



Crystalline structures and thermal properties of poly(ethylene-*co*- α,ω -nonconjugated diene)s prepared by zirconocene catalysts

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Abstract

Crystalline structures and thermal properties of poly(ethylene-*co*- α,ω -nonconjugated diene)s, [diene = 1,5-hexadiene (HD), 1,7-octadiene (OD), and 1,9-decadiene (DD)] have been investigated in relation to insertion mode of the dienes. In the case of poly(ethylene-*co*-HD), the copolymer containing high *cis*-1,3-cyclopentane units shows lower melting point depression with increasing the comonomer content than the copolymers containing high *trans*-1,3-cyclopentane units. In the case of poly(ethylene-*co*-OD) and poly(ethylene-*co*-DD), the copolymers containing pendant vinyl groups show higher ΔH_m than that of the copolymers with cyclic units or branching structures. Thermal degradation of the copolymers has been investigated under nitrogen atmosphere and the degradation of the copolymers containing the cyclic structures begins at lower temperature than the copolymers containing pendant vinyl groups.

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1. Introduction

Metallocene catalysts are effective catalysts for polymerization of various olefins, and have made possible syntheses of novel polyolefins. The catalysts show high activity in homo-polymerization of α,ω -nonconjugated dienes and copolymerization with ethylene or propylene [1–14]. Three types of insertion modes take place in the (co)polymerization of α,ω -nonconjugated dienes, as illustrated in Scheme 1. When 1,2-insertion takes place without cyclization, pendant vinyl group is formed in the polymer (Scheme 1a). When 1,2-insertion is followed by cyclization, 1,3-disubstituted cycloalkane unit is formed in the polymer (Scheme 1b). Crosslinked-branching or crosslinking occurs by reaction of the pendant vinyl group with other propagating chain end (Scheme 1c).

We have reported copolymerization of ethylene and α,ω -nonconjugated dienes, 1,5-hexadiene (HD) [12], 1,7-octadiene (OD), and 1,9-decadiene (DD) [14], with various zirconocene catalysts. HD was taken into the copolymer

preferentially by the cyclization mechanism, as shown in Scheme 1b, consisting of *cis*- and *trans*-1,3-cyclopentane units. The insertion mode of OD and DD could be controlled by the ligand structure of the zirconocene catalysts used. OD was taken in the copolymer by 1,2-insertion (1-hexenyl branch) and/or cyclization (1,3-disubstituted cycloheptane unit). DD formed 1-octenyl branches (1,2-insertion) or crosslinked-branching structures.

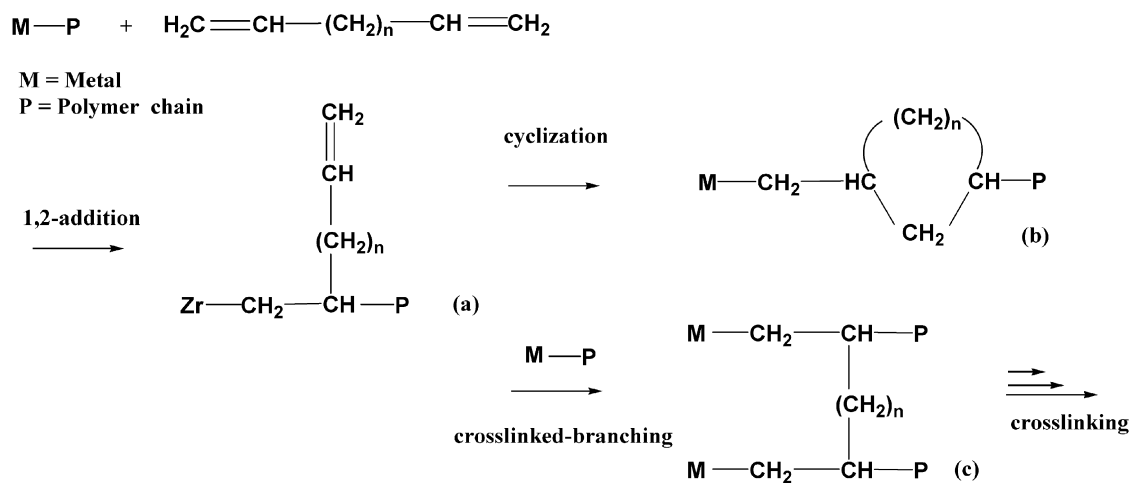
The properties of the poly(ethylene-*co*- α,ω -nonconjugated dienes)s should be affected by the nature of dienes as well as the insertion mode of dienes. In this paper, we have investigated the relationship between insertion mode of the α,ω -nonconjugated dienes and the crystalline structures and thermal properties of the poly(ethylene-*co*- α,ω -nonconjugated dienes)s.

