and Diolefin

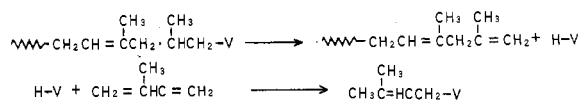
Homopolymerization of either an olefin or a diolefin can be achieved with the Ziegler-Natta catalysts, but their copolymerization is difficult because diolefins

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.



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:



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

(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 - $(i\text{-Bu})_3\text{Al}$ -Benzoic Acid Catalyst System

polym temp, °C	k , min^{-1}	$[\text{P}^*]$, ^a M	k_{tr}/k_p	k_p , $\text{M}^{-1} \text{min}^{-1}$	k_{tr} , $\text{M}^{-1} \text{min}^{-1}$
-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 $[\text{P}^*]$ = concentration of the active species, [propylene] = 3.71 M, [butadiene] = 3.71 M, TiCl_4 = [benzoic acid] = 6.69×10^{-3} M, $[(i\text{-Bu})_3\text{Al}]$ = 15.7×10^{-3} M; toluene as solvent.

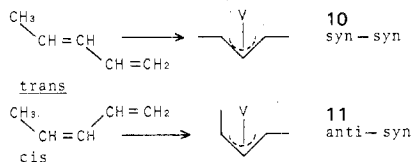
Table III
Effect of Polymerization Temperature on Rate Constants and Concentrations of Active Species in the VOCl_3 - $(i\text{-Bu})_3\text{Al}$ - $(i\text{-PrO})_3\text{Al}$ Catalyst System

polym temp, °C	k , min^{-1}	$[\text{P}^*]$, ^a M	k_{tr}/k_p	k_p , $\text{M}^{-1} \text{min}^{-1}$	k_{tr} , $\text{M}^{-1} \text{min}^{-1}$
-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}

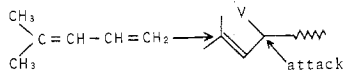
^a [Propylene] = 2.76 M, [butadiene] = 2.76 M, $[\text{VOCl}_3]$ = 3.89×10^{-3} M, $[(i\text{-Bu})_3\text{Al}]$ = 19.5×10^{-3} M, $[(i\text{-PrO})_3\text{Al}]$ = 4.67×10^{-3} M; toluene as solvent.

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.



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 $[\text{P}^*]$) 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})

$$R_p = k_{PB}K_B[\text{P}_P^*][\text{BD}] + k_{BP}K_P[\text{P}_B^*][\text{PP}] \quad (1)$$

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

$$k_{PB}K_B[\text{P}_P^*][\text{BD}] = k_{BP}K_P[\text{P}_B^*][\text{PP}] \quad (2)$$

sites, $[\text{P}^*] = [\text{P}_B^*] + [\text{P}_P^*]$, may be assumed to be constant during polymerization, eq 3 is derived. A $2[\text{P}^*]/R_p = 1/(k_{PB}K_B[\text{BD}]) + 1/(k_{BP}K_P[\text{PP}])$ (3)

linear relation was found between $1/R_p$ and $1/[\text{BP}]$ or $1/[\text{PP}]$, from which $k_{PB}K_B$ and $k_{BP}K_P$ for a titanium catalyst were evaluated as 67.4 and 9.6 $\text{M}^{-1} \text{min}^{-1}$, 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 ($\text{VO}(\text{acac})_2$) and Et_3Al yields mainly 1,2-polybutadiene, whereas that of $\text{VO}(\text{acac})_2$ and Et_2AlCl yields *trans*-1,4-polybutadiene. The alternating copolymer is obtained by the ternary system of $\text{VO}(\text{acac})_2$, Et_3Al , and Et_2AlCl as illustrated in Figure 1.

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

(17) I. Maruyama, Dissertation, Kyoto University, 1976.

(18) M. Taniguchi, Dissertation, Kyoto University, 1976.

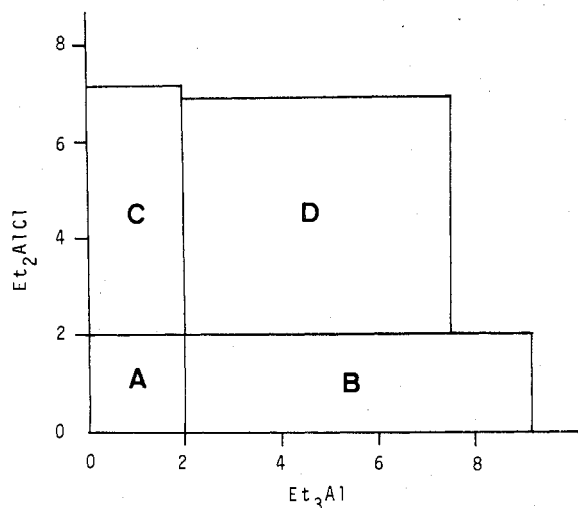
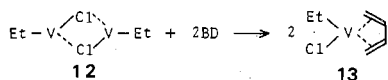


