

# Copolymerization of Ethylene/Nonconjugated Dienes over a Bis(2-methyl indenyl) Zirconium Dichloride/Methylaluminumoxane Catalyst System

HYOUNG-JOON JIN,<sup>1</sup> CHANG-HO CHOI,<sup>1</sup> EUN-SOO PARK,<sup>1</sup> IK-MO LEE,<sup>2</sup> JIN-SAN YOON<sup>1</sup>

<sup>1</sup> Department of Chemical Science Engineering, Inha University, 402-751 Incheon, Korea

<sup>2</sup> Department of Chemistry, Inha University, 402-751 Incheon, Korea

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**ABSTRACT:** Ethylene was copolymerized with 1,5-hexadiene (1,5-HD), 1,4-hexadiene (1,4-HD) and 1,7-octadiene (1,7-OD) with bis(2-methyl indenyl) zirconium dichloride/methylaluminumoxane. 1,5-HD units formed the *trans*-structured cyclopentane rings and 1-butenyl side chains, and cross-linking took place during ethylene/1,5-HD (E15HD) copolymerizations. The lower the polymerization temperature was, the larger the amount of hot xylene (XYL)-insoluble fraction was. Copolymers of ethylene/1,7-OD (E17OD) did not have any cyclic structures and were nearly insoluble in XYL when produced below 60°C. In contrast, all the copolymers of ethylene/1,4-HD (E14HD) were completely soluble in XYL. The broadest differential scanning calorimetry melting peak was found for E15HD and then for E17OD, and the narrowest was found for E14HD due to the presence or the absence of the cyclic structures and cross-linking. Addition of 1,7-OD or 1,4-HD as a comonomer reduced the polymerization rate and the molecular weight of the respective copolymers much more than that of 1,5-HD. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1048–1058, 2002; DOI 10.1002/app.10397

**Key words:** copolymerization; polyethylene; metallocene catalysts

## INTRODUCTION

Copolymerizations of ethylene and dienes have been carried out to synthesize functional polyolefins with unreacted vinyl groups.<sup>1–3</sup> The functional polyolefins enhance adhesion and printability of polyolefins and can be used as interfacial modifiers for blends of polyolefins with polar polymers.

Homogeneous metallocene catalysts have been known to be more effective in the copolymerization of dienes than heterogeneous Ziegler–Natta catalysts.<sup>4–6</sup> Homopolymerization of 1,5-hexadiene (1,5-HD) and copolymerization of ethylene/1,5-HD (E15HD) have been performed,<sup>7–9</sup> and Mülhaupt and colleagues investigated ethylene/styrene/1,5-HD terpolymerization using the constrained geometry catalyst.<sup>10</sup>

Cyclopentene rings can be formed, as well as 1-butenyl side chains, and cross-linking can also take place during E15HD copolymerizations,<sup>11</sup> resulting in a complicated molecular structures of E15HD.

In this study, ethylene was copolymerized with

Correspondence to: J.-S. Yoon (jsyoon@inha.ac.kr).

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**Table I Copolymerization of Ethylene with 1,5-HD with (2-MeInd)<sub>2</sub>ZrCl<sub>2</sub>/MAO<sup>a</sup> Catalyst System**

Sample Code	$T_p$ (°C)	[1,5-HD] (mol/L)	$T_m$ (°C)	$\chi_c$ (%)	Ins. <sup>b</sup> (%)	Activity <sup>c</sup> ( $\times 10^5$ )	$M_w \times 10^{-3}$ (g/mol)	$M_w/M_n$
00E15HD00		0.0	137.8	69.8	0	2.08	2,530	2.8
00E15HD005	0	0.05	129.2	49.5	98.5	1.85	n.d.	n.d.
00E15HD01		0.1	125.0	43.7	97.1	1.95	n.d.	n.d.
00E15HD025		0.25	116.5	42.1	97.6	1.75	n.d.	n.d.
20E15HD00		0.0	136.3	62.5	0	4.12	1,550	2.6
20E15HD001	20	0.01	126.1	31.3	75.3	4.95	1,440	3.0
20E15HD005		0.05	120.3	28.1	76.6	5.22	631	2.0
20E15HD01		0.1	116.1	22.1	87.2	5.70	683	2.1
40E15HD00		0.0	137.2	65.3	0	3.00	870	2.3
40E15HD001	40	0.01	125.6	37.9	0	2.54	470	2.1
40E15HD003		0.03	122.7	32.6	0	2.88	430	1.9
40E15HD005		0.05	119.5	28.2	0	3.01	300	2.2
40E15HD01		0.1	115.3	23.5	0	3.56	320	2.2
60E15HD00	60	0.0	135.6	69.3	0	3.02	190	2.5
60E15HD001		0.01	125.7	36.8	0	2.20	210	2.3
60E15HD003		0.03	121.6	33.6	0	2.54	170	3.0
60E15HD005		0.05	117.5	29.2	0	2.88	160	2.8
60E15HD01	80	0.1	112.3	24.3	0	3.39	100	3.1
80E15HD01		0.1	118.1	33.7	0	3.46	79	4.3

$T_p$  = polymerization temperature;  $T_m$  = melt peak temperature;  $\chi_c$  = degree of crystallinity measured from the DSC melting endotherm;  $M_w$  = weight-average molecular weight;  $M_n$  = number-average molecular weight.