2. Experimental section

2.1. Materials

Poly(ethylene-*co*- α,ω -nonconjugated dienes)s were

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Scheme 1.

prepared by various zirconocene catalysts, bis(cyclopentadienyl)zirconium dichloride (**1**), bis(pentamethylcyclopentadienyl)zirconium dichloride (**2**), dimethylsilylenebis(cyclopentadienyl)zirconium dichloride (**3**), bis(indenyl)zirconium dichloride (**4**), ethylenebis(indenyl)zirconium dichloride (**5**), dimethylsilylenebis(indenyl)zirconium dichloride (**6**), diphenylmethylene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride (**7**), using methylaluminoxane (MAO) as a cocatalyst at 40 °C. The polymerization procedures have been reported previously [12,14]. The resulting copolymers were extracted with boiling *o*-dichlorobenzene (ODCB) and separated into soluble and insoluble fractions. The solution of extracted polymer was precipitated in a large excess of ethanol. The precipitate was recovered by filtration and dried in vacuo at 60 °C for 6 h.

2.2. Analytical procedures

Molecular weight and molecular weight distribution of boiling ODCB-soluble fraction of the copolymers were measured at 140 °C by means of gel permeation chromatography (Tosoh HLC-8121 GPC/HT) using ODCB as a solvent and calibrated with standard polystyrene samples. ¹³C NMR spectra were recorded at 130 °C using a JEOL Lambda-400 Fourier transform NMR spectrometer in the pulse Fourier transfer (FT) mode. Polymers were dissolved in trichlorobenzene/benzene-*d*₆ (9/1 v/v) (up to 10 wt%). In the ¹³C NMR measurements, the pulse angle was 45°, and 5000–10,000 scans were accumulated in 5.2 s of pulse repetition. The comonomer content of the copolymers with pendant vinyl groups and/or cyclic structures was determined by ¹³C NMR spectra using integrals of secondary carbons signals. The DD content of poly(ethylene-*co*-DD) with crosslinking-branching was determined by ¹³C NMR spectra using integrals of tertiary carbons signals. Content and insertion mode of dienes were determined by the ¹H and ¹³C NMR spectra as previously reported [12,14]. DSC measurement was conducted using a Seiko DSC6200 (Seiko Instruments Inc.) at a heating rate of

10 °C/min, after preheating to 200 °C and precooling to –150 °C at a rate of 10 °C/min. Samples for X-ray diffraction measurements were melted at 180 °C and were pressed under 10 MPa pressed followed by quenching in 30 °C water. Wide angle X-ray diffraction (WAXD) patterns of the copolymers were recorded on a Rigaku RAD-IIC using Cu K α radiation. Thermogravimetry (TG) analysis of the copolymers was carried out with a TG-DTA (Rigaku Thermo Plus 8120) from room temperature to 600 °C under nitrogen atmosphere.

Table 1
Structures and thermal properties of EHD prepared by zirconocene catalysts

Sample	Catalyst	HD (mol%) ^a	<i>cis/trans</i> (%/%) ^b	<i>M</i> _n (× 10 ⁻⁴) ^c	<i>M</i> _w / <i>M</i> _n ^c	<i>T</i> _m (°C) ^d
1	1	0.5		8.4	4.1	127.3
2	1	2.0		9.3	2.8	122.2
3	1	2.3		9.0	3.2	120.5
4	1	5.6	15.2/84.8	9.6	4.1	109.0
5	1	9.2	19.5/80.5	9.4	3.4	98.6
6	2	0.7		1.7	4.3	130.6
7	2	1.1	82.3/17.7	0.9	7.3	127.8
8	2	9.0	83.6/16.4	0.8	6.5	120.8
9	2	10.9	80.1/19.9			116.5
10	3	0.6		1.6	4.3	122.4
11	3	2.8		2.5	4.6	120.4
12	3	4.3	28.7/71.3	1.8	4.6	106.7
13	4	0.9		33.1	2.1	129.9
14	4	1.0		32.3	2.2	127.8
15	4	1.6		25.1	2.4	122.7
16	4	3.1	17.1/82.9	21.2	3.2	109.9
17	6	1.8		7.4	2.6	120.3
18	6	6.6	23.3/76.7	10.1	3.8	112.6
19	6	11.0	24.2/75.8	7.4	3.4	91.7
20	7	3.3		9.9	2.5	111.9
21	7	8.1	31.0/69.0	12.4	2.9	100.9
22	7	14.8	29.6/70.4	9.1	2.7	89.6

^a Determined by ¹³C NMR spectroscopy.

^b [*cis*]/[*trans*] ratio of 1,3-cyclopentane units determined by ¹³C NMR spectroscopy.

