Copolymerization of Propylene and 1,5-Hexadiene with Stereospecific Metalloocene/Al(i-Bu)3/[Ph3C][B(C6F5)4]

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ABSTRACT: Copolymerizations of propylene (P) with 1,5-hexadiene (1,5-HD) were carried out with isospecific rac-1,2-ethylenebis(1-indenyl)Zr(NMe2)2 [rac-(EBI)Zr(NMe2)2, 1] and syndiospecific isopropylidene(cyclopentadienyl)(9-fluorenyl)ZrMe 2 [i-Pr(Cp)-(Flu)ZrMe2, 2] compounds combined with Al(i-Bu)3/[Ph3C][B(C6F5)4] as a cocatalyst system. Microstructures of poly(propylene-co-1,5-HD) were determined by 1H NMR, 13C NMR, Raman spectroscopies and X-ray powder diffraction. The isospecific 1/Al(i-Bu)3/[Ph3C][B(C6F5)4] catalyst showed much higher polymerization rate than 2/Al(i-Bu)3/[Ph3C][B(C6F5)4] system, however, the latter system showed higher incorporation of 1,5-HD (rP = 16.25, r1,5-HD = 0.274) than the former system (rP = 8.85, r1,5-HD = 0.274). The high value of rP × r1,5-HD far above 1 demonstrated that the copolymers obtained by both catalysts are somewhat blocky. The insertion of 1,5-HD proceeded by enantiomorphic site control; however, the diastereoselectivity of the intramolecular cyclization reaction of 1,2-inserted 1,5-HD was independent of the stereospecificity of metallocene compounds, but dependent on the concentration of 1,5-HD in the feed. The insertion of the monomers by enantiomorphic site control could also be realized by Raman spectroscopy and X-ray powder diffraction of the polymers. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 1590–1598, 2000

Keywords: propylene; 1,5-hexadiene; copolymerization; stereospecific; metalloenes

INTRODUCTION

Marvel and Stille first reported the cyclopolymerization of nonconjugated 1,5-hexadiene (1,5-HD) in 1958,1 however much attraction has not been paid to this subject for a long time. Recently, Waymouth and coworkers reported that various nonconjugated diolefins, such as 1,5-HD, 1,4-pentadiene, and 1,7-octadiene undergo cyclopolymerization by various metallocene catalysts.2 The cyclopolymerization of 1,5-HD by optically active metalloocene catalysts led to optically active trans-diisotactic poly(methylene-1,3-cyclopentane) (PMCP) as a major product.2

Copolymerizations of ethylene and/or propylene with nonconjugated dienes with various metalloocene catalysts are a useful method to synthesize polyolefins with cyclic backbone. Polyolefins with cyclic units in backbone show high glass-transition temperatures and high transparency and thus these materials are suitable for optical and medical applications.3 Copolymerizations of olefin/nonconjugated dienes can be an alternative method of olefin/cycloolefin copolymerization, because homo- and copolymerization of cycloolefins show low productivity. Marques et al. and Luft et al. studied ethylene/1,5-HD copolymerization with metallocene catalysts.4 Ethylene/1,5-HD co-
polymerization and ethylene/styrene/1,5-HD terpolymerization with constrained geometry catalyst were reported by Mühlaupt and coworkers.\textsuperscript{5} Shiono et al. investigated propylene/1,5-HD and propylene/1,7-octadiene copolymerizations with various metalloocene catalysts.\textsuperscript{6}

In this study, we described the effect of metalloocene stereospecificity on propylene/1,5-HD copolymerization with two metalloocene catalysts, isospecific rac-1,2-ethylenebis(1-indenyl)Zr(NMe\textsubscript{2})\textsubscript{2} [rac-(EBI)Zr(NMe\textsubscript{2})\textsubscript{2}, 1] and syndiospecific isopropylidenecyclopentadienyl(9-fluorenyl)ZrMe\textsubscript{2} [i-Pr(Cp)(Flu)ZrMe\textsubscript{2}, 2], combined with Al(i-Bu)\textsubscript{3}/[Ph\textsubscript{3}C][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] as a cocatalyst system. In addition, the microstructure of poly(propylene-co-1,5-HD) was investigated.

