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Crystalline Structure and Thermal Property of Polyethylene and Isotactic Polypropylene Containing Cyclopentane Units in the Main Chain

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ABSTRACT: Polyethylene and isotactic polypropylene having 1,2- or 1,3-disubstituted cyclopentane structures were prepared by copolymerization of ethylene or propylene with cyclopentene (CPE) or 1,5-hexadiene (HD) using zirconocene catalysts. Effect of the cyclopentane structures on the melting point and crystalline structure of the copolymers was investigated. In the case of ethylene-based copolymers, polyethylene containing 1,3-disubstituted cyclopentane structure, poly(ethylene-*co*-HD), showed a lower degree of melting-point depression and decreasing crystallinity with increasing cyclopentane contents than polyethylene containing 1,2-disubstituted cyclopentane structure, poly(ethylene-*co*-CPE). Expansion of crystalline unit cell, especially along the *a*-axis, with increasing cyclopentane content was observed in the wide-angle X-ray diffraction patterns of the poly(ethylene-*co*-HD). The phenomenon indicated incorporation of 1,3-disubstituted cyclopentane structure in the crystalline phase of polyethylene. On the other hand, both poly(propylene-*co*-CPE) and poly(propylene-*co*-HD) showed similar profiles in the relationship between the comonomer content and the melting point or the crystallinity of the copolymers.

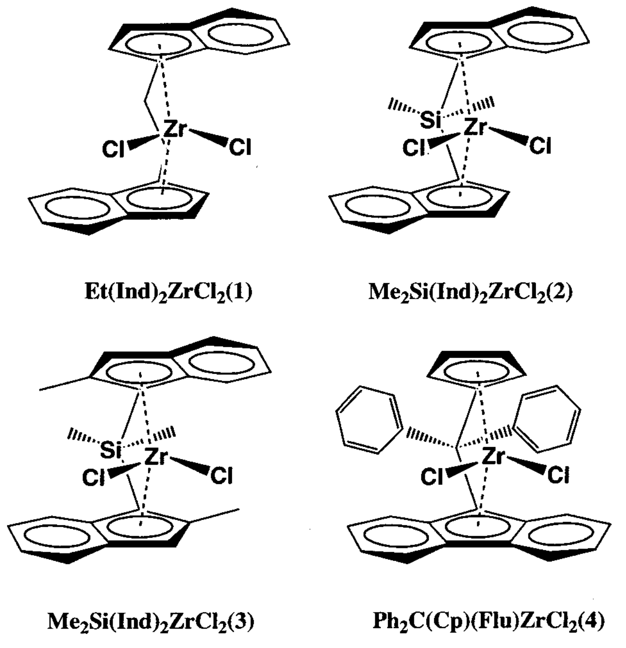
Introduction

Polyethylene and polypropylene containing cyclic structures in the main chain are useful materials with high glass-transition temperature and excellent transparency. The properties of these copolymers can be widely controlled by changing content and structure of the cyclic unit. These copolymers can be synthesized via two different methods using transition-metal complexes, which are effective catalysts for polymerization of cycloolefins and diolefins. One of the two methods is copolymerization of ethylene[1] or propylene[1b,2] with cycloolefin without ring-opening propagation. The other is copolymerization of ethylene[3] or propylene[4] with α,ω-nonconjugated diene involving cyclization propagation.

A number of authors have reported syntheses of polyethylene and isotactic polypropylene containing cyclopentane structures using zirconocene catalysts. Copolymerization of ethylene and cyclopentene (CPE) with zirconocene catalysts preferentially gave polyethylene with 1,2-disubstituted cyclopentane structure.[1a,w] On the other hand, the ligand structure of isospecific zirconocene catalysts affected the propagation mode of CPE in propylene/CPE copolymerization, and the ratio of 1,2- and 1,3-disubstituted cyclopentane structures was found to be widely controlled by the catalyst used.[2c] In the case of copolymerization of ethylene or propylene with 1,5-hexadiene (HD), HD was copolymerized via cyclization propagation, and (methylene-)1,3-disubstituted cyclopentane structure was formed in the main chain of polyethylene or polypropylene.[3,4]

Previous reports of cycloolefin copolymers focused attention on synthesis, structure, and property of amorphous copolymers with high content of cyclic units. In this study, we investigated thermal property and structure of crystalline polyethylene and isotactic polypropylene in relation to the content of 1,2- and 1,3-disubstituted cyclopentane units prepared by the copolymerization of ethylene or propylene with CPE or HD using zirconocene catalysts, *rac*-ethylenebis(indenyl)zirconium dichloride (**1**), *rac*-dimethylsilylenebis(indenyl)zirconium dichloride (**2**), *rac*-dimethylsilylenebis(2-methylindenyl)zirconium dichloride (**3**), and diphenylmethylene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride (**4**), which are listed in Scheme 1.