^c Determined by GPC using polystyrene standard samples.

^d Melting temperature measured by DSC.

Table 2
Structures and thermal properties of EOD prepared by zirconocene catalysts

Sample	Catalyst	OD (mol%) ^a	C/V (%/%) ^b	$M_n (\times 10^{-4})^c$	M_w/M_n^c	T_m (°C) ^d	ΔH_m (J/g) ^e
23	1	1.4	32.6/67.4	2.7	1.7	117.0	152.6
24	1	4.9	31.3/68.7	2.2	3.2	93.4	93.8
25	3	1.9	29.1/70.9	0.8	2.7	116.4	149.4
26	3	4.9	25.1/74.9	1.0	2.7	80.1	62.9
27	3	8.1	19.9/80.1	4.2	6.2		
28	5	4.6	100/0	3.3	2.8	108.3	80.1
29	5	7.7	100/0	2.9	3.3	89.2	49.1
30	5	12.9	100/0	2.8	5.8	70.8	14.2
31	6	4.1	100/0	4.8	4.9	115.1	86.0
32	6	5.9	100/0	4.6	5.7	87.2	50.1
33	7	n.d.		2.2	10.3	85.8	34.0
34	7	n.d.		7.7	3.5	64.2	8.6
35	7	5.6	26.3/16.1 ^f	4.8	6.4	54.9	5.0

^a Determined by ¹³C NMR spectroscopy.

^b [Cycloheptane]/[pendant vinyl] ratio of OD units determined by ¹³C NMR spectroscopy.

^c Determined by GPC using polystyrene standard.

^d Melting temperature measured by DSC.

^e Heat of fusion measured by DSC.

^f Including 57.6 % of crosslinked-branching units.

3. Results and discussion

3.1. Crystalline structure and DSC analysis of poly(ethylene-co- α,ω -conjugated diene)s

3.1.1. Poly(ethylene-co-HD) (EHD)

Structures and thermal properties of EHD are summarized in Table 1. HD was incorporated by cyclization mechanism consisting *cis*- and *trans*-1,3-cyclopentane

units. The copolymers prepared by the catalyst 2 contain high *cis*-1,3-cyclopentane units due to bulkiness of the catalyst ligand. The crystal of the copolymer shows characteristic transition from orthorhombic to hexagonal with increasing the HD content [15,16]. Relationship between HD content and melting point (T_m) is illustrated in Fig. 1. The T_m of the copolymer containing high *cis*-1,3-cyclopentane units is higher than that of the copolymer containing high *trans*-1,3-cyclopentane units. We have

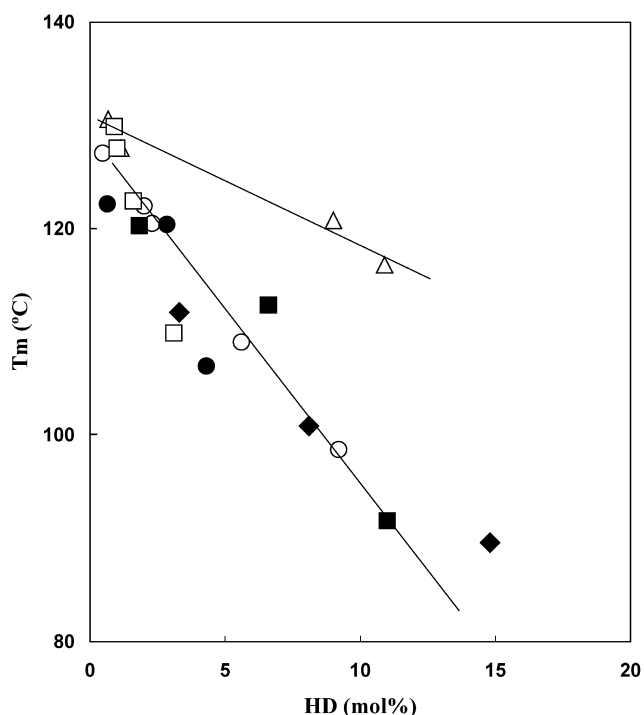


Fig. 1. Relationship between HD content and T_m of EHD prepared by the zirconocene catalysts 1 (○), 2 (△), 3 (●), 4 (□), 6 (■) and 7 (◆).