**EXPERIMENTAL**

**Materials**

All reactions were carried out under a purified nitrogen atmosphere using standard dry box and Schlenk techniques. Propylene (donated by SK Co., Korea) of polymerization grade was purified by passing it through columns of Fisher RIDOX catalyst and molecular sieve 5A/13X. 1,5-hexadiene was distilled from CaH\textsubscript{2}. Solvents were distilled from Na/benzophenone and stored over molecular sieves (4A). Triisobutyl aluminum [Al(i-Bu)\textsubscript{3}] was obtained from Aldrich and used without further purification. Metalloocene compounds, rac-(EBI)Zr(NMe\textsubscript{2})\textsubscript{2} and Me\textsubscript{2}C(Cp)(Flu)ZrMe\textsubscript{2},\textsuperscript{8} and anionic [Ph\textsubscript{3}C][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}]\textsuperscript{3} compounds were synthesized according to literature procedures.

**Polymerization**

Copolymerizations were carried out in a 250-mL glass reactor equipped with a magnetic stirrer and a thermometer. In a dry box, the reactor was filled with 80 mL of toluene, Al(i-Bu)\textsubscript{3}, 1,5-HD, and metalloocene compound. The reactor was immersed in a constant-temperature bath previously set to the desired temperature. When the reactor temperature had been equilibrated to the bath temperature, propylene was introduced into the reactor after removing the argon gas under a vacuum. When no more absorption of propylene into toluene was observed, a prescribed amount of [Ph\textsubscript{3}C][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] dissolved in toluene was injected into the reactor and then the polymerization was started. The polymerization rate was determined at every 0.01 s from the rate of consumption and was measured by a hot-wire flowmeter (model 5850 D, Brooks Instrument Div.) connected to a personal computer through an analog to digital converter. Polymerization was quenched by the addition of methanol. The polymer obtained was filtered, washed with an excess amount of methanol and dried in vacuum at 50 °C for 24 h.

**Characterization**

\textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra of the polymers were recorded at 110 °C on a Varian Unity Plus 300 spectrometer. Samples were prepared by dissolving the polymer in CDCl\textsubscript{3}-tetrachloroethane (1/5, v/v). Melting curves were recorded with a DuPont differential scanning calorimeter (DSC, Model 910) at a 10 °C/min. The intrinsic viscosities of polymers were determined in 1,2,4-trichlorobenzene at 135 °C using an Ubbelohde viscometer. Raman spectra were recorded on a Brucker IFS55 FTIR spectrometer with the Raman modules (FRA 106), CaF\textsubscript{2} beamsplitter, and Ge detector. The excitation source was a diode pumped Nd: YAG laser operated at 1064 nm. The laser power was 350 mW. The crystalline structure of the polymer was determined by a wide-angle X-ray diffractometer (Rigaku 2013) using Cu K\textalpha at 40 kV, 50 Ma with a scan speed of 2 °/min.

**RESULTS AND DISCUSSION**

**Copolymerization Activity and Copolymer Composition**

Copolymerization of propylene and 1,5-HD was carried out at 30 °C in the presence of isospecific catalyst, 1 and syndiospecific catalyst, 2. Figures 1 and 2 show the polymerization rate (R\textsubscript{p}) curves as a function of time obtained by using 1/Al(i-Bu)\textsubscript{3}/[Ph\textsubscript{3}C][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] and 2/Al(i-Bu)\textsubscript{3}/[Ph\textsubscript{3}C][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}], respectively. We have carried out the polymerization for 20 min in order to minimize the variation of 1,5-HD comonomer concentration during polymerization. Polymerizations reach maximum rate within 5 min in the presence of small amount of the comonomer, however, the induction period becomes longer as the amount of comonomer increases.

The polymerizations obtained by using 1/Al(i-Bu)\textsubscript{3}/[Ph\textsubscript{3}C][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] show quite different ki-
netic behaviors compared to 2/Al(i-Bu)_3/[Ph_3C][B(C_6F_5)_{4}]_4 catalyst at various [1,5-HD]/[IP] ratios of (a) 0, (b) 0.1, (c) 0.3, (d) 0.6, (e) 1.0, (f) 2.0, and (g) 3.0. Polymerization conditions: \( P_{\text{propylene}} = 5 \) psig, \( T_p = 30^\circ C \), [Al]/[Zr] = 80, [(Ph_3C)(B(C_6F_5)_{4})]/[Zr] = 1, and toluene = 80 mL.