Scheme 1. Zirconocene Catalysts Used in the Present Investigation



Et(Ind)$_2$ZrCl$_2$(1) **Me$_2$Si(Ind)$_2$ZrCl$_2$(2)**

Me$_2$Si(Ind)$_2$ZrCl$_2$(3) **Ph$_2$C(Cp)(Flu)ZrCl$_2$(4)**

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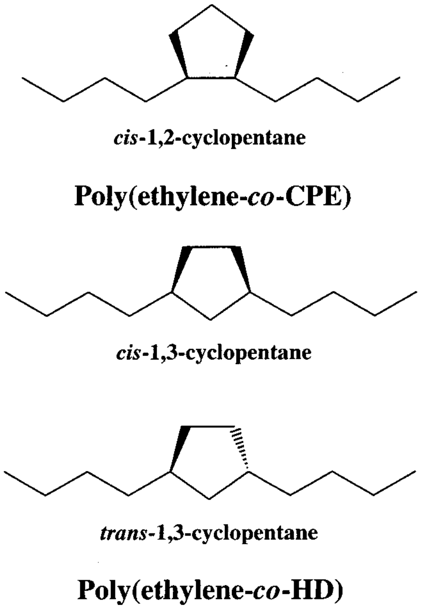
Table 1. Structure and Property of Poly(ethylene-*co*-CPE) and Poly(ethylene-*co*-HD)

sample	catalyst	comonomer nature	comonomer content (mol %)	cis^a (%)	$M_n{}^b$ ($\times 10^{-4}$)	$M_w/M_n{}^b$	$T_m{}^c$ (°C)	$X_c{}^d$ (%)	$d_{110}{}^e$ (Å)	$d_{200}{}^e$ (Å)	axial length (Å)[f] a axis	axial length (Å)[f] b axis
1	**2**		0		10.6	3.6	129.8	64.7	4.16	3.80	7.60	4.80
2	**2**	CPE	3.5	100	13.2	2.6	102.8	37.9	4.25	3.85	7.70	4.90
3	**2**	CPE	4.8	100	7.2	2.3	96.0	34.1	4.24	3.85	7.70	4.89
4	**2**	CPE	12.9	100	5.8	1.9	66.0	15.6	nd[g]	nd[g]		
5	**2**	HD	1.8		7.4	2.6	120.3	61.8				
6	**2**	HD	3.1	19.2	9.3	2.5	114.3	47.1	4.24	3.91	7.82	4.89
7	**2**	HD	5.8	28.7	9.9	2.6	102.8, 112.9	40.7	4.26	3.99	7.98	4.92
8	**2**	HD	11.0	24.2	7.4	3.4	91.7	30.5	4.35			
9	**4**		0		20.9	2.1	131.8	60.9	4.18	3.76	7.52	4.82
10	**4**	CPE	2.5	100	4.8	2.0	106.9	46.3	4.25	3.84	7.69	4.90
11	**4**	CPE	6.1	100	7.3	1.9	90.6	29.6	4.24	3.87	7.75	4.90
12	**4**	CPE	13.4	100	6.5	1.8	71.0	17.6	nd[g]	nd[g]		
13	**4**	HD	3.3		9.9	2.5	111.9	46.6				
14	**4**	HD	8.1	31.0	12.4	2.9	100.9	43.3	4.32	4.16	8.32	4.98
15	**4**	HD	14.8	29.6	9.1	2.7	89.6	30.8	4.43	nd[g]		

[a] Proportion of *cis*-structure of cyclopentane units: *cis*-1,2-disubstituted and *cis*-1,3-disubstituted cyclopentane in poly(ethylene-*co*-CPE) and poly(ethylene-*co*-HD), respectively. [b] Determined by GPC using polystyrene standard. [c] Determined by DSC. [d] X_c denotes crystallinity of copolymer determined by DSC. [e] Bragg distance of (110) and (200) phases. [f] Calculated from (110) and (200) reflections of WAXD assuming orthorhombic crystal of polyethylene. [g] Not detected.

Scheme 2. Structure of Poly(ethylene-*co*-CPE) and Poly(ethylene-*co*-HD)



Results and Discussion

Crystalline Structure of Polyethylene Containing Cyclopentane Units. Polyethylenes containing cyclopentane units were prepared by copolymerization of ethylene and cyclopentene or 1,5-hexadiene with bridged zirconocene catalysts, **2** and **4**. The structures and melting point of copolymers are summarized in Table 1. The copolymerization with CPE produced polyethylene containing *cis*-1,2-disubstituted cyclopentane structure exclusively (Scheme 2). On the other hand, the copolymerization with HD gave the polyethylene with *cis*- and *trans*-1,3-disubstituted cyclopentane structures (Scheme 2). DSC endothermic curves of poly(ethylene-*co*-CPE) and poly(ethylene-*co*-HD) prepared the catalyst **2** are shown in Figures 1 and 2, respectively. DSC curves of poly(ethylene-*co*-CPE) showed single melting peak, as shown Figure 1, and indicated narrow distribution of copolymer composition. A narrow distribution of copolymer composition of the copolymer was confirmed by cross-fractionation chromatography (CFC).[1w,5] In the case of poly(ethylene-*co*-HD), the DSC curves of the copolymer, with the exception of sample 7, also showed single melting peak. As shown in the DSC curves of sample 7 (Figure 2c), poly(ethylene-*co*-HD) with about 6 mol % of HD units tends to show double melting peaks. Composition distribution of poly(ethylene-*co*-HD) was investigated with CFC,[3d] and a narrow distribution of copolymer composition of the poly(ethylene-*co*-HD) with double melting peaks was confirmed.[5] One possibility to assume that two types of crystalline structures exist in poly(ethylene-*co*-HD) with specific content of HD. DSC curves of poly(ethylene-*co*-CPE) and poly(ethylene-*co*-HD) prepared by the catalyst **4** showed single melting peak and indicated a narrow distribution of copolymer composition.[6]