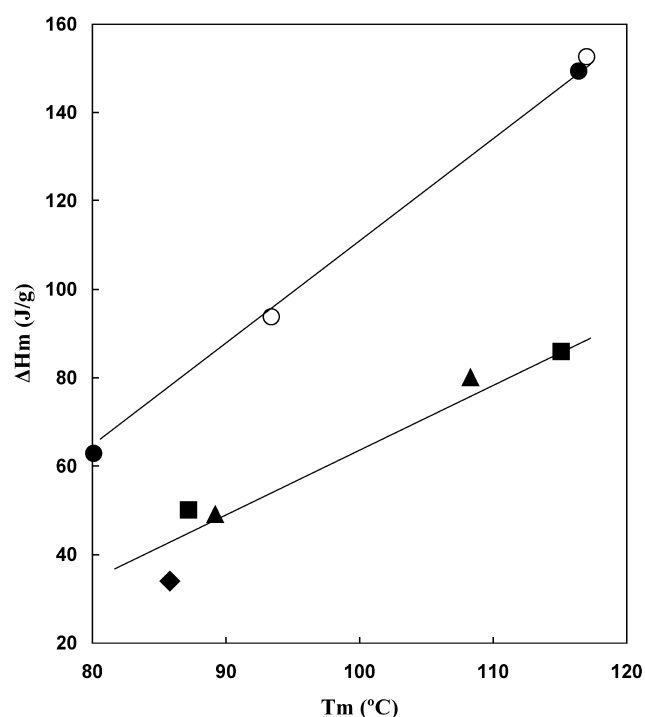


Fig. 2. Relationship between T_m and ΔH_m of EOD prepared by the zirconocene catalysts 1 (○), 3 (●), 5 (▲), 6 (■) and 7 (◆).