Figure 1. \( R_p \) versus time curves obtained by the 1/Al(i-Bu)_3/[Ph_3C][B(C_6F_5)_{4}]_4 catalyst at various [1,5-HD]/[IP] ratios of (a) 0, (b) 0.1, (c) 0.3, (d) 0.6, (e) 1.0, (f) 2.0, and (g) 3.0. Polymerization conditions: \( P_{\text{propylene}} = 5 \) psig, \( T_p = 30^\circ C \), [Al]/[Zr] = 80, [(Ph_3C)(B(C_6F_5)_{4})]/[Zr] = 1, and toluene = 80 mL.

Figure 2. \( R_p \) versus time curves obtained by the 2/Al(i-Bu)_3/[Ph_3C][B(C_6F_5)_{4}]_4 catalyst at various [1,5-HD]/[IP] ratios of (a) 0, (b) 0.1, (c) 0.3, (d) 0.6, (e) 1.0, and (f) 2.0. Polymerization conditions: \( P_{\text{propylene}} = 5 \) psig, \( T_p = 30^\circ C \), [Al]/[Zr] = 80, [(Ph_3C)(B(C_6F_5)_{4})]/[Zr] = 1, and toluene = 80 mL.

Figure 3. Effect of 1,5-HD concentration on the average polymerization rate. Polymerization conditions are the same as those in Figures 1 and 2, and the catalysts are (a) 1 and (b) 2.

The comonomer content incorporated in the copolymer was determined by \(^{13}\)C NMR spectroscopy according to the literature. A more detailed kinetic study, possibly using a specifically labeled monomer and comonomer would be necessary to explain the difference. The highly electrophilic character of the cationic zirconocene species, in particular the ones issued from 2/Al(i-Bu)_3/[Ph_3C][B(C_6F_5)_{4}]_4 system, is likely responsible for the observed low activity.

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are summarized in Table I together with polymerization results and Figure 4, which shows the plot of 1,5-HD percentage in feed versus 1,5-HD percentage in copolymer. The calculation of copolymerization parameters according to Kelen–Tüdös plot resulted in $r_P = 16.25$, $r_{1,5\text{-HD}} = 0.34$ ($r_P \times r_{1,5\text{-HD}} = 5.53$) with $1/[\text{Al}/(i\text{-Bu})]/[\text{Ph}_3\text{C}]_2\text{[B(C}_6\text{F}_5\text{F}_4])]/[\text{Zr}] = 1$, toluene = 80 mL.

Table I. Results of Copolymerization of Propylene and 1,5-Hexadiene$^a$

<table>
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<tr>
<th>Run No.</th>
<th>Cat.</th>
<th>[1,5-HD] in Feed (mol %)</th>
<th>[Zr] (µmol)</th>
<th>$T_p$ (°C)</th>
<th>[1,5-HD] in Copolymer$^b$ (mol %)</th>
<th>Trans$^b$ (%)</th>
<th>Cyclization$^c$ (%)</th>
<th>$\tilde{R}_p$</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_f$ (J/g)</th>
<th>$[\eta]^f$</th>
<th>$X_c^g$ (%)</th>
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<td>2.63 n.d.$^b$</td>
<td>111.5</td>
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<td>111.5</td>
<td>5.65</td>
<td>0.299</td>
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<td>6.65</td>
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<td>99.47</td>
<td>0.06 n.d.$^b$</td>
<td>111.3</td>
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<td>0.299</td>
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<td>0.03 n.d.$^b$</td>
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<td>30</td>
<td>22.00</td>
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<td>97.35</td>
<td>0.01 n.d.$^b$</td>
<td>111.5</td>
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<td>30</td>
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<td>100</td>
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<td>12.39</td>
<td>0.352</td>
<td>—</td>
<td>—</td>
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</table>

$^a$ Polymerization conditions: $P_{\text{propylene}} = 5$ psig, $[\text{Al}]/[\text{Zr}] = 80$, $[[\text{Ph}_3\text{C}]_2\text{[B(C}_6\text{F}_5\text{F}_4])]/[\text{Zr}] = 1$, toluene = 80 mL.