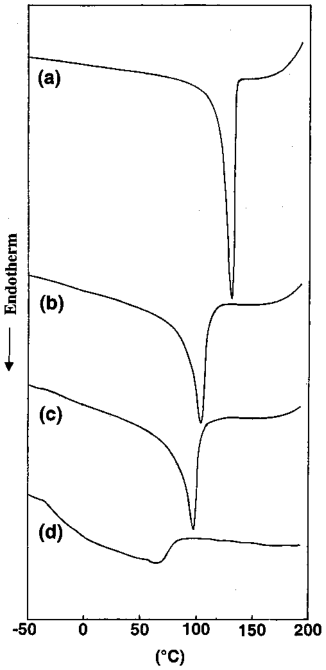


Figure 1. DSC melting curves of poly(ethylene-*co*-CPE)s prepared by the catalyst **4**: (a) CPE, 0 mol % (sample 1); (b) CPE, 3.5 mol % (sample 2); (c) CPE, 4.8 mol % (sample 3); (d) CPE, 12.9 mol % (sample 4).

The relationship between the comonomer content and the melting point of poly(ethylene-*co*-CPE) and poly-

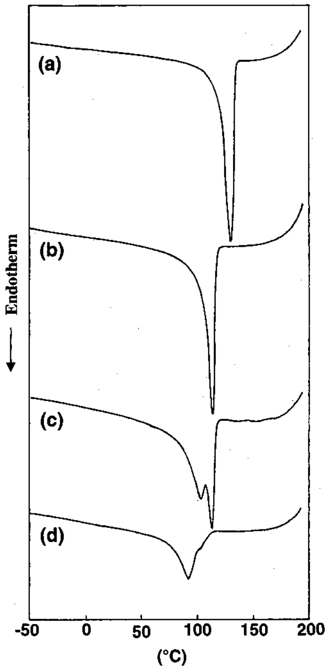


Figure 2. DSC melting curves of poly(ethylene-*co*-HD)s prepared by the catalyst **4**: (a) HD, 0 mol % (sample 1); (b) HD, 3.1 mol % (sample 6); (c) HD, 5.8 mol % (sample 7); (d) HD, 11.0 mol % (sample 8).

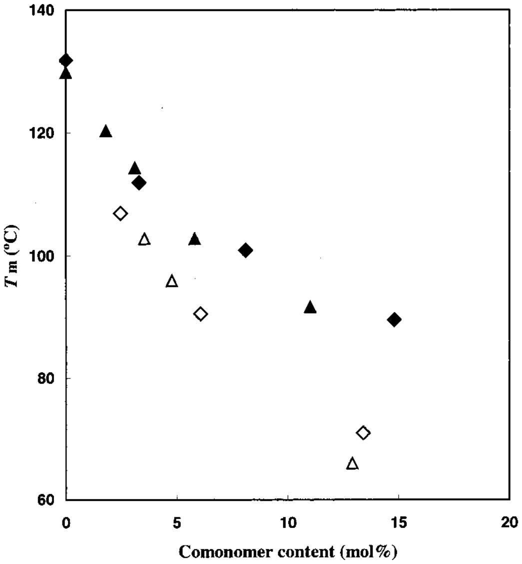


Figure 3. Relationship between comonomer content and melting temperature (T_m) of poly(ethylene-*co*-CPE) obtained with the catalysts **2** (△) and **4** (◇) and poly(ethylene-*co*-HD) obtained with the catalyst **2** (▲) and **4** (◆).

(ethylene-*co*-HD) is shown in Figure 3. Poly(ethylene-*co*-HD) exhibited a lower degree of melting-point depression with increasing comonomer content than poly(ethylene-*co*-CPE). The relationship between the comonomer content and the crystallinity of the copolymers is illustrated in Figure 4. Poly(ethylene-*co*-HD) showed higher crystallinity than poly(ethylene-*co*-CPE), and this relationship is similar to that observed with the melting point.

The crystalline structure of the ethylene-based copolymers was investigated by wide-angle X-ray diffraction (WAXD). The WAXD patterns of poly(ethylene-*co*-CPE) and poly(ethylene-*co*-HD) are shown in Figures 5 and 6, respectively. In the case of poly(ethylene-*co*-CPE), the intensity of reflection peaks due to (110) and (200) crystal planes (peaks at $2\theta = 21°$ and 23.5° of polyethylene, respectively) decreased with increasing CPE content (Figure 5). On the other hand, in the case of poly(ethylene-*co*-HD), the intensity of the (200) reflection peak remarkably decreased with increasing HD content, and 2θ values of both reflections shifted to lower angles (Figure 6). The 2θ values in WAXD of poly(ethylene-*co*-HD) including higher cyclopentane units indicate pseudohexagonal crystalline phase as observed in poly(ethylene-*co*-propylene).[6] Poly(ethylene-*co*-HD) including 5.8 mol % of HD (sample shows the WAXD pattern with feature between orthorhombic crystal and pseudohexagonal crystal, as shown in Figure 6c). Double melting peaks in the DSC analysis of the copolymer, as shown in Figure 2c, should be derived from the coexistence of two types of crystals.

