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The Polymerization of 2,4-Hexadiene. Stereoregular Polymer and the Mechanistic Study for Its Preparation

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ABSTRACT: The polymerization of 2,4-hexadienes has been carried out by various catalysts. High polymers were obtained from all isomers either by Lewis acids or transition-metal catalysts. Some transition-metal catalysts gave the stereoregular polymer composed of the erythrodiiso trans-1,4-tactic sequence. The study showed that the properties of transition metal and the isomeric form of monomer are important factors for the determination of configuration of the polymer. The crystalline polymer was prepared only with the trans,trans isomer by cobalt and titanium catalysts. The ligands in the catalyst and the polymerization solvent have little effect on the stereoregulation. *trans,trans*-2,4-Hexadiene was much more reactive than the corresponding trans,cis and cis,cis isomers by the transition-metal catalyst. This is in contrast to the result in the cationic polymerization. On the basis of these experimental results, the mechanism of the diene polymerization by transition-metal catalysis was discussed.

Extensive work has been reported on the polymerization of diene compounds, especially butadiene and isoprene, by transition-metal catalysts and their mechanisms.[1-5] We reported in a preliminary note[6] that 2,4-hexadiene could be polymerized to high polymers by using transition-metal catalysts or Lewis acids and that a crystalline polymer (*erythrodiiso trans-1,4-tactic*) was obtained using some of the former catalysts which gave the 1,4-cis polymer from butadiene[1,2,7] and the 1,4-cis or 1,2-trans polymer from 1,3-pentadiene.[8-10] The remarkable difference in the microstructure of the polymers obtained from similar diene compounds prompted us to an extensive investigation for the chemical structure of the crystalline polymer obtained from 2,4-hexadiene, the optimum condition for the preparation of the crystalline polymer, and then the mechanism of the polymerization by transition-metal catalysts.

To elucidate the difference in stereocontrol in the polymerization of diene compounds, several mechanisms have been proposed from the point of the coordination of the monomer or the structure of the propagating active end.[11-18] Recently, much information has been derived on the structure of the terminal active unit by the nmr technique.[19,20] Nevertheless, the mechanism of stereoregular polymerization of diene compounds by transition-metal catalysts still remains unsolved. It would be desirable for clarification of the polymerization mechanism to examine the polymerization of 2,4-hexadiene, which has three isomeric forms, by transition-metal catalysts.

In this communication, the detailed results of the polymerization of isomeric forms of 2,4-hexadiene are described. The microstructure of the polymer will be determined by various spectroscopy and then the condition for the preparation of stereoregular polymer will be examined. In addition, the mechanism of the stereoregular polymerization will be discussed on the basis of the above-mentioned results.

Experimental Section

(A) Monomers. The mixture of trans,trans and trans,cis isomers of 2,4-hexadiene were synthesized by the reaction of crotonaldehyde and ethylmagnesium bromide, followed by hydrolysis and subsequent dehydration of the alcohol (bp 80–81°, yield 51%). The isomer ratio of the mixture was determined by gas chromatography (column: silicon DC 550 on celite 545, 4.5 m) with helium as a carrier gas at 80°. The isomer ratio was trans,trans:cis,trans = 1:0.7. The cis,cis isomer could not be produced by this method. The cis,cis isomer was prepared by the isomerization of 1-*cis*-4-hexadiene (supplied from Toray Co. Ltd.) with Fe(acac)$_3$–Et$_3$Al as catalyst.[21] The isomer ratio of the product was trans,trans:trans,cis:cis,cis = 1:6:3.

The isomers were separated from their mixture by fractional distillation through a spinning band column. It was found by gas chromatography that each of the isomers thus separated had an isomeric purity of greater than 90%. These isomers were dried over calcium hydride before use in the polymerization.

(B) Solvents. Benzene and *n*-hexane were purified by ordinary methods and dried in a flask coated with sodium mirror.

(C) Catalysts. Commercial samples of boron trifluoride etherate, titanium tetrachloride, and organoaluminum compounds (($C_2H_5)_2AlCl$ and $(C_2H_5)_3Al$) were purified by distillation under reduced pressure and stored under nitrogen at 0° as *n*-hexane solutions. Transition-metal acetylacetonates (M(acac)$_n$) were recrystallized from their benzene–hexane solutions and dried in high vacuum. M(acac)$_n$–Al$(C_2H_5)_2$Cl catalysts were prepared by adding *n*-hexane solution of Al$(C_2H_5)_2$Cl to mixtures of M(acac)$_n$ in benzene or *n*-hexane and shaking the solution for 30 min at 30°. The ratio of Al/Co was from 5 to 100. Commercial cobaltus halides (Cl, Br, and I) were purified by recrystallization from methanol solutions. Cobaltus halide pyridine complexes (CoX_2–2Py) were prepared by reacting CoX_2 (1 mol) with pyridine (2 mol) in ethyl alcohol and recrystallized from their ethanol solutions.

Transition-metal catalysts were prepared by introducing the reagents into a polymerization apparatus in the following order: polymerization solvents, transition metal compounds, and then aluminum compounds.