$^b$ Determined by $^{13}$C NMR.

$^c$ Determined by $^1$H NMR.

$^d$ Unit is $10^6$ g-PP/mol-Zr h.

$^e$ Not detected.

$^f$ In 1,2,4-trichlorobenzene at 135 °C.

$^g$ Determined by XRD.

$^h$ In 1,2,4-trichlorobenzene at 135 °C.

Figure 4. Copolymerization diagrams of propylene and 1,5-HD. The catalysts used are (a) 1 and (b) 2.
interesting to note that the intrinsic viscosity of copolymer shows different behavior, depending on the catalyst used (Table I). The intrinsic viscosity ([\eta]) of copolymer produced by 2 decreases according to the increase of the amount of 1,5-HD incorporated. On the other hand, the intrinsic viscosity of copolymer by 1 increases as the amount of 1,5-HD incorporated in copolymer increases. The copolymer with 25.2% of 1,5-HD (Run No. 7) incorporated shows higher value than polypropylene (Run No. 1). It is not clear why these results are obtained. It may be assumed that some amount of crosslinking has occurred during polymerization through the unsaturated double bonds generated by 1,2-added 1,5-HD that fails to cyclopolymerize and remain in the polymer backbone as shown in Scheme 1. The unsaturated bonds remaining in the side chain cause the crosslinking, resulting in the increase of molecular weight of the polymer.

**Characterization of Copolymer**

In order to get more insight into the microstructure of the copolymers obtained by isospecific 1 and syndiospecific 2 compounds, the microstructure of poly(propylene-co-1,5-HD) was investigated with \(^{13}\)C NMR spectroscopy. Shiono et al. investigated detailed microstructure of the copolymers by using \(^1\)H NMR, \(^{13}\)C NMR, and DEPT (distortionless enhancement of polarization transfer) spectroscopies. Figure 5 shows the \(^{13}\)C NMR spectra of representative copolymers synthesized by 1 and 2 compounds (see also Table I). The stereochemistry in copolymerization of propylene and 1,5-HD is dependent on the stereospecificity of catalysts used. Waymouth and coworkers investigated the effect of metalloocene geometry on the diastereoselectivity (selectivity of cis- or trans-cyclization) in the 1,5-HD homopolymerization and concluded that diastereoselectivity was affected by the steric effect of ligand and bite angle associated with the metalloocene catalyst precursors. Cavello et al. carried out conformational calculations on the diastereoselectivity and reported a good agreement with polymerization results. We can define the stereoregulations of isolated methylene-1,3-cyclopentane (MCP) units next to propylene units as cis-m, cis-r, trans-m, and trans-r as shown in Scheme 2, if we assume that compound 1 polymerizes propylene and 1,5-HD isospecifically based on enantiomorphic site control [Scheme 2(a,b)], and compound 2 polymerizes them syndiospecifically [Scheme 2(c,d)]. The resonances at 31.9, 32.1, 32.5-32.6, 33.1, and 33.7-33.8 ppm in Figure 5 are assigned to cis-r, cis-homosequential units of MCP, cis-m, trans-homosequential units of MCP, trans-r and trans-m of 3,4 carbon (see Scheme 1) in cyclopentane, respectively. The resonance of 43.9 ppm is assigned to homosequential units of 6 carbon in cyclopentane. The appearance of homosequential units of MCP indicates that compounds 1 and 2 copolymerize propylene and 1,5-HD to form blocky structure as already identified by \(r_P \times r_{1,5-HD}\) values. In addition, no cis-r

![Scheme 1](image1)

![Figure 5](image2)

![Scheme 2](image3)
Scheme 3

(31.9 ppm) is observed and the molar ratios of trans-m to trans-r is close to 1.02 for the copolymer obtained by compound 1, and no trans-m unit is expectedly observed and the molar ratio of cis-m to cis-r is close to 0.96 for the copolymer obtained by compound 2, demonstrating that the insertion of propylene and 1,5-HD is accomplished predominantly by the enantiomorphic site control. The trans/cis ratios measured by using resonance ratio of 3,4 carbon in cyclopentane units are higher with 2 than with 1 (Table I). This result agrees with that of homopolymerization of 1,5-HD carried out by the same catalysts.14