<sup>a</sup> [Zr] =  $5.9 \times 10^{-5} M$ ; [Al]/[Zr] = 2000; polymerization time = 1 h; ethylene = 1 atm.

<sup>b</sup> XYL-insoluble fraction.

<sup>c</sup> Activity in g of polymer/(mol of Zr h atm).

1,5-HD, 1,7-octadiene (1,7-OD) and 1,4-hexadiene (1,4-HD) over bis(2-methyl indenyl) zirconium dichloride/methylaluminoxane [(2-MeInd)<sub>2</sub>ZrCl<sub>2</sub>/

MAO]. The catalyst activity, molecular weight, and thermal properties of the resulting copolymers were explored.

**Table II Copolymerization of Ethylene with 1,7-OD with (2-MeInd)<sub>2</sub>ZrCl<sub>2</sub>/MAO<sup>a</sup> Catalyst System**

Sample Code	$T_p$ (°C)	[1,7-OD] (mol/L)	$T_m$ (°C)	$\chi_c$ (%)	Ins. <sup>b</sup> (%)	Activity <sup>c</sup> ( $\times 10^5$ )	$M_w \times 10^{-3}$ (g/mol)	$M_w/M_n$
20E17OD01	20	0.1	115.6	27.8	99.2	1.24	n.d.	n.d.
40E17OD001		0.01	126.5	37.5	93.2	1.52	n.d.	n.d.
40E17OD003	40	0.03	118.1	29.4	97.5	2.36	n.d.	n.d.
40E17OD005		0.05	108.8	25.2	99.9	2.90	n.d.	n.d.
40E17OD01		0.1	93.1	12.6	99.9	3.35	n.d.	n.d.
60E17OD001		0.01	125.5	38.2	98.2	1.3	n.d.	n.d.
60E17OD003	60	0.03	122.1	29.5	98.7	1.6	n.d.	n.d.
60E17OD005		0.05	118.3	22.6	99.9	2.17	n.d.	n.d.
60E17OD01		0.1	110.9	5.1	99.9	2.56	n.d.	n.d.
80E17OD01		80	0.1	115.5	8.9	0	0.66	6

$T_p$  = polymerization temperature;  $T_m$  = melt peak temperature;  $\chi_c$  = degree of crystallinity measured from the DSC melting endotherm;  $M_w$  = weight-average molecular weight;  $M_n$  = number-average molecular weight; n.d. = not defined.

<sup>a</sup> [Zr] =  $5.9 \times 10^{-5} M$ ; [Al]/[Zr] = 2000; polymerization time = 1 h; ethylene = 1 atm.

<sup>b</sup> XYL-insoluble fraction.

<sup>c</sup> Activity in g of polymer/(mol of Zr h atm).

**Table III Copolymerization of Ethylene with 1,4-HD with (2-MeInd)<sub>2</sub>ZrCl<sub>2</sub>/MAO<sup>a</sup> Catalyst System**

Sample Code	$T_p$ (°C)	[1,7-OD] (mol/L)	$T_m$ (°C)	$\chi_c$ (%)	Ins. <sup>b</sup> (%)	Activity <sup>c</sup> ( $\times 10^5$ )	$M_w \times 10^{-3}$ (g/mol)	$M_w/M_n$	Content of Diene (mol %)
0E14HD001	0	0.01	123.8	36.8	0	0.9	348	2.8	1.3
0E14HD003		0.03	121.6	33.9	0	0.8	328	2.9	1.5
0E14HD005		0.05	119.3	30.2	0	0.6	305	2.7	1.9
0E14HD01		0.1	116.7	28.3	0	0.4	300	2.8	2.2
20E14HD001		0.01	122.0	40.4	0	2.6	450	2.3	0.6
20E14HD003	20	0.03	121.1	38.9	0	2.2	165	2.3	0.7
20E14HD005		0.05	119.8	37.9	0	1.5	180	2.2	0.7
20E14HD01		0.1	115.3	33.6	0	1.0	130	2.2	1.3
40E14HD001	40	0.01	124.3	47.6	0	2.8	130	2.2	1.0
40E14HD003		0.03	120.8	41.2	0	2.5	130	2.1	1.3
40E14HD005		0.05	119.1	40.3	0	2.1	120	1.9	1.4
40E14HD01		0.1	115.7	35.6	0	1.1	97	1.8	2.0
60E14HD001		0.01	124.6	49.4	0	1.2	100	2.2	1.0
60E14HD003	60	0.03	121.4	47.2	0	0.8	80	2.1	1.4
60E14HD005		0.05	120.8	46.7	0	0.7	58	2.2	2.0
60E14HD01		0.1	111.4	38.9	0	0.5	49	2.3	2.5

$T_p$  = polymerization temperature;  $T_m$  = melt peak temperature;  $\chi_c$  = degree of crystallinity measured from the DSC melting endotherm;  $M_w$  = weight-average molecular weight;  $M_n$  = number-average molecular weight.

<sup>a</sup> [Zr] =  $5.9 \times 10^{-5}$  M; [Al]/[Zr] = 2000; polymerization time = 1 h; ethylene = 1 atm.