The axial length of unit cell in the copolymers, assuming orthorhombic crystal, is illustrated in Figures 7 and 8. In the case of poly(ethylene-*co*-CPE), incorporation of a small amount of CPE (2.5 mol %) caused a

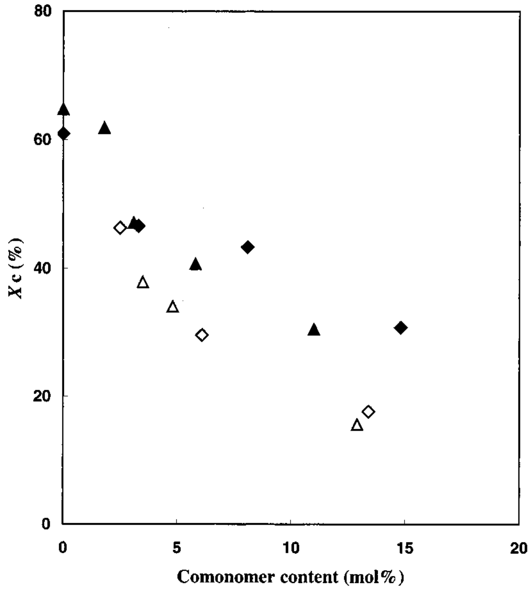


Figure 4. Relationship between comonomer content and crystallinity (X_c) of poly(ethylene-*co*-CPE) obtained with the catalyst **2** (△) and **4** (◇) and poly(ethylene-*co*-HD) obtained with the catalyst **2** (▲) and **4** (◆).

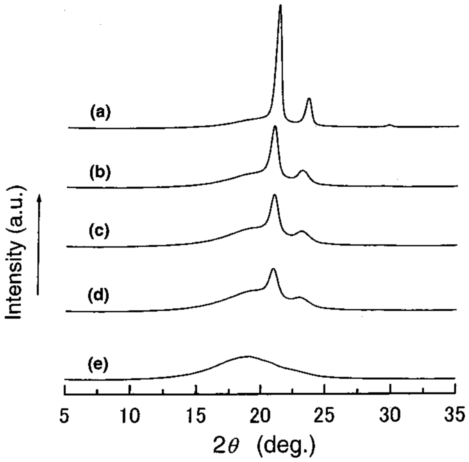


Figure 5. WAXD pattern of poly(ethylene-*co*-CPE) obtained with the catalyst **2** or **4**: (a) CPE, 0 mol %; (b) CPE, 2.5 mol %; (c) CPE, 4.8 mol %; (d) CPE, 6.1 mol %; (e) CPE, 12.9 mol %.

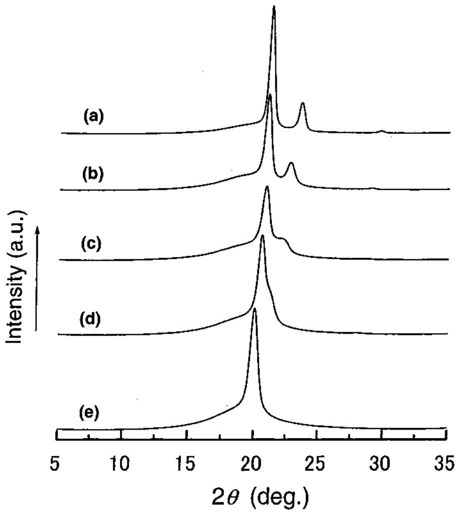


Figure 6. WAXD patterns of poly(ethylene-*co*-HD) obtained with the catalyst **2** or **4**: (a) HD, 0 mol %; (b) HD, 3.1 mol %; (c) HD, 5.8 mol %; (d) HD, 8.1 mol %; (e) HD, 14.8 mol %.

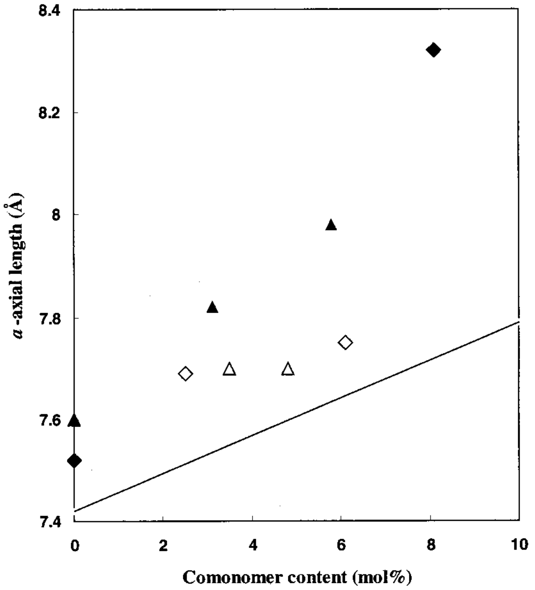


Figure 7. Relationship between comonomer content and *a*-axial length of poly(ethylene-*co*-CPE) obtained with the catalyst **2** (△) and **4** (◇), poly(ethylene-*co*-HD) obtained with the catalyst **2** (▲) and **4** (◆), and poly(ethylene-*co*-propylene) (straight line).

slight expansion of both *a*- and *b*-axial lengths. However, the axial length was almost unaffected by further incorporation of cyclopentane units. On the other hand, the *a*-axial length of the poly(ethylene-*co*-HD) unit cell increased linearly with increasing comonomer content, while the *b*-axial length was not apparently affected by comonomer content.