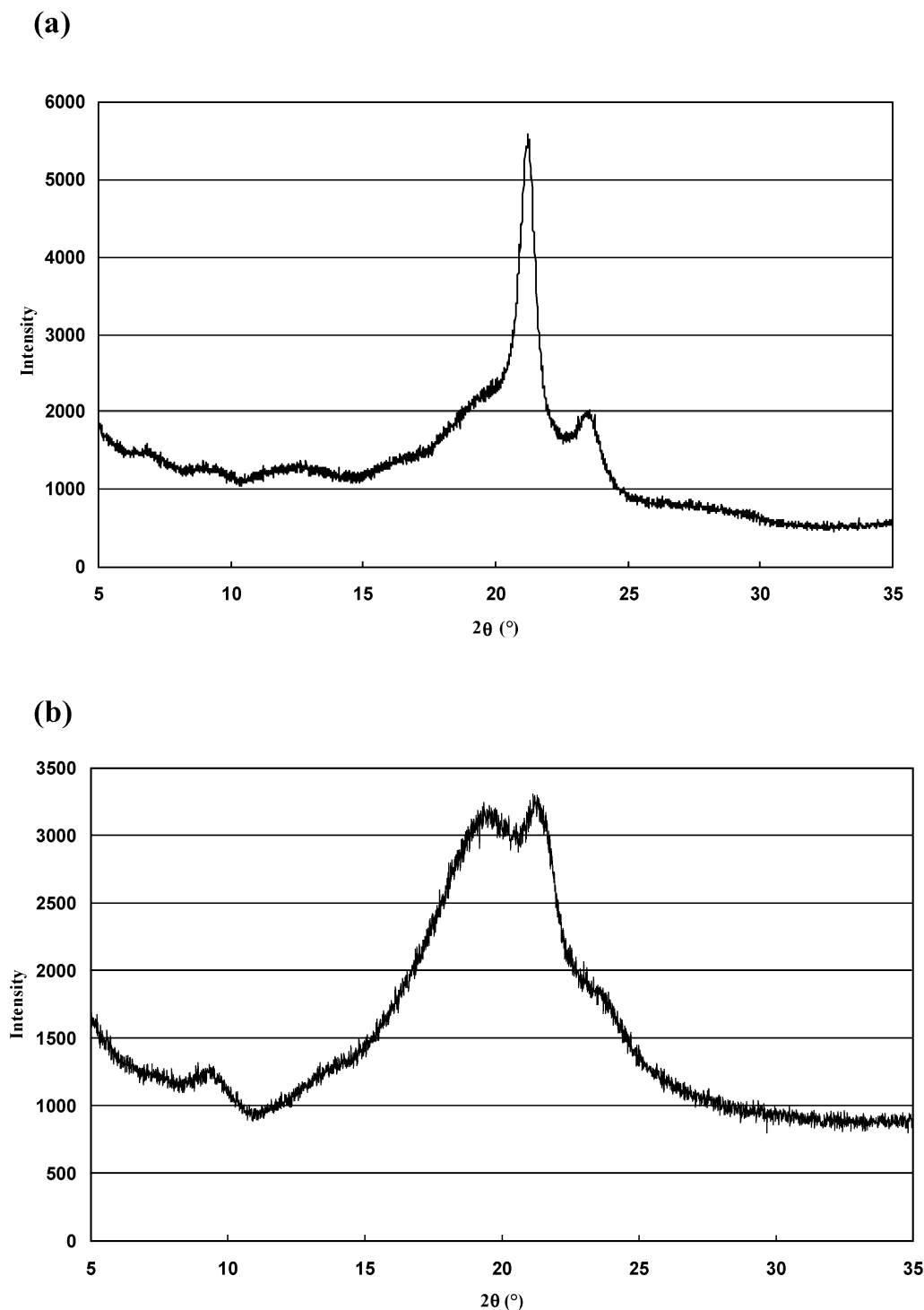


Fig. 3. WAXD patterns of EOD containing pendant vinyl group and 1,3-cycloheptane unit: (a) sample 24 (OD, 4.9 mol%), (b) sample 27 (OD, 8.1 mol%).

investigated crystalline structures of EHD containing both *cis*- and *trans*-1,3-cyclopentane units by oxidative degradation method and found out that the *cis*-1,3-cyclopentane units are preferentially taken in crystalline part of the copolymer [16]. The gradual melting point depression of the EHD containing high *cis*-1,3-cyclopentane units should be derived from that preferential including of the *cis*-units prevent lamellae size of the crystalline part from shrinking.

3.1.2. Poly (ethylene-co-OD) (EOD)

Structures and thermal properties of EOD are summarized in Table 2. OD in the copolymers was incorporated by 1,2-insertion mechanism and/or cyclization mechanism consisting 1-hexenyl branch and 1,3-cycloheptane unit, respectively. Relationship between T_m and ΔH_m of the copolymers is shown in Fig. 2. EOD containing pendant vinyl groups showed higher ΔH_m than that containing the 1,3-cycloheptane units.