(D) Polymerization. The polymerizations by transition-metal catalysts were carried out in glass cylindrical tubes, having a side arm which was connected with a vacuum–nitrogen apparatus in order to remove the air from the reactor and to introduce nitrogen. The polymerizations were terminated by adding a small amount of methanol. The reaction mixture was then poured into a large amount of methanol containing aqueous HCl. The precipitated polymers were thoroughly washed with methanol and dried under vacuum at room temperature. They were usually purified by dissolving them in benzene and washing the solution with aqueous HCl in order to remove all inorganic moieties and then they were reprecipitated with methanol and dried under vacuum. The procedure for the cationic polymerization has been described elsewhere.[22] High-vacuum techniques were used for the anionic polymerization and radical polymerization. These methods have been shown in another communication.[23]

(E) Physical Examination of the Polymer. Intrinsic viscosities were determined in toluene at 30°, using a Ubbelohdetype viscometer. A nmr examination was performed with a Varian XL 100 spectrometer and a JEOL JNM-4H-100 spectrometer using solu-

Table I
Polymerization of 2,4-Hexadiene by Various Catalysts[a]

Catalysts	Al/M	Solvents	Polym temp, °C	Polym time, hr	Yield, %	Mp, °C	[η]
AIBN		Benzene	60	20	3	Liquid	
BuLi		THF	−78	20	11	Liquid	
$TiCl_4$		CH_2Cl_2	30	19	74	Amorph	0.18
Et_2AlCl		Benzene	30	19	82	Amorph	0.23
$TiCl_4$–Al(*i*-Bu)$_3$	1.6	*n*-Hexane	30	19	47	78	0.13
VCl_4–Al(*i*-Bu)$_3$	3.0	*n*-Hexane	30	19	9	Amorph	0.10
Co(acac)$_2$–Et_2AlCl	10.0	Benzene	30	19	32	78	0.16

[a] [Monomer] = 2.4 mol/l., [catalyst] = 10^{-1}–10^{-3} mol/l.

Table II
The Polymerization of Three Isomers by Homogeneous Transition-Metal Catalysts[a]

Isomer	Solvent	Polym time, hr	Yield, %	Mp, °C
	Co(acac)$_2$–Et_2AlCl Catalyst			
Trans, trans	*n*-Hexane	10	41	87
Trans, cis	*n*-Hexane	10	16	Amorph
Cis, cis	*n*-Hexane	10	12	Amorph
	Ti(acac)$_2$–Et_2AlCl Catalyst			
Trans, trans	*n*-Hexane	10	12	72
Trans, cis	*n*-Hexane	10	10	Amorph
Cis, cis	*n*-Hexane	10	10	Amorph
	Ni(acac)$_2$–Et_2AlCl Catalyst			
Trans, trans	*n*-Hexane	48	73	Amorph

[a] Polym temp = 30°; [M(acac)$_2$] = 7.2×10^{-3} mol/l., M = transition metal, Al/M = 10, [monomer] = 2.4 mol/l.

tions of polymers in $CDCl_3$ or CCl_4. ^1H nmr spectra were obtained in the continuous wave mode at 100 MHz using both spectrometers (sweep width 1000 Hz and radiofrequency field 40–60 db), and ^{13}C nmr spectra were obtained in the natural abundance at 25.2 MHz from the Fourier transform of the ^{13}C free induction decay using a Varian XL-100 spectrometer (5000 Hz and radiofrequency field 30 db). In order to give a satisfactory signal-to-noise ratio for all signals of interest, 5000 pulses, each of width 30 μsec, needed to be accumulated. Field-frequency stabilization was maintained by locking on the ^1D signal of $CDCl_3$ which was solvent. Infrared spectra were taken with a Nippon Bunko IR-S spectrometer, using films obtained by evaporating benzene solutions of the polymers on NaCl plates. In the case of stereoregular polymers, annealing of the film for some hours at about 35° is necessary for crystallization. X-Ray diffraction patterns were taken by using nickel-filtered Cu Kα radiation. An oriented specimen was obtained by cold drawing at 0°.

The thermal behavior of the crystalline polymer was investigated by a differential scanning calorimeter manufactured by Rigaku Denki (No. 8055). The melting point of the crystalline polymers was determined by a hot-stage polarizing microscope with crossed Nicols.

(F) Reactivity of Geometrical Isomers. The polymerization was carried out using a mixture of isomeric monomers. At specified intervals of time, small portions of the reaction mixture were sampled out with a syringe and quenched by the addition of methanol containing a small amount of toluene as internal standard. The residual monomer was determined by the use of a Shimazu Model GC-2C gas chromatograph with helium as a carrier gas (4.5 m column of silicon DC 550 on Celite 545, 80°).

Results and Discussion

Polymerizability of 2,4-Hexadiene. In order to see the polymerizability of 2,4-hexadiene the polymerization was carried out by various kinds of catalysts (Table I). Monomer used was a 1:1 mixture of the trans,trans isomer and the cis,trans isomer. By employing free-radical initiators and anionic initiators, 2,4-hexadiene was only slightly polymerized to viscous oligomers. The anionic polymerization system colored orange-red indicating that the carbanion was formed. A high polymer was obtained by Friedel-Crafts catalysts and transition-metal catalysts. The polymers obtained by most of these catalysts were amorphous, having predominantly the 1,4-trans unit as judged from their ir and ^1H nmr spectroscopy. No cross-linked polymer was produced under our polymerization conditions. Crystalline polymers were obtained by Co(acac)$_3$–$AlEt_2Cl$ and $TiCl_4$–$AlEt_3$.