The experimental observations of melting temperature and WAXD of polyethylenes containing cyclopentane structures strongly indicate isomorphism of poly(ethylene-*co*-HD). In the case of polyethylene with 1,2-disubstituted cyclopentane structures, poly(ethylene-*co*-CPE), most of the cyclopentane groups are excluded from crystalline phase. On the other hand, the 1,3-disubstituted cyclopentane structures can be incorporated in the crystalline phase and expand the unit cell of polyethylene as observed in poly(ethylene-*co*-HD).

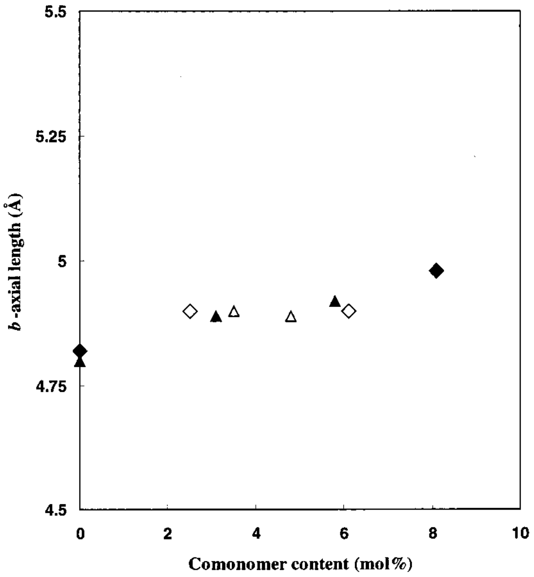


Figure 8. Relationship between comonomer content and *b*-axial length of poly(ethylene-*co*-CPE) obtained with the catalyst **2** (△) and **4** (◇) and poly(ethylene-*co*-HD) obtained with the catalyst **2** (▲) and **4** (◆).

Poly(ethylene-*co*-propylene), containing up to 30 mol % of propylene, has been known as a typical polyolefin showing isomorphism.[7] A structural similarity of poly(ethylene-*co*-HD) and poly(ethylene-*co*-propylene) can be found in the size of side-chain branches. Imaginary covalent linking of two adjacent side-chain methyl groups in poly(ethylene-*co*-propylene) would produce a 1,3-disubstituted cyclopentane unit. Present poly(ethylene-*co*-HD) and a literary poly(ethylene-*co*-propylene)[7e] are compared for the *a*-axial length/comonomer content relationship in Figure 7. With all errors of absolute values of axial length between present data and literary data,[8] slopes of the plots should reflect the side-chain structure of copolymers. Poly(ethylene-*co*-HD) showed a higher degree of expansion with increasing comonomer content than poly(ethylene-*co*-propylene), indicating more effectiveness of a cyclopentane unit in affecting the unit cell structure than a methyl group.

Crystalline Structure of Isotactic Polypropylene Containing Cyclopentane Units. Isotactic polypropylenes containing cyclopentane units were prepared by copolymerization of propylene and CPE or HD with isospecific zirconocene catalysts **1**, **2**, and **3**. The propylene sequence in the copolymers was kept high isotacticity much the as polypropylene. The content and structure of cyclopentane units in the copolymers are summarized in Table 2.[9] In the case of propylene/CPE copolymerization, the zirconocene catalysts **1** and **2** gave the copolymers containing both 1,2- and 1,3-disubstituted cyclopentane structures. On the other hand, only 1,2-propagation of CPE occurred in the copolymerization with the catalyst **3** (Scheme 2).[2c] In the propylene/HD copolymerization, HD propagated exclusively via the addition−cyclization mechanism, yielding *cis*- and *trans*-methylene-1,3-cyclopentane structures in the main chain of isotactic polypropylene (Scheme 3).[4]