<sup>b</sup> XYL-insoluble fraction.

<sup>c</sup> Activity in g of polymer/(mol of Zr h atm).

## EXPERIMENTAL

### Materials

Bis(2-methyl indenyl) zirconium dichloride was prepared and recrystallized by precipitation in CH<sub>2</sub>Cl<sub>2</sub> after the reaction of lithium salt of 2-*R*-indene with ZrCl<sub>4</sub> · 2THF (THF = tetrahydrofuran) in toluene medium.

Methylaluminoxane (MAO; Akzo Chemical Co., MMAO-4 type, 11.6 wt % Al in toluene, and MMAO-3A type, 8.4 wt % Al in toluene) was used without further purification.

Toluene was refluxed for over 8 h in the presence of sodium and benzophenone and was used after a second distillation.

Purity of ethylene gas was more than 99.5%, and we removed trace impurities by passing the gas successively through CaCl<sub>2</sub> and CaSO<sub>4</sub>.

1,5-HD (97%), 1,4-HD (99%, mixture of *cis* and *trans*), and 1,7-OD (98%) were purchased from Aldrich Co. (Milwaukee, WI) and were purified by vacuum distillation.

### Ethylene Homopolymerization

All polymerization reactions were carried out in a 500-mL glass reactor with a magnetic stirrer. Toluene (100 mL) was used as a reaction medium.

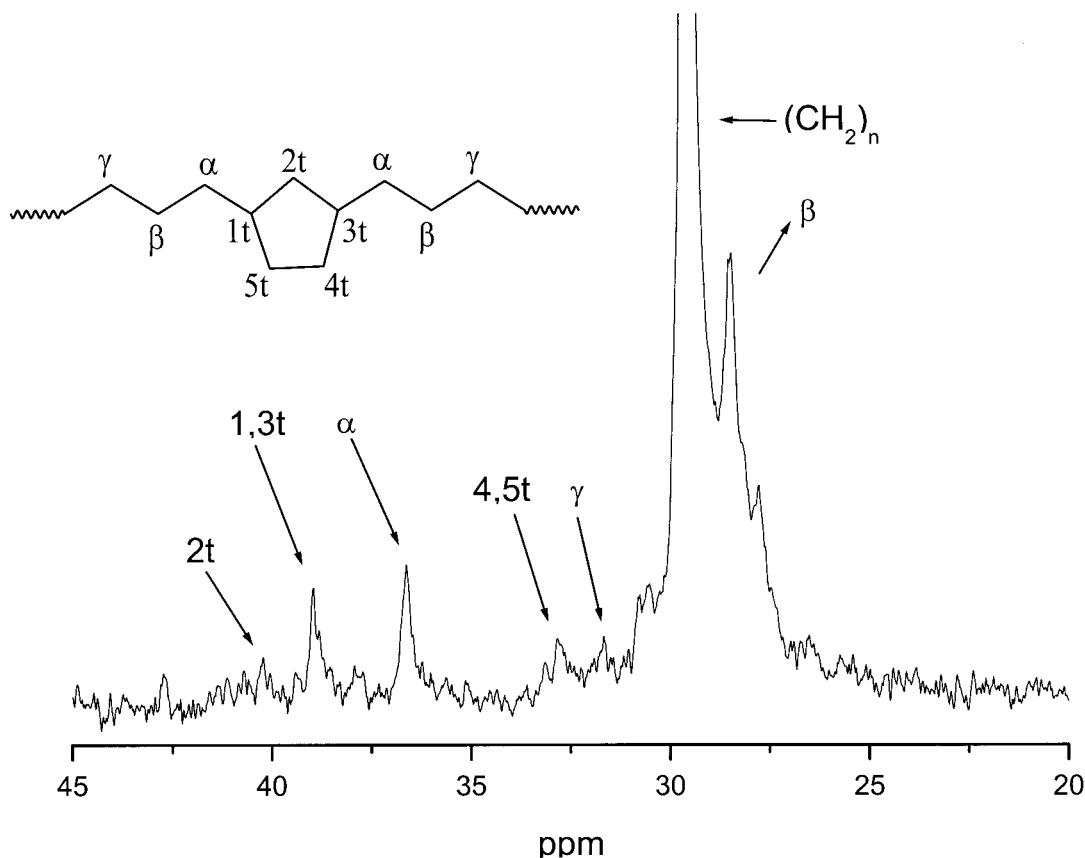
Ethylene gas was introduced first at 1 atm, and MAO and the catalyst ( $5.9 \times 10^{-5}$  M) were added subsequently. The ratio of concentration of co-catalyst to that of catalyst ([Al]/[Zr]) was maintained at 2000. The reaction time was 1 h, and the reaction was terminated by the addition of a mixed solution of methanol and HCl. The products were washed with plenty of methanol three times and were dried in a vacuum oven (30°C) until a constant weight was attained.

### Copolymerization of Ethylene/Nonconjugated Diene

The same reactor described previously was used. Ethylene gas was first introduced at 1 atm, and comonomers (1,5-HD, 1,4-HD, and 1,7-OD) were added in different concentrations. The copolymerization was initiated by the addition of MAO and catalyst ( $5.9 \times 10^{-5}$  M). The Al/Zr mole ratio was also maintained at 2000, and the reaction was carried out for 1 h. Drying and washing of the products were accomplished by the same procedure as followed in the ethylene polymerization.