The degree of cyclization of 1,2-inserted 1,5-HD was determined by 1H NMR spectroscopy (Table I).15 At the low concentration of 1,5-HD in the feed, the degree of cyclization approaches 100%, however, the value decreases somewhat as the concentration of the comonomer increases, demonstrating that 1,5-HD concentration in the polymerization medium influences the cyclization selectivity. The selectivity of 1,2-added 1,5-HD cyclization could be interpreted in the point of competition between intramolecular cyclization and intermolecular propagation reaction.16 As shown in Scheme 3, in the first step only one 1,5-HD double bond is involved, to form [Zr-1,5-HD]* active species. The active species can either yield a cyclic structure, by reacting intramolecularly with the residual double bond, or attack one of the double bonds of another monomer, propylene, or 1,5-HD. In the second case, instead of a cyclic structural unit, an unsaturated linear structural unit is left behind in the growing chain. As the intramolecular cyclization of 1,2-inserted 1,5-HD is unimolecular and the intermolecular propagation is bimolecular, the intermolecular propagation can be activated at higher concentration of the comonomer, resulting in the ratio of intramolecular cyclization/intermolecular propagation increases at more dilute conditions.

The ratio between the mole fraction \( f_c \) of cyclic structural units and the mole fraction \( f_u \) of unsaturated structural units can be expressed quantitatively by the ratio between the rate of the reactions yielding the two kinds of structural units:

\[
\frac{f_u}{f_c} = \frac{k_c[Zr-1,5-HD]^*}{n k_p[Zr-1,5-HD]^*[M]} \tag{1}
\]

where \( k_c \) and \( k_p \) are the rate constants of the intramolecular and the intermolecular reactions, respectively, and \([M]\) is the monomer (propylene or 1,5-HD) molar concentration. The \( n \) value is 1 when \( M \) is propylene and 2 when \( M \) is 1,5-HD because there are two points of attack, the two unsaturations, in 1,5-HD of \([Zr-1,5-HD]^*\) species onto the monomer molecules. Assuming that the intramolecular and the intermolecular reactions are the only insertion of 1,5-HD, \( f_u + f_c = 1 \) and letting cyclization ratio \( r_c = k_c/k_p \), one obtains from eq 1:

\[
\frac{1}{f_c} = 1 + \frac{n[M]}{r_c} \tag{2}
\]

This simple relation shows that, by increasing the monomer concentration, the mole fraction \( f_c \) must decrease.

The increase of intermolecular propagation at higher 1,5-HD concentration could also be identified by FT Raman spectra of poly(propylene-co-1,5-HD)s. Figures 6 and 7 show the Raman spectra of poly(propylene-co-1,5-HD)s synthesized by 1 and 2, respectively. The presence of the peak at 1640 cm\(^{-1}\) resulting from C=O stretching vibration [Fig. 6(f,g) and Fig. 7(e,f)] demonstrates the intermolecular propagation of 1,2-inserted 1,5-HD. FT Raman spectra provide a good opportunity to investigate the crystalline structure of polymers. As shown in Figures 6 and 7, the intensities of the peaks at \( \sim 310, \sim 398, \sim 809, \sim 841, \sim 900, \sim 998, \) and \( \sim 1168 \) cm\(^{-1}\) resulting from the crystalline helix bands of isotactic polypropylene (Fig. 6) and those at \( \sim 867, \sim 977, \) and \( \sim 1005 \) cm\(^{-1}\) resulting from the helix structure of syndiotactic polypropylene (Fig. 7)17–19 decrease monotonously as the amount of 1,5-HD incorporated in the copolymer increases, demonstrating that the
crystallinity of the copolymer decreases as the amount of 1,5-HD incorporated in the copolymer increases. FT Raman spectra of poly(propylene-co-1,5-HD) obtained by 1 are quite different from those obtained by 2, since the crystalline structure of the resulting copolymers are evidently different from each other depending on the stereospecificity of the metallocene compound. Comparing the spectrum of polypropylene homopolymer [Fig. 6(a)] obtained by 1 with the spectra of copolymers [Fig. 6(b) through (g)] obtained by 1 and the spectrum of polypropylene [Fig. 7(a)] with the spectra of copolymers [Fig. 7(b) through (f)] obtained by 2, the isotactic and the syndiotactic configurations of polypropylene are retained in the copolymers, even if the crystallinity decreases as the amount of 1,5-HD increases. This result indicates that the insertion of propylene is accomplished by the enantiomorphic site control.