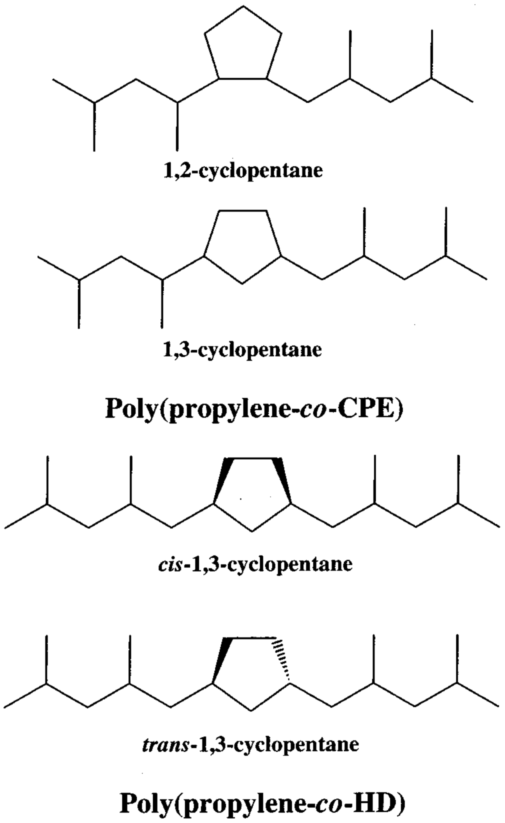
DSC curves of poly(propylene-*co*-CPE) and poly(propylene-*co*-HD) showed a single melting peak[10] and indicated a narrow distribution of copolymer composition. The relationship between comonomer content and melting temperature is illustrated in Figure 9. The melting temperature of the copolymers and polypropylene was dependent on not only the comonomer content but also the ligand structure of zirconocene

Table 2. Structure and Property of Poly(propylene-*co*-CPE) and poly(propylene-*co*-HD)

		comonomer						
sample	catalyst	nature	content (mol %)	1,3-insertion unit[a] (%)	$M_n{}^b$ ($\times 10^{-4}$)	$M_w/M_n{}^b$	$T_m{}^c$ (°C)	$X_c{}^d$ (%)
16	**1**		0		1.1	2.1	126.9	41.8
17	**1**	CPE	2.0	51.6	1.1	1.7	114.9	29.2
18	**1**	CPE	3.6	59.8	0.79	1.8	103.5	23.5
19	**1**	CPE	5.8	60.8	0.45	1.8	83.3	11.8
20	**1**	HD	2.1	100	1.3	1.9	109.9	22.3
21	**1**	HD	4.1	100	1.2	2.1	99.7	19.2
22	**1**	HD	7.0	100	0.7	3.0	78.0	13.8
23	**2**		0		4.0	1.9	141.2	47.2
24	**2**	CPE	1.4	16.7	1.8	1.9	128.1	37.7
25	**2**	CPE	3.7	25.9	1.2	1.7	104.6	28.3
26	**2**	CPE	5.3	28.2	0.80	1.9	97.6	21.5
27	**2**	HD	1.8	100	2.5	1.8	123.6	31.4
28	**2**	HD	3.2	100	2.4	1.8	111.9	29.2
29	**2**	HD	6.2	100	2.1	1.8	85.7	14.4
30	**3**		0		6.7	1.7	147.7	53.3
31	**3**	CPE	1.5	0.0	3.0	1.8	132.1	41.0
32	**3**	CPE	2.1	0.0	2.7	1.9	123.2	37.9
33	**3**	CPE	4.1	0.0	1.8	2.1	108.1	27.9
34	**3**	CPE	6.1	0.0	0.85	2.0	89.6	17.4
35	**3**	HD	1.3	100	4.8	1.7	134.3	42.4
36	**3**	HD	2.4	100	5.5	1.7	127.7	35.8
37	**3**	HD	3.5	100	6.1	1.9	115.3	24.7
38	**3**	HD	6.1	100	9.8	2.1	98.1	12.6

[a] Proportion of 1,3-disubstituted cyclopentane units: proportion of *cis*-1,3-disubstituted cyclopentane units in poly(propylene-*co*-HD) is about 34% with the catalyst **2** and 29% with the catalyst **3**.[4,8] [b] Determined by GPC using polystyrene standard. [c] Determined by DSC. [d] X_c denotes crystallinity of copolymer determined by DSC.

Scheme 3. Structure of Poly(propylene-*co*-CPE) and Poly(propylene-*co*-CPE)



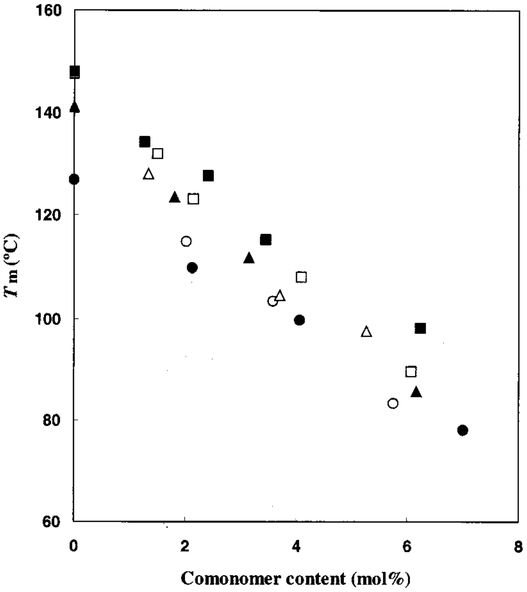


Figure 9. Relationship between comonomer content and melting temperature (T_m) of poly(propylene-*co*-CPE) obtained with the catalyst **1** (○), **2** (△), and **3** (□) and poly(propylene-*co*-HD) obtained with the catalyst **1** (●), **2** (▲), and **3** (■).