### Characterization of Polymers

<sup>13</sup>C-NMR and <sup>1</sup>H-NMR spectra of the products were recorded at 130°C on a Fourier transform



**Figure 1**  $^{13}\text{C}$ -NMR spectra of E15HD copolymer (80E15HD10) synthesised at 80°C.

NMR spectrometer (Bruker AC-250 FT-NMR (Bruker Instruments, Billerica, MA)) operating at 62.896 MHz. NMR samples were prepared by dissolution of 20–50 mg of the polymers in 0.3 mL of 1,2-dichlorobenzene- $d_4$ .

Molecular weight and molecular weight distribution of the polymers were obtained by gel permeation chromatography (Waters 150 C plus (Waters Instruments, Rochester, MN) with a differential refractometer detector and a column composed of Styragel<sup>®</sup> HT6E, HT5, and HT3) with 1,2,4-trichlorobenzene (1.0 mL/min) as an eluent at 135°C with polystyrene (Showadenko SL-105, Japan) as a standard.

The thermal properties of the polymers were determined by differential scanning calorimetry (DSC; PerkinElmer DSC 7, Norwalk, CT). We removed the thermal history of the products, due to the different reaction temperatures, by scanning to 180°C with a heating rate of 10°C/min first and cooling at 5°C/min to room temperature. Then, the crystallized samples were reheated at

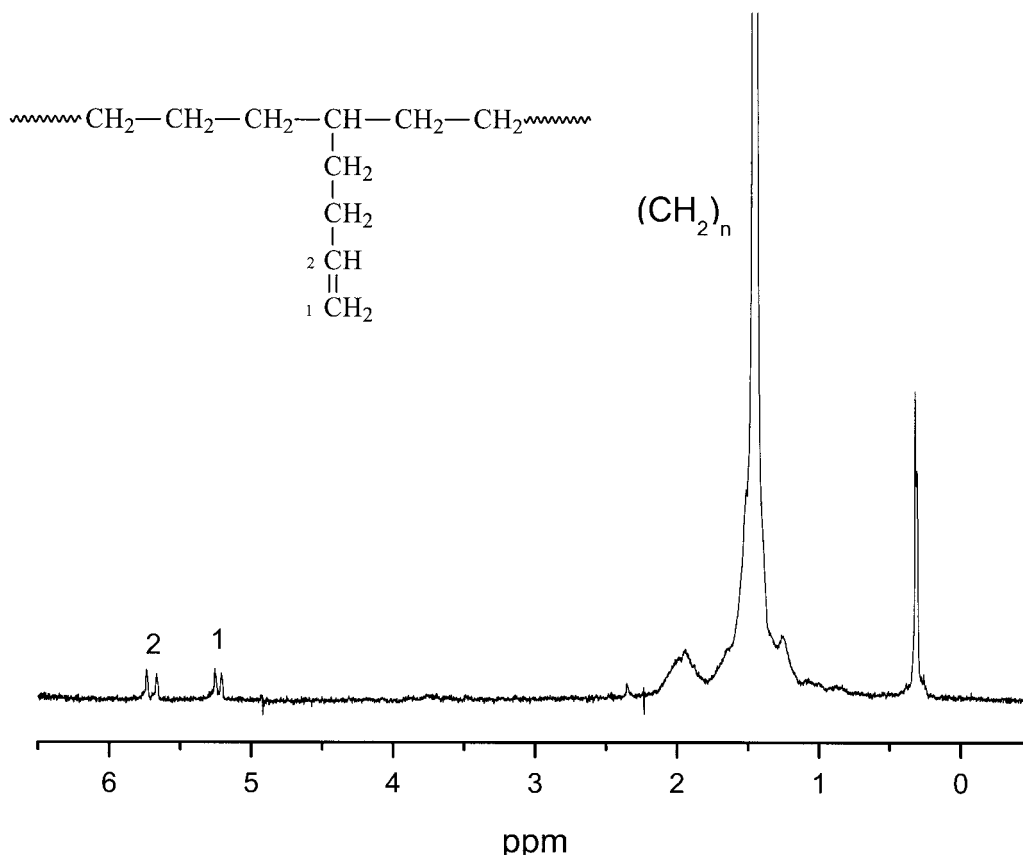
10°C/min to 180°C, and the second scan DSC thermogram was obtained.

The insoluble fraction of the copolymers was isolated by xylene Soxhlet extraction at 160°C for 12 h according to ASTM D-2765-84. The insoluble fraction thus obtained was dried at 150°C for another 48 h.

Crystallinity of the copolymers was presented as the ratio of the melting enthalpy of the DSC thermogram to that of a perfect polyethylene crystal (290 J/g).<sup>12</sup>

## RESULTS AND DISCUSSION

Ethylene and 1,5-HD were copolymerized over (2-MeInd)<sub>2</sub>ZrCl<sub>2</sub>/MAO, and the results are summarized in Table I. The catalyst activity increased as the temperature was raised from 0 to 20°C. A further increase in the polymerization temperature reduced the catalyst activity. The synergistic effect, meaning that the addition of



**Figure 2**  $^1\text{H}$ -NMR spectra of E15HD copolymer (20E15HD10) synthesised at 20°C.

comonomer enhances the catalyst activity, appeared clearly at 20°C. However, at the other temperatures, a definite conclusion on the synergistic effect was hard to draw. Lee and colleagues<sup>13</sup> reported that the synergistic effect<sup>7–21</sup> in an ethylene/1-hexene copolymerization was observed at 0°C but not at higher temperatures.