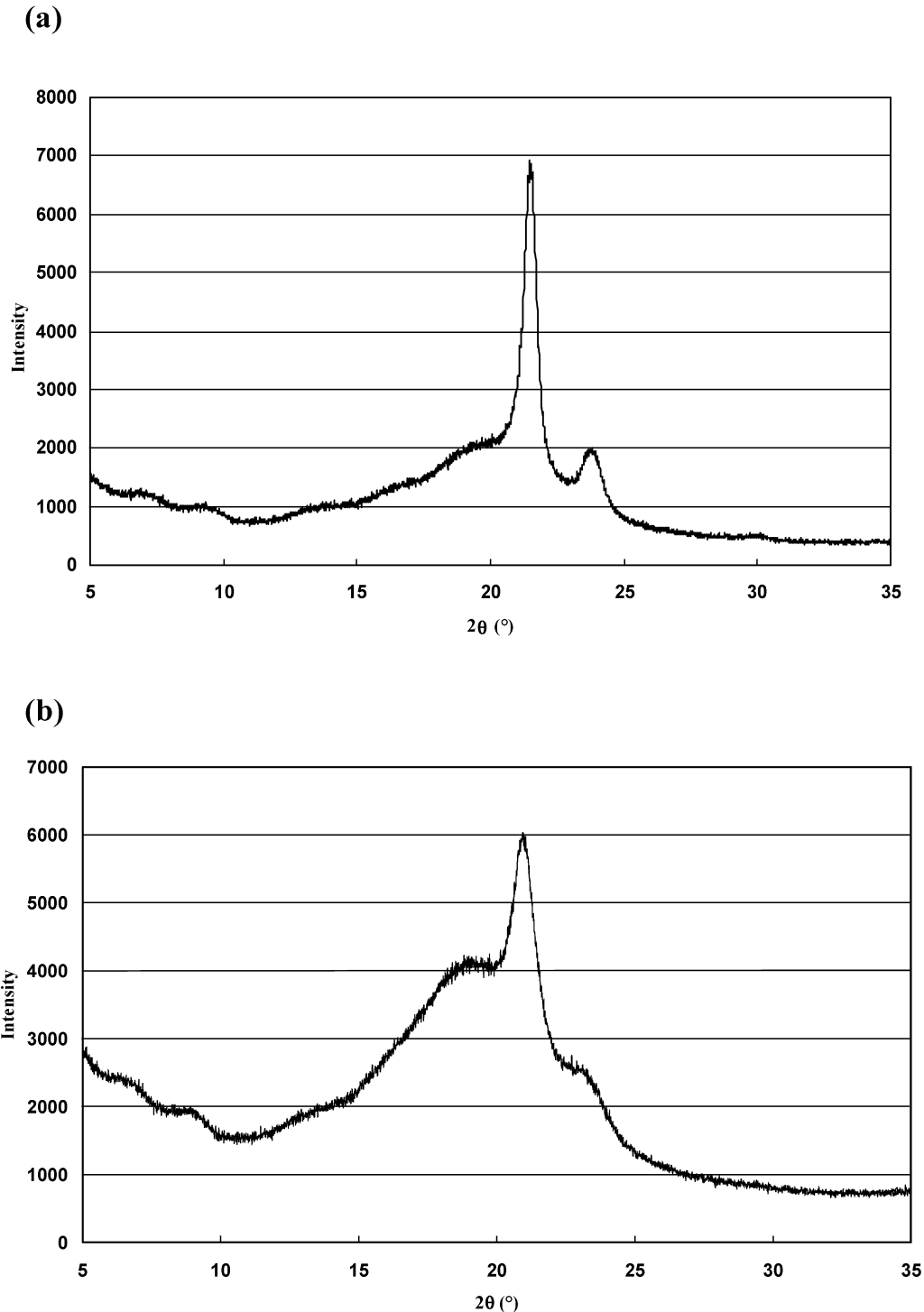


Fig. 4. WAXD patterns of EOD containing 1,3-cycloheptane unit: (a) sample 31 (OD, 4.1 mol%), (b) sample 29 (OD, 7.7 mol%).

The difference should be derived from the number of branching in the inserted OD units; the 1,3-cyclopentane structure has two branches while the pendant vinyl structure has one branch per each unit. Crystalline structures of EODs were studied by WAXD. The typical WAXD patterns of EODs containing pendant vinyl and/or 1,3-cycloheptane groups are illustrated in Figs. 3 and 4, respectively. In the WAXD patterns of the copolymers containing both the

pendant vinyl and 1,3-cycloheptane groups (Fig. 3), the intensity of reflection peaks due to (110) and (200) crystal planes decreased with increasing the OD content. The same tendency was observed in the WAXD patterns of the copolymers containing only the 1,3-cycloheptane group in Fig. 4. In the case of EHD including the 1,3-cyclopentane units, transition from an orthorhombic crystal to a hexagonal crystal was observed with increasing the HD

Table 3
Structures and thermal properties of EDD prepared by zirconocene catalysts

Sample	Catalyst	DD (mol%) ^a	Structure of DD units ^b	$M_n (\times 10^{-4})^c$	M_w/M_n^c	T_m (°C) ^d	ΔH_m (J/g) ^e
36	1	1.8	V	2.7	2.1	106.5	107.9
37	1	4.5	V	1.6	5.6	76.7	45.6
38	2	0.8	V	1.4	12.2	125.3	170.2
39	2	2.9	V	0.8	2.6	117.8	137.2
40	3	0.9	V	0.8	2.3	120.3	146.2
41	3	2.2	V	1.0	2.1	104.0	108.3
42	3	4.1	V	1.2	3.0	72.8	25.1
43	4	0.6	V	16.7	2.8	117.0	139.2
44	6	4.3	C-B	16.2	3.8	80.9	12.1
45	6	5.3	C-B	6.3	3.2	69.0	4.8
46	7	2.9	C-B	6.7	3.1	80.0	10.2

^a Determined by ¹³C NMR spectroscopy.

^b V = pendant vinyl, C-B = crosslinked-branching determined by ¹³C NMR spectroscopy.

^c Determined by GPC using polystyrene standard.

^d Melting temperature measured by DSC.

^e Heat of fusion measured by DSC.

content [15]. The characteristic phenomenon was accompanied by incorporation of the 1,3-cyclopentane units in the crystalline phase. On the other hand, the WAXD patterns of EOD including the 1,3-cycloheptane units (Fig. 4) shows that the copolymer formed orthorhombic crystal independent of the OD content. The different behaviors of the two kinds of copolymers indicate that the 1,3-cycloheptane units are difficult to be incorporated in the crystalline phase of polyethylene due to the sizable cyclic structure.

3.1.3. Poly(ethylene-co-DD) (EDD)

Structures and thermal properties of EDD are summarized in Table 3. Relationship between T_m and ΔH_m of the copolymer is shown in Fig. 5. EDD having pendant vinyl groups showed higher ΔH_m than that having crosslinked-branching structures. The typical WAXD patterns of EDDs are shown in Fig. 6a and b. The WAXD pattern of the copolymers including the pendant vinyl groups (Fig. 6a) shows the reflection peaks due to (110) and (200) planes of the orthorhombic crystal. On the other hand, the WAXD pattern of the copolymers including the crosslinked-branching structures (Fig. 6b) shows broad reflection patterns. The WAXD profiles indicate that crosslinked-branching structures in the copolymer disturb the crystalline phase of the copolymer more strongly than pendant vinyl groups. The result explains the result that the copolymers with pendant vinyl groups show higher ΔH_m values than those with crosslinked-branching structures.