catalyst used, and the melting temperature of the polymers decreased in the following order: catalyst **3** > **2** > **1**.[11] The difference is derived from the isotacticity and regioregularity of the propylene sequence of the copolymers. However, the degree of melting temperature depression on the copolymer composition was not affected by the ligand structure of zirconocene catalyst used. Poly(propylene-*co*-CPE) and poly(propylene-*co*-HD) prepared by the same catalyst showed a similar relationship. The crystallinity of either copolymer decreased with increasing cyclopentane units in a similar manner independent of the cyclopentane structure, as shown in Figure 10. These results indicate that any types of cyclopentane structures, 1,2- or 1,3-disubstituted cyclopentane and methylene-1,3-disubstituted cyclopentane, are excluded from crystalline phase of isotactic polypropylene.

Crystalline structures of the copolymers prepared by the catalyst **3** are summarized in Table 3. The WAXD pattern of poly(propylene-*co*-CPE) and poly(propylene-*co*-HD) prepared by the catalyst **3** is shown in Figures 11 and 12, respectively. In the case of poly(propylene-

Table 3. Crystalline Structure of Poly(propylene-*co*-CPE) and Poly(propylene-*co*-HD) Prepared by Catalyst 3

	comonomer					axial length (Å)[b]	
sample	nature	content (mol %)	d_{110}[a] (Å)	d_{040}[a] (Å)	d_{130}[a] (Å)	*a* axis	*b* axis
30		0	6.32	5.30	4.82	6.71	21.20
32	CPE	2.1	6.32	5.53	4.82	6.68	22.12
33	CPE	4.1	6.32	5.37	4.82	6.70	21.48
34	CPE	6.1	6.41	5.46	4.90	6.80	21.84
36	HD	2.4	6.27	5.30	4.82	6.65	21.20
37	HD	3.5	6.32	5.33	4.82	6.71	21.32
38	HD	6.1	6.27	5.30	4.82	6.65	21.20

[a] Bragg distance of (110), (040), and (130) phases. [b] Calculated from (110) and (040) reflections of WAXD assuming monoclinic crystal of isotactic polypropylene.

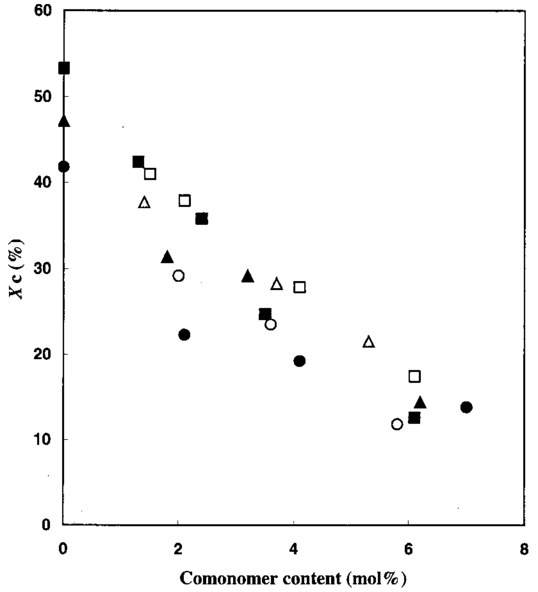


Figure 10. Relationship between comonomer content and crystallinity (X_c) of poly(propylene-*co*-CPE) (□) and poly(propylene-*co*-HD) (■) prepared by the catalyst **3**.

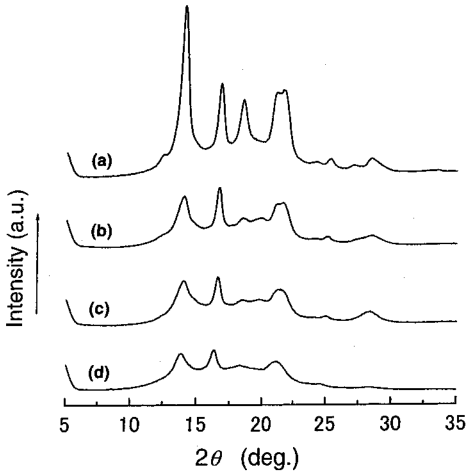


Figure 11. WAXD pattern of poly(propylene-*co*-CPE) prepared by the catalyst **3**: (a) CPE, 0 mol %; (b) CPE, 2.1 mol %; (c) CPE, 4.1 mol %; (d) CPE, 6.1 mol %.

co-CPE), a reflection peak derived from the (130) crystal plane of α-form, $2\theta = 18°$, disappeared, and a small reflection peak derived from the γ-form, $2\theta = 20°$, could be detected. On the other hand, in the case of poly(propylene-*co*-HD), intensity of all reflection peaks derived from α-phase of isotactic polypropylene decreased with increasing cyclopentane units in the copolymer without changing phase distance. Cyclopentane units in the both poly(propylene-*co*-CPE) and poly(propylene-*co*-HD) are isolated from each other. It seems reasonable to suppose that the difference of crystalline structure should not be derived from the length of propylene sequence in the copolymers but be derived from the difference of cyclopentane structure in the copolymers, 1,2-disubstituted or 1,3-disubstituted cyclopentane structure.