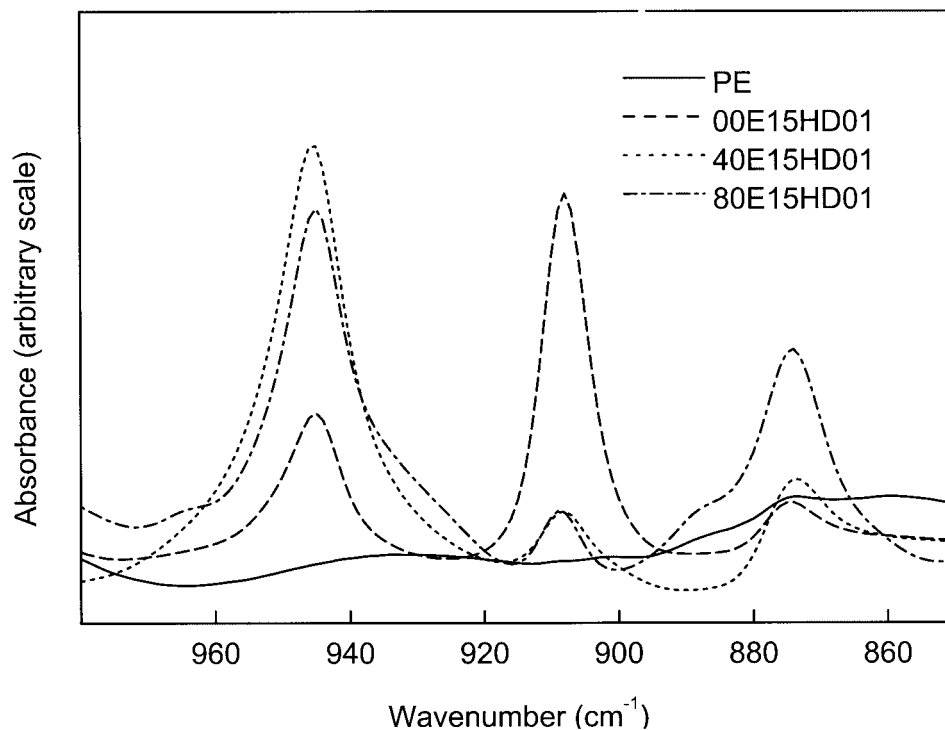
Table II shows the results on ethylene/1,7-octadiene (E17OD) copolymerizations using (2-MeInd)<sub>2</sub>ZrCl<sub>2</sub>/MAO. The catalyst activity was lower compared to that for E15HD copolymerizations. Fink and colleagues<sup>14</sup> and Lee and colleagues<sup>13</sup> also observed that the catalyst activity for ethylene/ $\alpha$ -olefin copolymerizations decreased as the chain length of the  $\alpha$ -olefin increased.

The results on ethylene/1,4-hexadiene (E14HD) are shown in Table III. The catalyst activity for the E14HD copolymerizations was lower than for the E15HD copolymerizations. The synergistic effect was absent at all polymerization temperatures. Chien and colleagues<sup>15</sup> also showed that the rate of copolymerization of E14HD, propylene/1,4-HD, and ethylene/propylene/1,4-HD over 1,2-bis(indene)

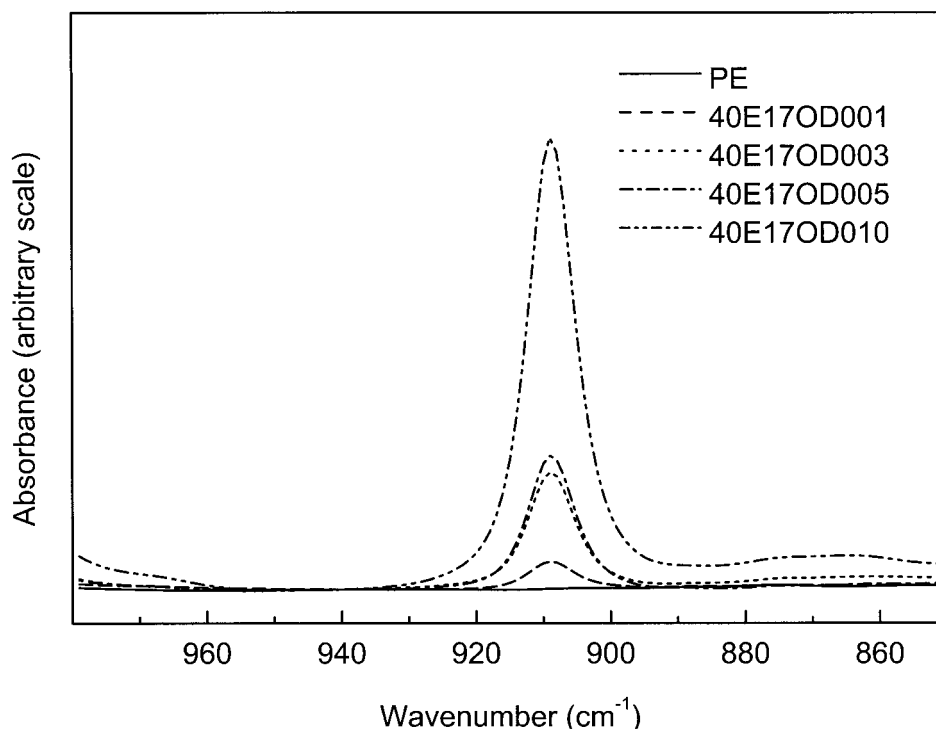
nyl)ethane zirconium dichloride (Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>)/MAO decreased due to the increase in the concentration of 1,4-HD.