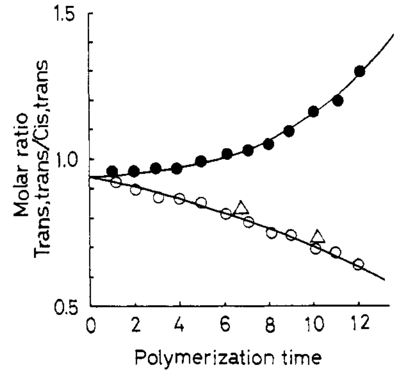

Figure 1. Variation of the residual isomer ratio of 2,4-hexadiene with polymerization time. Initial isomer ratio trans,trans:trans,cis = 0.94:1.0, polymerization temperature 30°: (○) Co(acac)$_2$–Et_2AlCl in benzene, (△) Co(acac)$_2$–Et_2AlCl in hexane, (●) Et_2AlCl in benzene.

The polymerizability of isomers was examined in the polymerization by Co(acac)$_3$–$AlEt_2Cl$ (Table II). The trans,trans isomer was much more reactive than the cis,trans and cis,cis isomers. The yield decreased in the order trans,trans > cis,trans > cis,cis. This result is in contrast to that in the cationic polymerization.[19] In order to confirm the relative reactivity of isomers, the rate measurements were performed for the mixtures of *trans,trans-* and *cis,trans-* 2,4-hexadiene by determining the change of isomer ratio with reaction time (Figure 1). Gas chromatography showed no isomerization of isomers and no formation of products other than normal polymers and oligomers during the polymerization in the case of homogeneous catalyst such as Co(acac)$_2$–$AlEt_2Cl$. Figure 1 also shows that the trans,trans isomer is much more reactive than other isomers in the polymerization by transition-metal catalysts. The structure of each isomer is shown in Figure 2. Figure 2 indicates that only trans,trans isomer can coordinate bidentately to the catalyst in the cissoid form since the bulkiness of the methyl group is likely to hinder sterically the bidentate coordination of other isomers to the catalyst. Similar results have been shown in the polymerization of 1,3-

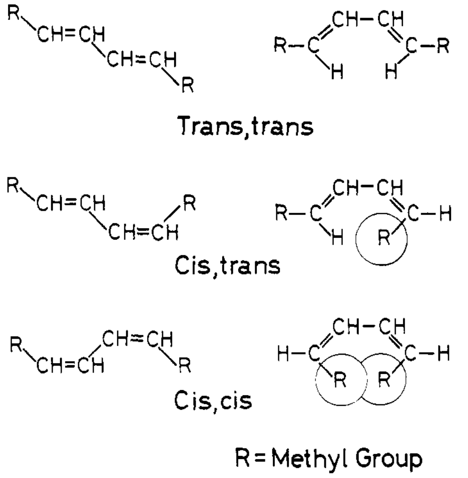

Figure 2. The conformation of each isomer of 2,4-hexadiene.

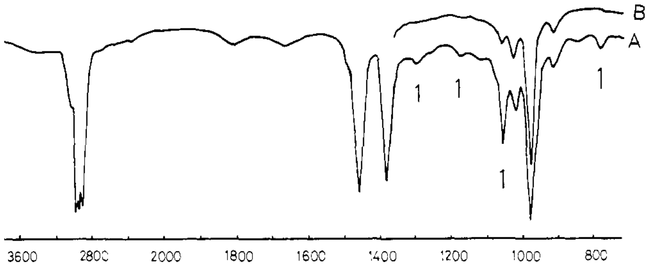

Figure 3. The ir spectra of crystalline poly(2,4-hexadiene): A, film; B, molten state.

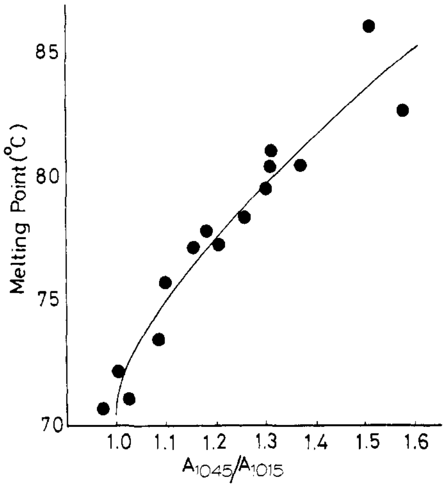

Figure 4. Relationship between melting point and A_{1045}/A_{1015}.

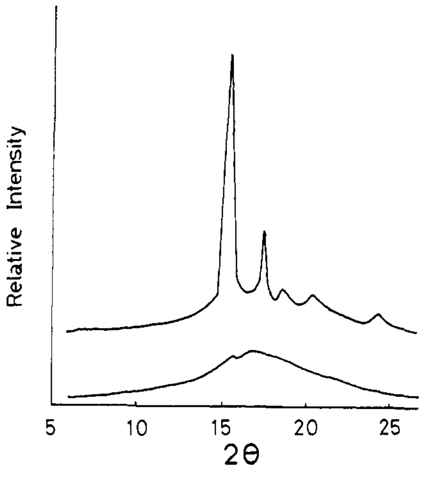

Figure 5. X-Ray spectra (Cu Kα), registered by a Geiger counter, of crystalline poly(2,4-hexadiene) (top) and amorphous poly(2,4-hexadiene) (bottom).