3.2. TG analysis

TG analysis of the copolymers has been carried out under nitrogen in the temperature range from room temperature to 600 °C. The results are summarized in Table 4 and the TG profiles of some samples are shown in Fig. 7. The polymers show similar TG profiles independent of the nature and the

insertion mode of the comonomers. Weight loss of the copolymers begins at lower temperature than that of polyethylene (homopolymer). Initiation temperatures of thermal degradation (T_d) in the copolymers containing cyclic units or branching structures were lower than those of copolymers containing pendant vinyl groups. One tertiary carbon is formed by 1,2-insertion of one α,ω -nonconjugated diene. On the other hand, two tertiary carbons are formed by cyclization and branching insertion of one α,ω -nonconjugated diene. These results made it clear that increase of the tertiary carbons in the copolymers reduces the T_d [17].

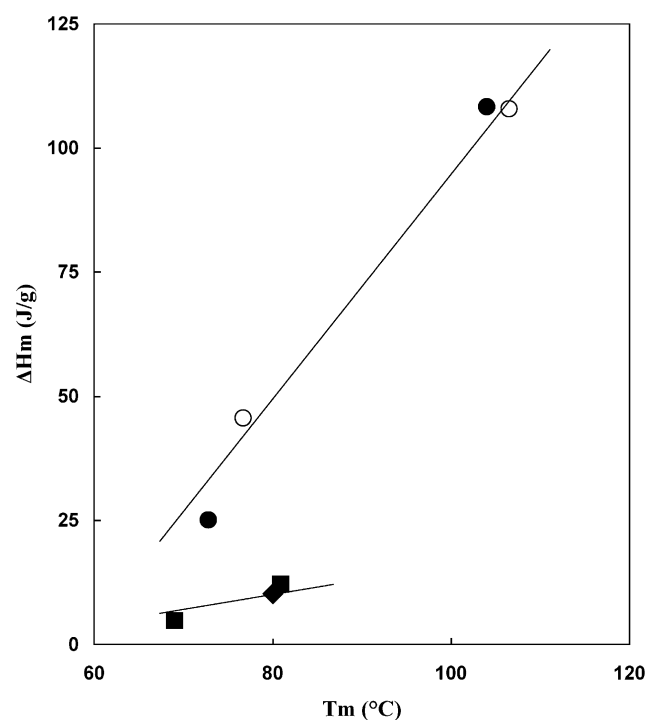


Fig. 5. Relationship between T_m and ΔH_m of EDD prepared by the zirconocene catalysts **1** (○), **3** (●), **6** (■) and **7** (◆).