Cyclopentane rings and 1-butenyl side chains were formed in E15HD copolymerizations.<sup>9,10</sup> Figure 1 is the  $^{13}\text{C}$ -NMR spectra of an E15HD copolymer produced at 80°C. The *trans*-structured cyclopentane ring had a characteristic peak at the chemical shift at 33.6–34.2 and 41.7 ppm.<sup>18</sup> However, the peaks which were expected to appear at 32.4–33.0 and 44.3 ppm<sup>19</sup> for the *cis*-structured cyclopentane rings, which were reported to be efficient in the enhancement of the thermal stability of polymers, were not observed.

According to Table I, the lower the copolymerization temperature was, the larger the amount of the hot xylene (XYL)-insoluble fraction. The cyclopentane ring formation prevailed over the 1,2-addition of 1,5-HD at higher temperatures,<sup>20</sup> and peaks for vinyl groups expected to be at 4.9–5.9 ppm were not observed in the  $^1\text{H}$ -NMR spectrum of the E15HD copolymer produced at 80°C. In contrast, in the XYL-soluble fraction of an E15HD

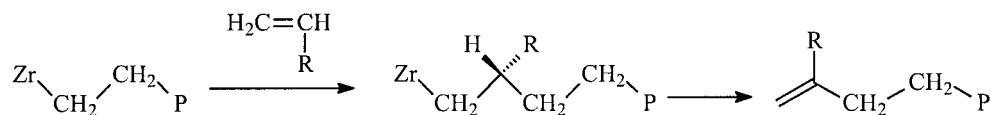


**Figure 3** Effect of polymerization temperature on the cyclization of 1,5-HD during the E15HD copolymerization (vinyl =  $910\text{ cm}^{-1}$ , five-membered rings =  $945$  and  $875\text{ cm}^{-1}$ ): Absorbance was divided by the sample thickness.

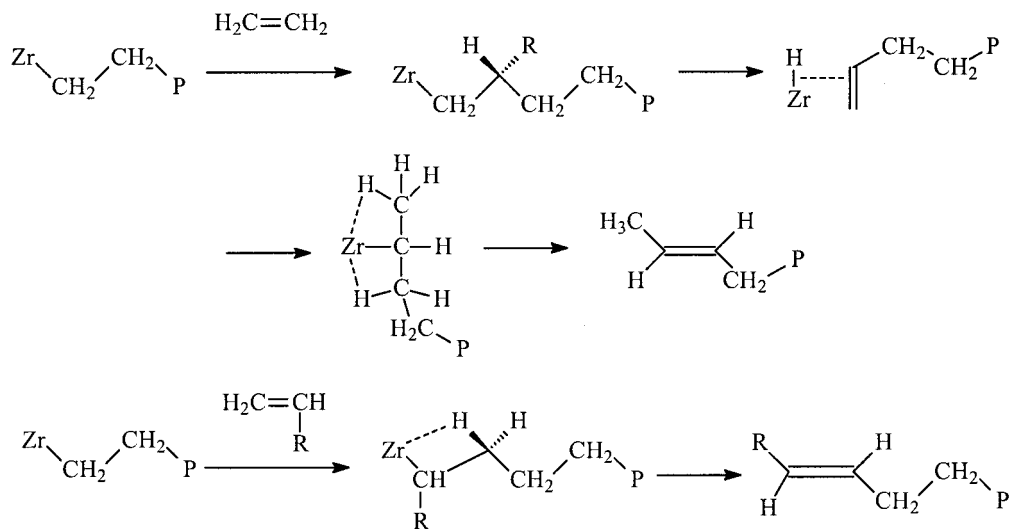


**Figure 4** Effect of concentration of 1,7-OD on the vinyl content of E17OD copolymers (vinyl =  $910\text{ cm}^{-1}$ ): Absorbance was divided by the sample thickness.

### 1) Vinylidene group



### 2) Trans-vinylidene group

Scheme 1<sup>21</sup>

copolymer produced at 20°C, peaks for vinyl groups turned up at 5.2 and 5.7 ppm in the <sup>1</sup>H-NMR spectra (Fig. 2), and the peaks were more intense than those for the methine protons of the cyclopentane rings at 2.35 ppm.