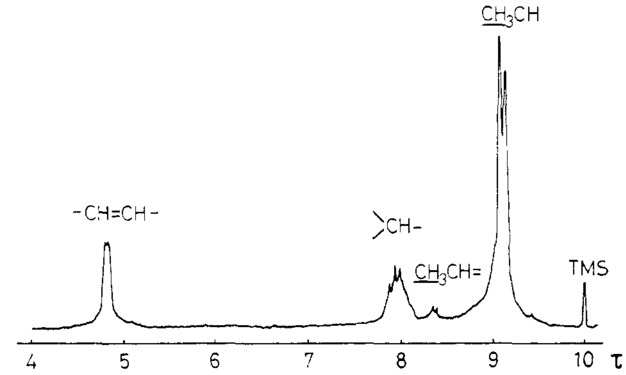

Figure 6. ^{1}H nmr spectrum of crystalline poly(2,4-hexadiene) (10% CCl_4 solution).

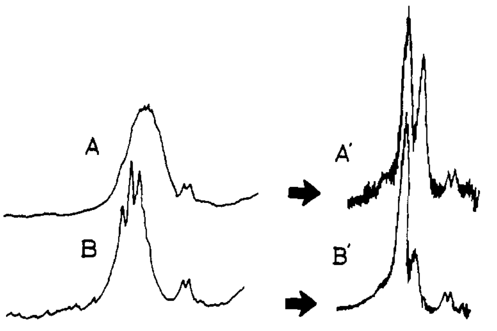

Figure 7. Methine proton resonance of poly(2,4-hexadiene) in $CDCl_3$ solution (10%) before and after decoupling of methyl proton: A, before decoupling of amorphous polymer; A′, after decoupling of amorphous polymer; B, before decoupling of crystalline polymer; B′, after decoupling of crystalline polymer.

pentadiene isomers by the same catalyst.[8,9,24] In this case, only *trans*-1,3-pentadiene, which can coordinate bidentately to Co through the two double bonds, was polymerized to high polymers. Both results suggest that the bidentate coordination of diene compounds to Co through the double bond might chemically activate the monomer. Isomerization occurred during the polymerization in the case of heterogeneous catalysts such as $TiCl_4$–$AlEt_3$.

The Structure of Crystalline Polymer. The ir spectrum of crystalline poly(2,4-hexadiene) was shown in Figure 3. The amorphous polymers obtained from each isomer and its mixtures showed the same spectra as the crystalline polymer except for crystalline-sensitive bands. The absorption band at 970 cm^{-1} is assigned to the out-of-plane deformation of trans C–H bonds, whereas no absorption bands due to the cis configuration of double bonds were found.[7,10,24-26] This result ruled out the presence of the cis-1,4 unit in the polymer. Absence of the cis configuration of double bonds in the polymer obtained from cis,cis isomer suggests that poly(2,4-hexadiene) is mainly composed of 1,4-trans unit. The crystalline-sensitive bands were assigned to 1300, 1190, 1045, and 780 cm^{-1} because these bands decreased and disappeared in the molten state and the CS_2 solution. The enhancement of the intensity at these bands with the increase of melting point of the crystalline polymer further confirms this assignment. The intensity ratio of 1045 to 1015 cm^{-1}, which did not change with the states, was correlated with the melting point of the crystalline polymer (Figure 4). The critical ratio above which the polymer has a melting point was 0.97.