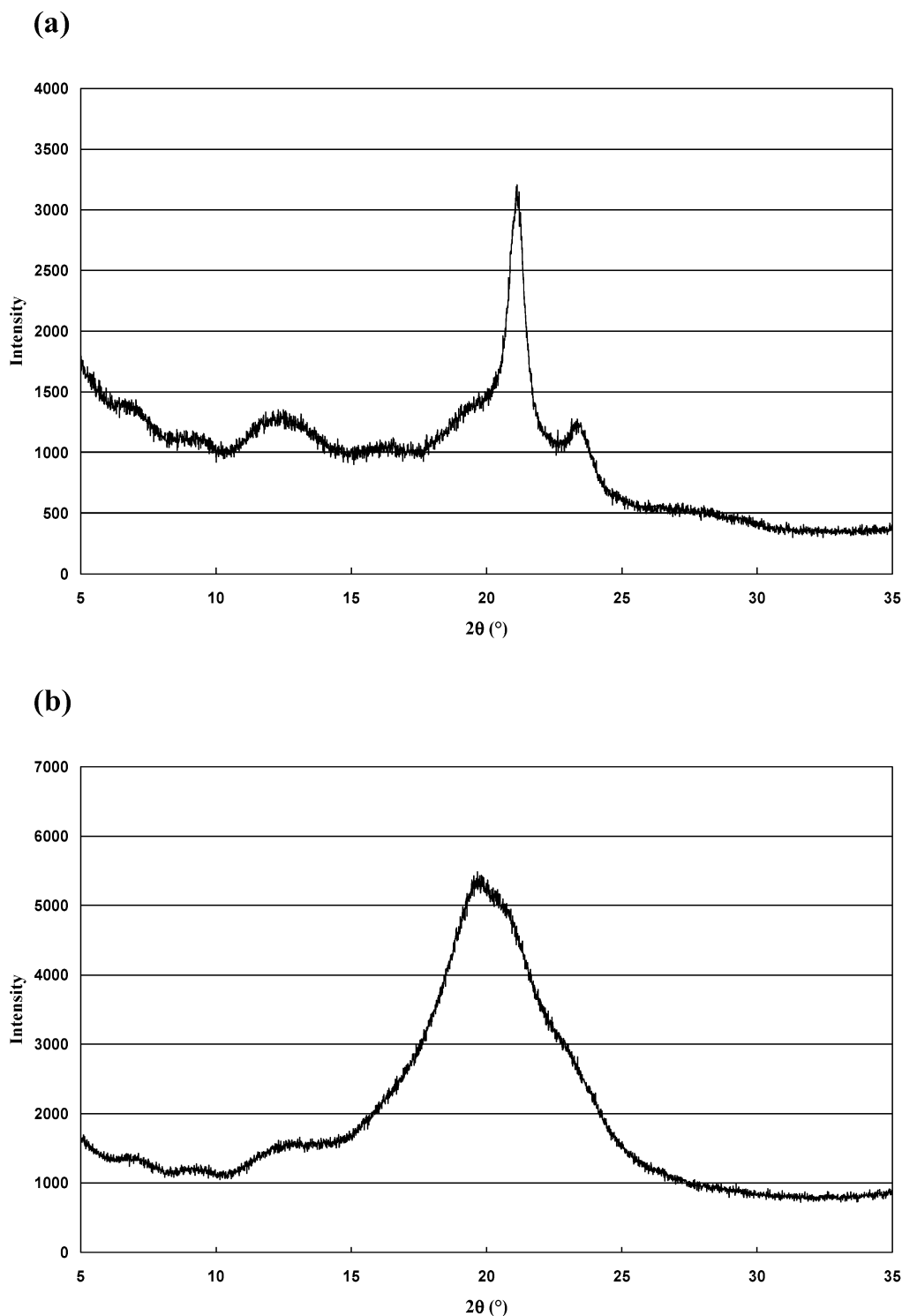


Fig. 6. WAXD patterns of EDD: (a) sample 41 (pendant vinyl DD, 2.2 mol%), (b) sample 44 (crosslinked-branching DD, 4.3 mol%).

4. Conclusion

The effect of insertion mode of α,ω -nonconjugated diene in copolymer with ethylene on the crystalline structures and thermal properties of the copolymers has been studied by WAXD, DSC and TG measurements. In the case of EHD,

the copolymers containing high *cis*-cyclopentane units show higher melting point than those of the copolymers with high *trans*-cyclopentane units. EODs containing pendant vinyl groups showed higher ΔH_m than that containing the 1,3-cycloheptane units. The crosslinked-branching structures in EDD disturb crystallization to drastically decrease the value

Table 4
Thermalgravimetric analysis of poly(ethylene-co-nonconjugated diene)s

Sample	Comonomer		Structure of diene units ^a	T_d (°C) ^b
	Nature	Content (mol%)		
47 ^c	–	0	–	340.5
19	HD	11.0	C	284.6
24	OD	4.9	C/V	311.6
32	OD	5.9	C	279.0
37	DD	4.5	V	306.3
45	DD	4.3	C-B	271.6

^a C = cyclic unit, V = pendant vinyl, C-B = crosslinked-branching.

^b Initial temperature of degradation.

^c Polyethylene prepared by the catalyst **6** for reference: $M_n = 1.1 \times 10^5$, $M_w/M_n = 3.6$, $T_m = 129.8$ °C.

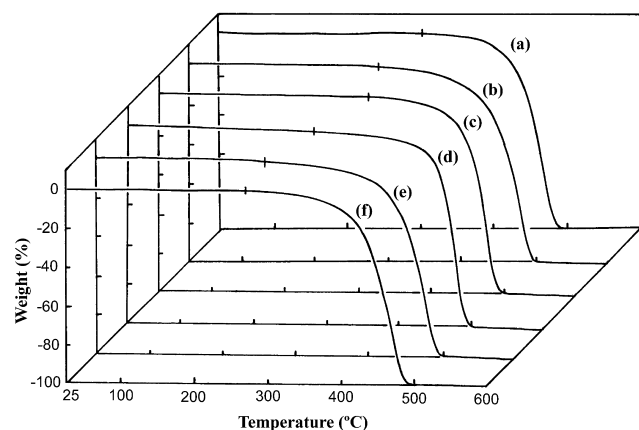


Fig. 7. TGA profiles of polyethylene (a) sample 47, EHD (b) sample 19, EOD (c) sample 24, EOD (d) sample 32, EDD (e) sample 37 and EDD (f) sample 45.

of ΔH_m . The TG analysis clearly showed that the tertiary carbons in the copolymers causes decrease of T_d . Precise control of the insertion mode of α,ω -nonconjugated dienes in the copolymer with ethylene should be one of the most effective methods to synthesize ethylene-based copolymers with characteristic properties.

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