Fourier transform infrared was used to monitor the relative frequency of cyclopentane rings (945 and 875 cm<sup>-1</sup>) and that of vinyl groups (910 cm<sup>-1</sup>) as shown in Figure 3. Absorbance of the IR light was divided by the thickness of the specimens to remove the sample thickness effect on the absorbance. The acronym, xE15HDy, means that the copolymer of E15HD was produced at x°C, where y is the concentration of 1,5-HD in the reaction medium. The peaks for cyclopentane rings became more intense compared to those for vinyl groups as the polymerization temperature increased.

According to Figure 4, E17OD copolymers did not have cyclic-structured units. The content of vinyl groups rose as the reaction medium of the copolymerization became richer in 1,7-OD. Besides the vinyl groups of the 1-hexenyl side

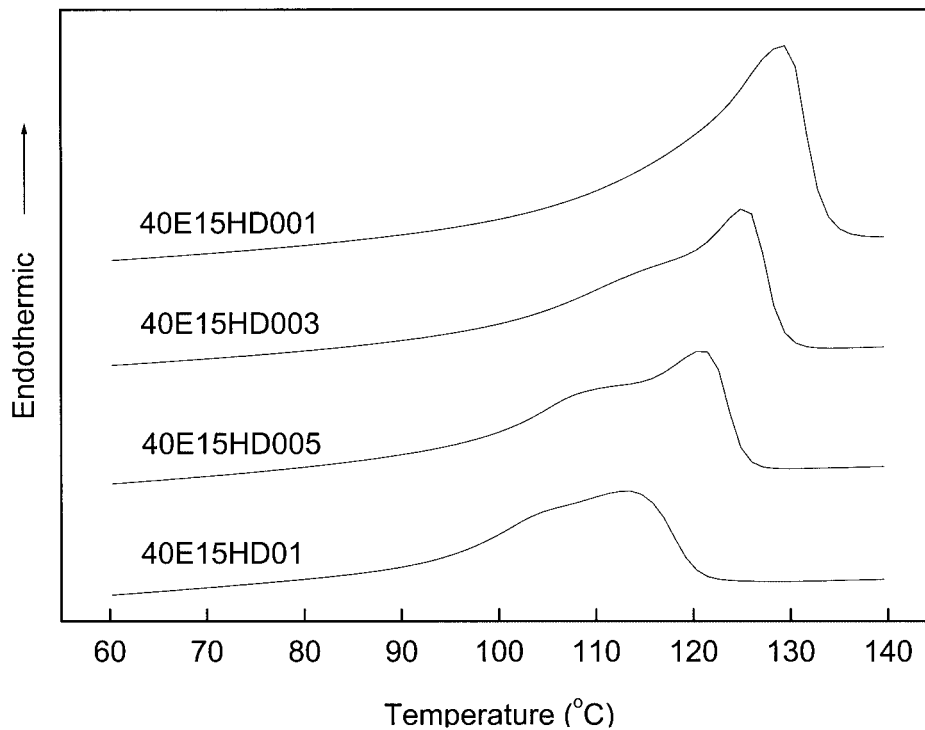
branches, vinylidene groups were also formed following the mechanism shown in Scheme 1,<sup>21</sup> as judged from peaks of 4.9 and 5.2 ppm in the <sup>1</sup>H-NMR spectra of the E17OD copolymer (Figure 5).

Table II shows that the XYL-insoluble fraction of E17OD copolymers was much larger than that of E15HD copolymers. In contrast, copolymers of E14HD did not have the XYL-insoluble fraction at all, as demonstrated in Table III, despite the fact that the E14HD copolymers had many vinyl groups, as shown in Figure 6. Therefore, the reactivity of the vinyl group was reduced greatly by substitution with the methyl group on the vinyl moiety.

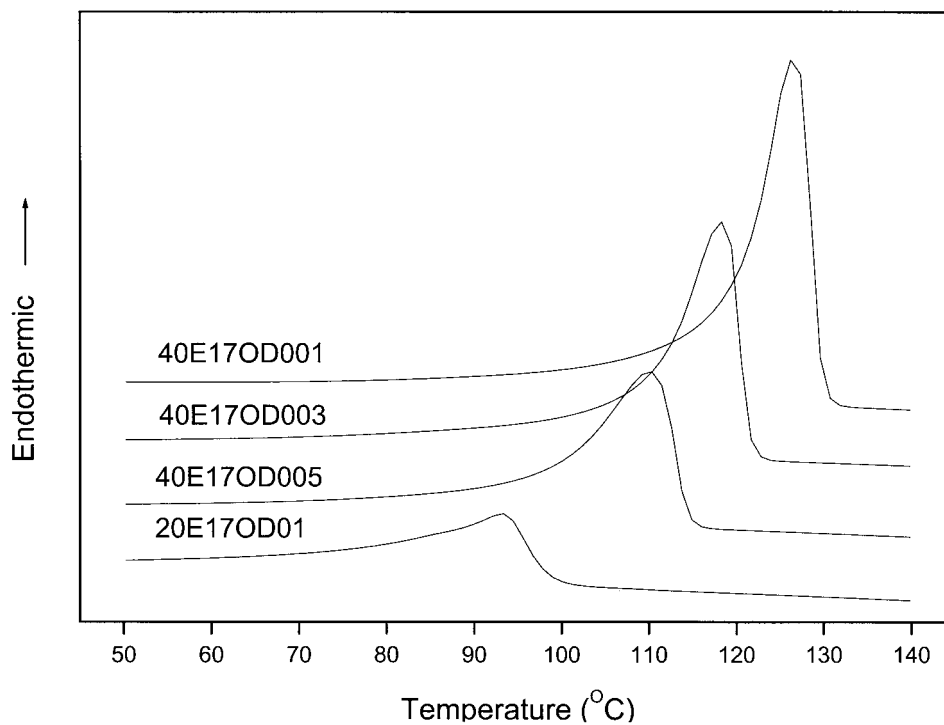
DSC thermograms of E15HD, E17OD, and E14HD copolymers are exhibited in Figures 7, 8, and 9, respectively. Melting peaks of the E15HD copolymers appeared at a lower temperature as the content of 1,5-HD rose, and they were much broader compared to those of ethylene/ $\alpha$ -olefin copolymers.<sup>13</sup> The narrowest melting peaks were found for the E14HD copolymers and next for the E17OD copolymers, and the broadest melting