X-Ray diffraction spectra, registered by a Geiger coun-

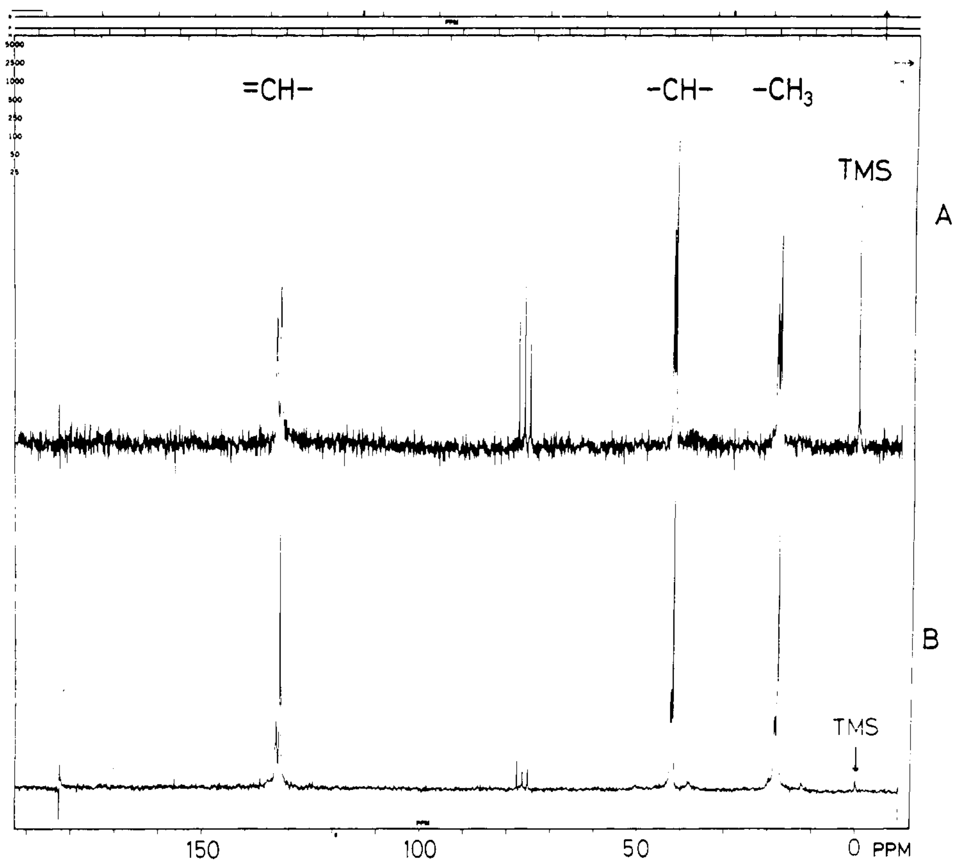

Figure 8. ^{13}C nmr spectra of poly(2,4-hexadiene): A, amorphous polymer (4.5% $CDCl_3$ solution); B, crystalline polymer (mp 78°, 10% $CDCl_3$ solution).

ter, of crystalline polymers obtained by $Co(acac)_3$–$AlEt_2Cl$ and of amorphons polymer obtained by $Ni(acac)_3$–$AlEt_2Cl$ were shown in Figure 5. Five reflexions by the coherent scattering appeared at 15.4, 17.6, 18.7, 20.6, and 24.5° in 2θ. The identity period along the chain axis is 2.3 Å, corresponding to one monomer unit. This result suggests that the crystalline polymer is not syndiotactic but either erythrodiisotactic or threodiisotactic.

The ^1H nmr spectrum of the crystalline polymer is shown in Figure 6. All peaks were assigned by use of spin decoupling. A small doublet absorption band at τ 8.37 changed to a singlet band by decoupling protons of the —CH= group and did not change by the decoupling of methine and methyl protons. Accordingly, this band was assigned to the methyl group in the side chain produced from the 1,2 addition. Strong doublet absorption at τ 9.12 was not influenced by decoupling a proton of the —CH= group. These results clearly show that the crystalline polymer is mainly composed of the 1,4-trans unit. The content of the 1,2 addition was determined by the ratio of the area of this band to that of the other methyl group. The content of the 1,2-addition unit was less than 10% in the crystalline polymer. ^1H nmr spectra of amorphous polymers were almost the same as that of the crystalline polymer except for the methine proton about τ 8.00, indicating that amorphous polymers are also mainly composed of the 1,4-trans unit. A difference between the crystalline polymer and the amorphous polymer is observed in the methine proton near τ 8.00 as shown in Figure 7. The broad absorption band due to the methine proton was separated into two clear doublet absorption bands at τ 7.94 and 8.05 by decoupling the methyl proton (τ 9.12). In the crystalline polymer, the absorption at τ 7.94 is much larger than the other absorption whereas amorphous polymer has absorption bands of almost the same intensity.

Since ir spectroscopy and ^1H nmr spectroscopy showed that 1,2 units and 1,4-cis units were small in all polymers obtained by transition-metal catalysts, two kinds of methine proton in these polymers suggest the presence of two kinds of the 1,4-trans unit, *i.e.,* the erytho trans-1,4 unit and the threo trans-1,4 unit.

To confirm this suggestion, ^{13}C nmr spectra of polymers were examined (Figure 8). The resonance spectra were easily assigned by the use of off-resonance technique. The resonances due to the methyl carbon were separated into two distinct bands at 23.33 and 24.01 ppm. The ratio ($A_{23.33}/A_{24.01}$) of intensities of these bands depends on the stereoregularity of the polymer. The higher the stereoregularity of the polymer, the higher the ratio. The same phenomena were also found in methine carbon at 47.34 and 47.82 ppm. Two kinds of methyl and methine are reasonably accounted for by the presence of the threo trans-1,4 unit and the erythro trans-1,4 unit.

Although no information concerning the configuration of the double bond was obtained from ^1H nmr spectroscopy, the two resonances in olefinic carbon were found at 137.90 and 138.81 ppm in ^{13}C nmr spectra of the polymers. The two resonances of the olefinic carbon might be due to the presence of cis- and trans-1,4 addition or the presence of the threo-1,4 units and erythro-1,4 units. The difference in chemical shifts of two resonances in the methine carbon in our results is much smaller than the difference in the methylene carbon between *trans*-1,4- and *cis*-1,4-polybutadiene.[27-29] Thus, the small difference in the distinct resonances in methine carbon and in olefinic carbon possibly come from the different configuration in the methyl group, *i.e.,* the erythro trans-1,4 unit and the threo trans-1,4 unit.

The melting behavior of the crystalline polymer by a differential scanning calorimeter was shown in Figure 9. Thermal analysis of polymer melting revealed two endothermic

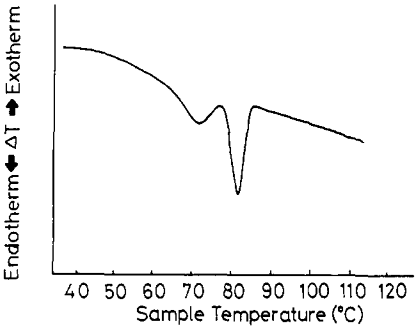

Figure 9. Differential scanning calorimetry of crystalline poly(2,4-hexadiene) (mp 82°), heating rate 10°C/min.