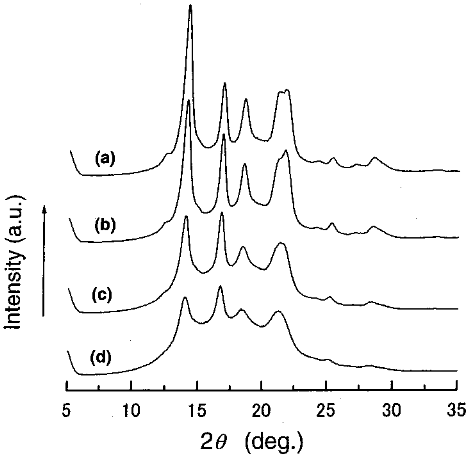


Figure 12. WAXD pattern of poly(propylene-*co*-HD) prepared by the catalyst **3**: (a) HD, 0 mol %; (b) HD, 2.4 mol %; (c) HD, 3.5 mol %; (d) HD, 6.1 mol %.

Conclusion

The cyclopentane units incorporated in the main chain of polyethylene affected the crystalline structure. In the case of poly(ethylene-*co*-CPE), 1,2-disubstituted cyclopentane structure was excluded from the crystalline phase. On the other hand, 1,3-disubstituted cyclopentane structure in poly(ethylene-*co*-HD) was incorporated in the crystalline phase and expanded the unit cell of crystalline polyethylene. This characteristic behavior observed in poly(ethylene-*co*-HD), so-called isomorphism, has not been reported previously for ethylene-based polyalkenes except for poly(ethylene-*co*-propylene). In the case of propylene-based copolymers, a similar relationship was found between cyclopentane content and melting point or crystallinity of the copolymer regardless of the structure of cyclopentane units incorporated. The difference between ethylene-based and propylene-based copolymers should have arisen from different crystalline structures of polyethylene and isotactic polypropylene, β-zigzag and 3/1-helix, respectively.

Experimental Part

Materials. Copolymers were prepared by zirconocene catalysts, ethylene-based copolymers by **2** or **4** and propylene-based copolymers by **1**, **2**, or **3**, using MAO as a cocatalyst (molar ratio of MAO[Al]/[Zr] = 1000) according to the literature.[1w,2c,3d,4] Copolymerizations were conducted in toluene at 40 °C under 1 atm of ethylene or propylene pressure. The copolymers obtained were extracted with boiling *o*-dichlorobenzene (ODCB) to remove catalyst residues (and cross-linked fraction in the poly(ethylene-*co*-HD).[3d]

Analytical Procedures. The comonomer content and the structure of incorporated cyclopentane units were determined by ^{1}H and ^{13}C NMR spectra recorded at 130 °C on a JEOL Lambda-400 Fourier transform NMR spectrometer.[1w,2c,3d,4] Molecular weight and molecular weight distribution 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. The melting temperature was measured by a Seiko DSC6200 (Seiko Instruments Inc.) at a heating rate of 10 °C/min after preheating and precooling to −150 °C. Crystallinity (X_c) of the ethylene-based copolymers and propylene-based copolymers was calculated from heat of fusion determined by DSC analysis using the following equation:

$$X_c\ (\%) = \Delta H_f/\Delta H_f^0 \times 100$$

where ΔH_f is the heat of fusion of the sample and ΔH_f^0 is the heat of fusion of folded-chain polyolefin crystals (269.9 J/g for polyethylene[12] and 208.3 J/g for isotactic polypropylene[13]).

Samples for X-ray diffraction measurements were melted at 180 °C for ethylene-based copolymer and at 200 °C for propylene-based copolymers and were pressed under 10 MPa pressure followed by quenching in 30 °C water. WAXD patterns of the copolymers were acquired on a MAC Science M18XCE using Cu Kα radiation.

Supporting Information Available: CFC diagrams of poly(ethylene-*co*-CPE) and poly(ethylene-*co*-HD) prepared by catalysts **2** and **4** and DSC endothermic curves of poly(propylene-*co*-CPE) and poly(propylene-*co*-HD) prepared by catalyst **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(5) CFC diagrams of poly(ethylene-*co*-CPE) and poly(ethylene-*co*-HD) prepared by catalysts **2** and **4** are available in the Supporting Information.

(6) DSC endothermic curves of poly(ethylene-*co*-CPE) and poly(ethylene-*co*-HD) prepared the catalyst **4** are available in the Supporting Information.

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(8) The present data of poly(ethylene-*co*-CPE) or poly(ethylene-*co*-HD) generally showed larger values of *a*-axial length than the literary data of poly(ethylene-*co*-propylene). The difference was also observed even in those values of polyethylene. The tendency may be derived from difference of preparation conditions of specimens.

(9) The proportion of *cis*-CPE to *trans*-CPE units in the poly(propylene-*co*-CPE) has not exactly determined. However, ^{13}C NMR spectra of the copolymers indicated that incorporated CPE unit preferentially formed *cis*-structure.[2c]

(10) DSC endothermic curves of poly(propylene-*co*-CPE) and poly(propylene-*co*-HD) prepared by catalyst **3** are available in the Supporting Information.

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