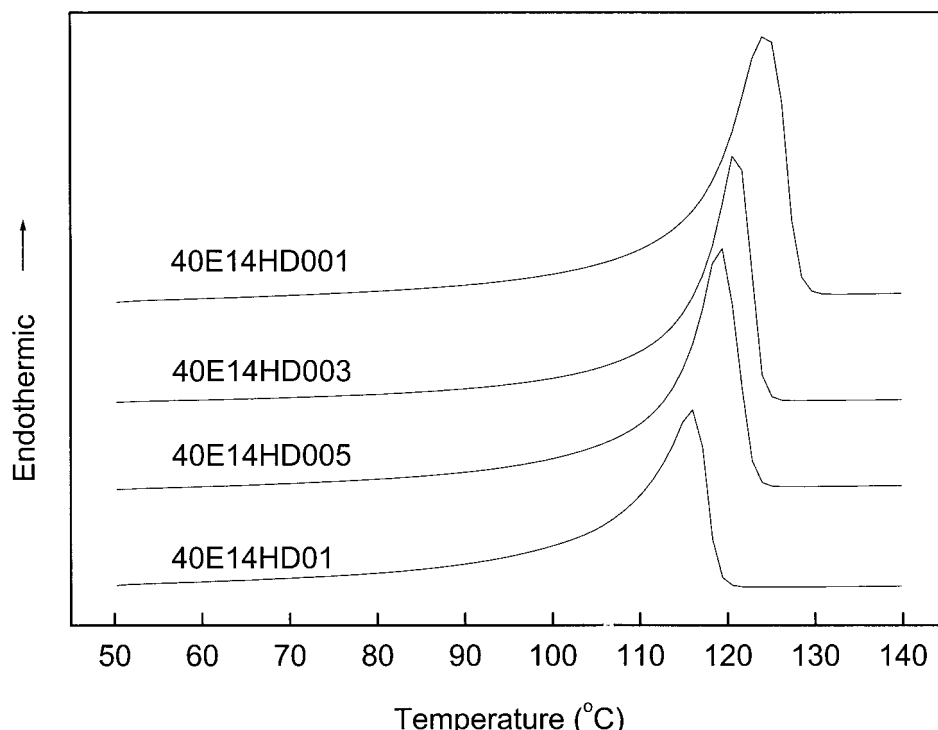




**Figure 7** DSC thermograms (second scan) of poly(ethylene-co-1,5-hexadiene) (E15HD) produced over  $(2\text{-MeInd})_2\text{ZrCl}_2/\text{MAO}$ .



**Figure 8** DSC thermograms (second scan) of poly(ethylene-co-1,7-octadiene) (E17OD) produced over  $(2\text{-MeInd})_2\text{ZrCl}_2/\text{MAO}$ .



**Figure 9** DSC thermograms (second scan) of poly(ethylene-co-1,4-hexadiene) (E14HD) produced over  $(2\text{-MeInd})_2\text{ZrCl}_2/\text{MAO}$ .

peaks were found for the E15HD copolymers. This is because the E15HD copolymers had different kinds of molecular structures, such as cyclopentane rings and 1-butenyl side chains.

The E17OD copolymers had a lot of cross-linked structures. In contrast, the E14HD copolymers were free both from cyclic structures and from cross-linking.

It is interesting to observe from Tables I and III that the crystallinity of the E14HD copolymers was higher than that of the E15HD ones when the two types of the copolymers had the same melting temperature. This is due to the fact that the melting peak temperature was determined mainly by the more crystallizable molecules in the copolymers. Cyclopentane rings should have restricted the crystallization of the E15HD copolymers more than 1-butenyl side chains did, and the different structures would reduce the average crystallinity of the copolymers, whose melting temperature was dominated by the copolymer molecules with fewer cyclopentane rings. In contrast, all the E14HD copolymer molecules crystallized to a similar extent, and therefore, narrower melting peaks appeared compared to those of the E15HD copolymers.

Molecular weight decreased as the polymerization temperature increased, as demonstrated in Tables I–III. Addition of 1,7-OD or 1,4-HD as comonomers reduced molecular weight of the copolymers much more than that of 1,5-HD.

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