Table III
Polymerization of 2,4-Hexadiene by Transition Metal Acetylacetonate-Et_2AlCl Catalysts[a]

$M(acac)_n$	Yield, %	Mp, °C	$[\eta]$
$Ti(acac)_3$	13	69	0.18
$V(acac)_3$	8	Amorph	0.13
$Cr(acac)_3$	20	Amorph	0.17
$Mn(acac)_3$	15	Amorph	0.16
$Fe(acac)_3$	12	Amorph	0.18
$Co(acac)_3$	54	78	0.14
$Co(acac)_2$	63	77	0.18
$Ni(acac)_2$	65	Amorph	0.15

[a] Solvent, benzene; polym temp, 30°; polym time, 48 hr; $[M(acac)_n] = 7.2 \times 10^{-3}$ mol/l.; Al/M = 10; [monomer] = 2.4 mol/l.

Table IV
Dependence of Microstructure of Poly(2,4-hexadiene) on the Monomer Isomer Ratio[a]

Catalyst	Solvent	Trans, trans/ trans, cis	1,2-unit/ 1,4-unit	Mp, °C
$Co(acac)_2-Et_2AlCl$	Benzene	4.2	0.08	82
$Co(acac)_2-Et_2AlCl$	Benzene	1.3	0.11	81
$Co(acac)_2-Et_2AlCl$	Benzene	0.3	0.13	Amorph
Et_2AlCl	Benzene	4.2	0.21	Amorph
$Co(acac)_2-Et_2AlCl$	*n*-Hexane		0.11	87
$Co(acac)_2-Et_2AlCl$	*n*-Hexane	3.8	0.10	81
$Co(acac)_2-Et_2AlCl$	*n*-Hexane	1.0	0.14	78
$Co(acac)_2-Et_2AlCl$	*n*-Hexane	0.3	0.16	Amorph
$Co(acac)_2-Et_2AlCl$	*n*-Hexane	0.0	0.15	Amorph
Et_2AlCl	*n*-Hexane	3.8	0.15	Amorph

[a] Polym temp, 30°; [monomer] = 2.4 mol/l.; $[Et_2AlCl] = 7.2 \times 10^{-2}$ mol/l.; Al/Co = 10.

peaks. The temperature of the final peak was consistent with the melting point measured by the hot-stage method. The cause of another peak remains unresolved.

We could not determine whether the crystalline polymer is mainly composed of the erythrodiiso trans-1,4-tactic unit or the threodiiso trans-1,4-tactic unit. An inspection of Stuart models revealed that the erythrodiisotactic structure was energetically more favorable than the threodiisotactic and hence it may be assumed that the configuration of the polymer is erythrodiiso trans-1,4 tactic.

The Optimum Condition for Stereoregular Polymerization. The nature of the transition metal in the catalyst is quite important for the stereoregular polymerization of butadiene.[1,3,11] Accordingly, the polymerization of 2,4-hexadiene by homogeneous catalysts, various kinds of transition-metal acetylacetonates, and diethylaluminum chloride was carried out under the same condition (Table III). 2,4-Hexadiene was polymerized by all catalysts, yielding *trans*-1,4-poly(2,4-hexadiene). The crystalline polymers were obtained only by catalysts containing Co or Ti. The former catalyst is better than the latter catalyst both in stereoregulation and the yield of the polymer. An amorphous polymer was yielded by $Ni(acac)_2$–$AlEt_2Cl$ and $V(acac)_3$–$AlEt_2Cl$ which was known to yield stereoregular poly(1,3-pentadiene) and poly(butadiene) under the same condition.[2,30,31] Thus, the effect of the properties of transition metal on the stereoregular polymerization is more sensitive in 2,4-hexadiene than in butadiene and 1,3-pentadiene. The unlikeness of crystallinity in 2,4-hexadiene is probably attributed to the lack of stereoregularity of the methyl group along the chain, because the irregularity of the polymer is mainly caused by the different content of two kinds of 1,4-trans structure, as shown in nmr spectroscopy.

The polymerization of 2,4-hexadiene isomers was carried out by $Co(acac)_3$–$AlEt_2Cl$ and $Ti(acac)_3$–$AlEt_2Cl$ (Tables II and IV). No isomerization was observed during the polymerization by both of the homogeneous catalysts. All isomers polymerized to high polymer were predominantly composed of the trans-1,4 structure. Crystalline polymer was obtained only from the trans,trans isomer which can make the cissoid form. In the mixture of trans,trans and trans,cis isomer, the larger the content of the former isomer, the higher the melting point of the polymer prepared. Amorphous polymer was obtained from other isomers by the homogeneous catalysts.

The polymerization of 2,4-hexadiene by $Co(acac)_3$–$AlEt_2Cl$ was carried out in heptane and benzene, respectively (Table IV). The configuration of the polymer obtained did not depend on the polymerization solvents, being in contrast to the result of 1,3-pentadiene in which this catalyst behaved very differently in aromatic solvents (cis-1,4-syndiotactic) and in aliphatic solvents (1,2-syndiotactic).[8] This result suggests that the conformation of the terminal active end and the coordination mode of monomer to catalysts were not affected by solvents in the polymerization of 2,4-hexadiene.