Figure 1. Mode of polymerization affected by the composition of the catalyst consisting of $\text{VO}(\text{Acac})_2$, Et_3Al , and Et_2AlCl . A: Vanadium exists as V^{4+} , giving no polymer. B: Vanadium exists as V^{2+} , giving 1,2-polybutadiene. C: Vanadium exists as a mixture V^{2+} and V^{3+} , 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
$\text{AlR}_n\text{X}_{3-n}-\text{VX}_4$	$\left\{ \begin{array}{l} \text{Al}(\text{OPr})_3 \\ \text{Zn}(\text{O-}i\text{-Pr})_2 \\ \text{Ca}(\text{CH}_3\text{COO})_2 \end{array} \right.$
$\text{AlR}_n\text{X}_{3-n}-\text{VO}(\text{OR})_{3-n}\text{X}_n$	$\left\{ \begin{array}{l} t\text{-BuCl, I}_2, \text{SOCl}_2, \\ \text{EtAlCl}_2, \text{SnCl}_4, \\ \text{CrO}_2\text{Cl}_2, \text{TiBr}_4 \end{array} \right.$
$\text{AlR}_n\text{X}_{3-n}-\text{VO}(\text{OR})_3$	

acteristic of divalent vanadium, whereas the ternary system of $\text{VO}(\text{acac})_2$, Et_2AlCl , and Et_3Al 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:



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

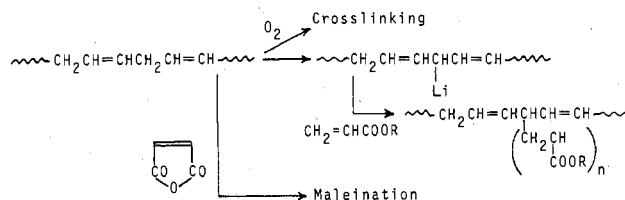
Table V
Formation of Cyclic and Linear Dimers of Butadiene Catalyzed by Nickel Salt and Reducing Agent Systems

Ni salt	NaBH_4 in ethanol ^a		CH_3ONa in 2-propanol ^a	
	A, % ^{b,c}	B, % ^{b,d}	A, % ^b	B, % ^b
$\text{NiBr}_2(n\text{-Bu}_3\text{P})_2$	80-82	7	58	28
$\text{NiCl}_2(n\text{-Bu}_3\text{P})_2$	30	11	43	19
$\text{Ni}(\text{NO}_3)_2(n\text{-Bu}_3\text{P})_2$	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.

at high elongation. The raw rubber has also good processability, showing high strength and elongation at break.

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.

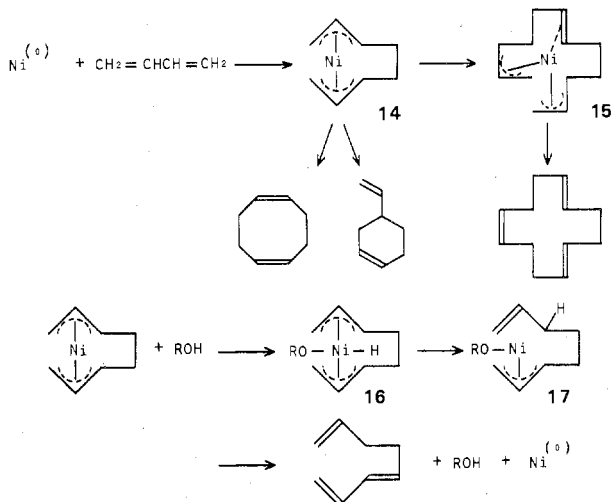
Oligomerization of Butadiene

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.

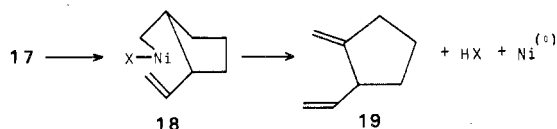
A mechanism involving a bis- π -allylic nickel and its hydrido complex as intermediates was proposed. The bis- π -allylic complex 14 or 15 was proposed by Wilke for cyclooligomerization.²⁰ In the presence of a weak protic compound such as an alcohol, the bis- π -allylic nickel may be protonated to form 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 Liebig's Ann. Chem.*, 727, 143 (1969).

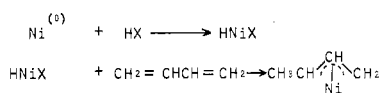


acidic compound is used, the intermediate 17 is more stable, which allows the insertion of a double bond to the nickel-carbon bond, i.e., 17 to 18, before deprotonation. In this way, 2-methylenevinylcyclopentane (19) is produced.¹ In support of this mechanism, 2-



methylenevinylcyclopentane-3-d was formed when a deuterated acid was employed.

It was reported by Tolman²¹ 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

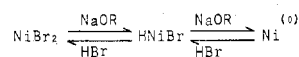


thus formed is able to induce the further insertion of butadiene to yield polybutadiene. In fact, Teyssié et al.⁵ found that reactivity in the polymerization of butadiene by the zerovalent nickel complex promoted by various acids increases with increasing acid strength. It is inferred that the zerovalent 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 con-

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

trolled acid strength, the protonation occurs after the coupling reaction and also induces the isomerization or the double bond insertion.

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 NiBr₂ or that of added HBr to Ni. This fact is associated with the formation of HNiBr and Ni⁰ from NiBr₂ or from zerovalent nickel as intermediates.



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 back-biting 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.

(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).