The quantification of the amount of 1,5-HD incorporated in the copolymers has been made by comparing the intensity of peak of Raman spectra. Carefully looking into the spectra of propylene [Fig. 6(a) and Fig. 7(a)] and 1,5-HD [Fig. 6(h) and Fig. 7(g)] homopolymers, and propylene/1,5-HD copolymers, the peaks at 1445 cm\(^{-1}\), which is assigned to be CH\(_2\) deformation and is recorded strong for poly(methylene-1,3-cycloptane), and 1464 cm\(^{-1}\), which is assigned to be CH\(_2\) bending vibrations\(^{17,19}\) and is the characteristic one for polypropylene as shown in Figures 6 and 7. Baselines were drawn between 1400 cm\(^{-1}\) and 1518 cm\(^{-1}\) for the determination of Raman intensities. Figure 8 shows \(I_{1445}/I_{1464}\) ratio versus the amount of 1,5-HD in copolymer determined by \(^{13}\)C NMR. As \(I_{1445}/I_{1464}\) ratios of isotactic and syndiotactic polypropylene are different from each other, the quantitative analyses were made for the copolymers synthesized by each catalyst. There are good linear relationships between \(I_{1445}/I_{1464}\) and the amount of 1,5-HD in copolymer for each catalyst expressed as:

\[
I_{1445}/I_{1464} = 0.023 [1,5-HD \text{ in copolymer}] + 0.338
\]

for catalyst 1

\[
I_{1445}/I_{1464} = 0.016 [1,5-HD \text{ in copolymer}] + 0.913
\]

for catalyst 2

The \(r^2\) value, which is a measure of the linear correlation between the experimental points (\(I_{1445}/I_{1464}\) in Raman spectra) and the actual
The amount of 1,5-HD in copolymer (determined by $^{13}$C NMR), is 0.996 for both cases.

The retention of configuration of polypropylene in the copolymers at the expense of the crystallinity according to the amount of 1,5-HD in copolymer could also be identified by the X-ray powder diffraction as shown in Figures 9 and 10. The broadening of the peaks remaining at the same position as the amount of 1,5-HD increases indicates the decrease of the crystallinity. The crystallinity determined by the X-ray powder diffraction is also summarized in Table I. Expectedly the copolymers become amorphous structures at the high concentration of 1,5-HD.

**CONCLUSION**

The isospecific 1/Al($i$-Bu)$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] catalyst showed much a higher polymerization rate than 2/Al($i$-Bu)$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] system, however, the latter system showed higher incorporation of 1,5-HD ($r_P = 8.85$, $r_{1,5}$-HD = 0.274) than the former system ($r_P = 16.25$, $r_{1,5}$-HD = 0.34). In the copolymerization of propylene and 1,5-HD the insertion of the monomers proceeded by enantioselective site control, however, the diastereoselectivity of the cyclization reaction of 1,2-inserted 1,5-HD was independent of the stereoselectivity of metallocene compounds and dependent on the monomer concentration in the

![Figure 8](image.png)

**Figure 8.** Relationship between Raman intensity ratio ($I_{1445}/I_{1464}$) and the amount of 1,5-HD in copolymer determined by $^{13}$C NMR spectroscopy. The catalysts used are (a) 1 and (b) 2.

![Figure 9](image.png)

**Figure 9.** XRD patterns for copolymers synthesized by the 1/Al($i$-Bu)$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] catalyst. Run No. in Table I is (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, and (h) 8.

![Figure 10](image.png)

**Figure 10.** XRD patterns for copolymers synthesized by the 2/Al($i$-Bu)$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] catalyst. Run No. in Table I is (a) 9, (b) 10, (c) 11, (d) 12, (e) 13, (f) 14, and (g) 15.
feed due to the competition of intramolecular cyclization and the intermolecular propagation. The insertion of the monomers made predominantly by enantiomorphic site control could be realized by both Raman spectroscopy and X-ray powder diffraction of the polymers. The copolymers obtained by 1 and 2 catalysts show somewhat blocky structure.

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REFERENCES AND NOTES