The effect of the ligand of the catalysts on the stereoregular polymerization of the polymer was also investigated in $AlEt_2Cl$–Co compounds (Table V). Table V shows that the nature of the ligand has a minor effect on the microstructure of the polymer. This result is remarkably different from that in the butadiene polymerization by π-C_3H_5NiX in which a drastic change of microstructure has been shown from cis 1,4 for X = Cl to trans 1,4 for X = I.[32-38]

The effect of Al/Co on the stereoregularity of the polymer was investigated (Table VI). When Al/Co is less than 5, the polymerization did not occur. The polymer having the maximum melting point was obtained at Al/Co = 10. On further increase of Al/Co, the melting point decreased and the yield of the polymer increased, owing to a cationic polymerization by residual $AlEt_2Cl$.[22]

Mechanism of Stereoregular Polymerization of 2,4-Hexadiene by $Co(acac)_3$–$AlEt_2Cl$. The mechanism based on the mode of the monomer coordination, bidentate or unidentate, to the catalyst has been proposed for the stereocontrol of diene polymerizations by transition metal catalysts.[3,8,37] Some researchers have proposed that the stereoregular polymerization of diene compounds does not depend on the coordination of the monomer to catalyst but on the structure of the propagating active end.[12-14]

2,4-Hexadiene is an interesting diene monomer from the point of mechanistic interpretation since it exists in three

Table V
The Effect of the Ligands of the Catalysts on the Microstructure of the Polymer[a]

Catalyst	Solvent	Yield, %	Mp, °C
$CoCl_2 \cdot 2Py-Et_2AlCl$	Benzene	35	84
$CoBr_2 \cdot 2Py-Et_2AlCl$	Benzene	29	85
$CoI_2 \cdot 2Py-Et_2AlCl$	Benzene	37	89
$Co(acac)_2-Et_2AlCl$	Benzene	28	81

[a] Polym temp, 30°; polym time 10 hr; [monomer] = 2.4 mol/l.; trans,trans/trans,cis = 1.3; $[CoX_2] = 7.2 \times 10^{-3}$ mol/l.; Al/Co = 10.

Table VI
The Effect of the Ratio of Et_2AlCl and $Co(acac)_2$ on the Crystallinity of the Polymer[a]

Al/Co	Yield, %	Mp, °C
5	0	
10	35	81
20	61	77
50	58	71
100	70	69

[a] Solvent, benzene; polym temp, 30°; polym time, 18 hr; [monomer] = 2.4 mol/l.; trans,trans/trans,cis = 1.0; $[Co(acac)_2] = 7.2 \times 10^{-3}$ mol/l.

geometrically isomeric forms. The crystalline polymer was obtained from the trans,trans isomer, which can make the cissoid form (Figure 2). In addition, the trans,trans isomer was much more reactive than other isomers in the polymerization by $Co(acac)_3-AlEt_2Cl$, while the cis,trans isomer was more reactive in cationic polymerization.[22] $Ti(acac)_3-AlEt_2Cl$, both with regard to polymer yield and the crystallinity of the polymer, was less active than $Co(acac)_3-AlEt_2Cl$. The difference between trans,trans and trans,cis isomers in the polymerization rate was not so pronounced with $Ti(acac)_3-AlEt_2Cl$ as that with $Co(acac)_3-AlEt_2Cl$. The polymerization of 2,4-hexadiene by $Ti(acac)_3-AlEt_2Cl$ might be carried out through the unidentate coordination of monomer to the catalyst, as proposed in the polymerization of 1,3-pentadiene by titanium catalyst.[1,2]

The above-mentioned results of polymerization by $Co(acac)_3-AlEt_2Cl$ indicate that the bidentate coordination of cobalt is an important factor for stereocontrol in the 2,4-hexadiene polymerization. However, the bidentate coordination of butadiene possibly leads to the *cis*-1,4-polybutadiene[1,3] whereas the obtained polymer of 2,4-hexadiene was predominantly composed of the 1,4-trans structure. The difference is likely to come from isomerization of propagating chain end. The formation of the 1,4-trans polymer can be derived from the isomerization of anti π-allyl terminal to the more stable syn π-allyl one or δ-allyl one after addition of the monomer coordinated bidentately[17,39,40] ($2 \rightleftharpoons 3 \rightleftharpoons 4$, Figure 10). The difference between polybutadiene and poly(2,4-hexadiene) in their microstructure is possibly ascribed to the thermodynamic stability of configuration of the active chain end.[17,39,40] The presence of methyl groups in the polymer is likely to make the anti π-allyl active chain end more unstable in 2,4-hexadiene than in butadiene. The minor effects of ligand and solvent on the stereoregularity of 2,4-hexadiene polymers support this assumption. That is to say, the isomerization to the stable syn π-allyl active end occurs in preference to other effects and hence the propagating chain ends are hardly affected with ligands and solvents. $Ni(acac)_2-AlEt_2Cl$, both with regard to the polymer yield and the preparation of crystalline polymer, was similar to $Co(acac)_3-AlEt_2Cl$ in the polymerization of butadiene.[2] In the case of 2,4-hexadiene, however, even the polymer obtained from the trans,trans isomer by the former catalyst was amorphous, although both catalysts showed the similar polymerization rate and both polymers obtained were composed of 1,4-trans structure (Table II). The polymerization with both catalysts is likely to proceed through the bidentate coordination of monomer since rate of polymerization is similar in both catalysts and the properties of Ni are similar to those of Co.[3,11] The difference observed may be due to the irregular structure of monomer unit caused by isomerization of the active end through hydride shift in $Ni(acac)_2-AlEt_2Cl$ (**$3 \rightleftharpoons 4 \rightleftharpoons 5 \rightleftharpoons 6$**, Figure 10), because the irregularity is produced by the random distribution of two kinds of trans-1,4 structures and π-allyl Ni complex might be more effective than π-allyl Co complex in isomerization.[41-44]

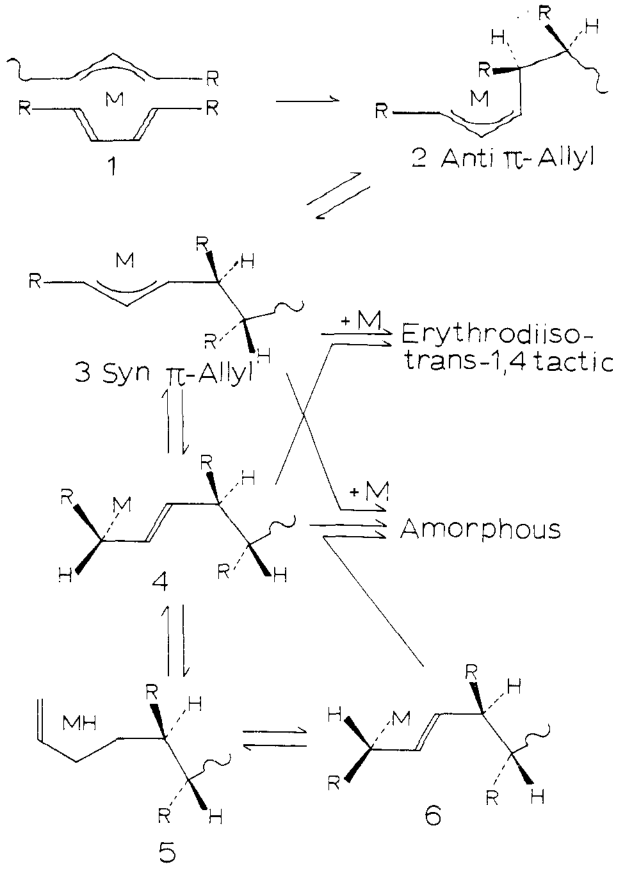

Figure 10. Structural formulas of propagating active ends and the polymers obtained from them.

Conclusion. The study on the stereoregular polymerization of three isomers of 2,4-hexadiene by homogeneous transition-metal catalysts showed that the kind of transition metals and the isomeric form of monomer are important factors for the preparation of crystalline polymers. The highly crystalline erythrodiiso trans-1,4-tactic polymer was obtained by $Co(acac)_2-AlEt_2Cl$ using only trans,trans isomers. Amorphous polymers were obtained from other isomers (trans,cis and cis,cis) although they were mainly composed of the trans-1,4 unit. No effect of ligands of cobalt and polymerization solvents on the stereoregularity was observed in the polymerization by cobalt salt–$AlEt_2Cl$, being in contrast to those in butadiene and 1,3-pentadiene.

The stereoregulation of the polymer obtained in the polymerization of diene compounds is not only due to the coordination mode of the monomer but also the thermodynamic stability of the propagating end.

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Polymerization of Propylene to Syndiotactic Polymer. VIII. Steric Control Forces

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ABSTRACT: The syndiotactic specific polymerization of propylene in the presence of homogeneous vanadium-based catalyst systems has been studied by ^{13}C nmr as a four-step copolymerization between "head-to-tail" and "tail-to-head" propylene. The activation barriers responsible for the prevailingly syndiotactic reaction pattern have been evaluated.

Propylene polymers obtained in the presence of vanadium-based syndiospecific catalyst systems contain a nonnegligible proportion of monomer units arranged in head-to-head ($-CH(CH_3)CH_2-CH_2-CH(CH_3)-$) and tail-to-tail ($-CH_2-CH(CH_3)CH(CH_3)-CH_2-$) sequences.[3] Preliminary data also seem to indicate that these polymer chains consist of long stereoblocks with a predominantly syndiotactic structure and of shorter stereoblocks with a sterically disordered structure.[4]

It has been suggested[5] that syndiotactic stereoblocks are formed by addition of the monomer to a growing chain ending in a substituted carbon atom, *i.e.*, by insertion of the monomer at a secondary metal–carbon bond.

Me ●— … + C_3H_6 → Me ●— ●— …

(Here, Me, ●—, —● indicate respectively the metal atom of the catalytic complex and the monomer units in the orientation $-CH(CH_3)CH_2-$ and $-CH_2CH(CH_3)-$.) Sterically disordered stereoblocks should instead form by addition of the monomer to a growing chain ending in a methylene carbon, *i.e.*, by insertion at a primary metal–carbon bond.

Me —● … + C_3H_6 → Me —● —● …

Consequently, the ends of each stereoblock should consist of one pair of head-to-head units (●— —●) and of one pair of tail-to-tail (—● ●—) units.

On the basis of these hypotheses, we have attempted to measure the forces of steric and arrangement controls involved in the polymerization considered by comparing the structures of the polymers obtained at different temperatures.

Results

According to the previous hypotheses, propylene polymerization in the presence of vanadium-based syndiospecific catalysts may be represented as a particular type of co-