Synthesis of Polyolefins with Unique Properties by Using Metallocene-Type Catalysts

Yukio Imanishi, Naofumi Naga, Michiyo Tsubooka*

Graduate School of Materials Science, Nara Institute of Science and Technology
8916-5, Takayama-cho, Ikoma, Nara, Japan 630-0101
Fax: +81-774-53-8207; E-mail: yukioima@muse.ocn.ne.jp

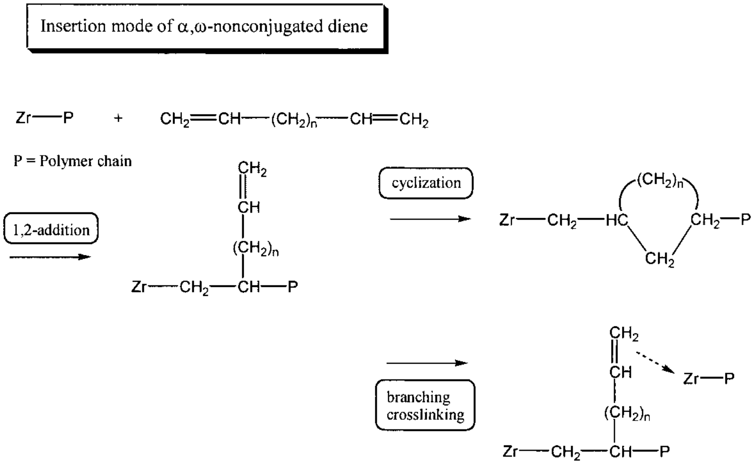
Summary: Copolymerization of ethylene and 1,5-hexadiene (HD) by zirconocene catalysts proceeded *via* cyclization-addition mechanism to form 1,3-didsubstituted cyclopentane structure in the polyethylene chain. The 1,3-cyclopentane structure was found to be taken in the crystalline structure of polyethylene (isomorphism) by partially chainging the *trans* zigzag chain into *gauche* conformation, thereby, inducing a transformation of orthorhombic crystal to pseudohexagonal crystal. Copolymerization of ethylene and cyclopentene (CPE) by zirconocene catalysts yielded copolymers having 1,2-disubstituted cyclopentane structure in the polyethylene chain. The 1,2-cyclopentane structure was not taken into the crystalline structure of polyethylene. The melting point (T_m) and the crystallinity (X_c) of polyethylene decreased by copolymerization of HD or CPE, and the T_m- and X_c-decreasing effect of CPE was stronger than HD. For copolymers of propylene and HD or CPE obtained with isospecific zirconocene catalyst, the isomorphism was not ovserved.

Keywords: copolymerization; ethylene; 1,5-hexadiene; isomorphism: zirconocene catalyst

Introduction

Metallocene catalysts are effective not only for the polymerization of common olefins but for cycloolefins and diolefins. Olefin copolymers containing cyclic structures have been developed for optical materials with high glass-transition temperature. The polyolefins with cyclic groups can be synthesized by (co)polymerization of α,ω-nonconjugated diene involving intramolecular cyclization[1] or (co)polymerization of cycloolefins without ring-opening reaction [2].

Three types of propagation reaction of α,ω-nonconjugated diene are possible in copolymerization with α-olefins such as ethylene and propylene as illustrated in Scheme 1.



Scheme 1.

The first is a repeated 1,2-addition-type reactions, producing pendant vinyl groups in the resulting copolymers. The second is an addition reaction of a double bond of diene immediately followed by intramolecular cyclization to form a cycloalkane structure. The third is a reaction of a pendant double bond in the polymer with other propagating chains, resulting in branching and crosslinking.

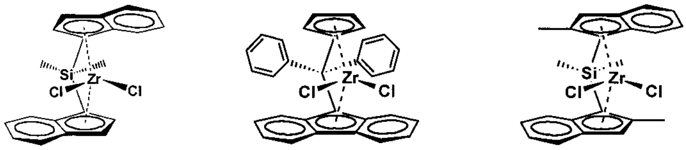
In the present investigation, we carried out copolymerization of ethylene or propylene with 1,5-hexadiene (HD) or cyclopentene (CPE) using stereospecific zirconocene catalysts, and investigated thermal properties and crystalline structure of resulting copolymers.

Experimental Part

Materials

Zirconocene catalysts (**1**—**3**) were commercially obtained from Aldrich Co., Ltd. and Boulder Science Co., Ltd., and used without further purification. A list of zirconocene catalysts is shown in Scheme 2. A hexane solution of methylisobutylaluminoxane (MMAO) and a toluene solution of methylaluminoxane (MAO) were donated from Tosoh Akzo Co., Ltd., and used without further purification. HD and CPE (Tokyo Kasei) were dried with CaH_2. Ethylene and propylene (Sumitomo Seika) were purified by passing through columns of NaOH, P_2O_5, and molecular sieves 3A.

List of zirconocene catalysts



Cat.1 $Me_2Si(Ind)_2ZrCl_2$ **Cat.2 $Ph_2C(Cp)(Flu)ZrCl_2$** **Cat.3 $Me_2Si(2\text{-}MeInd)_2ZrCl_2$**

Scheme 2.

Copolymerization

Copolymerization of ethylene or propylene was carried out in a 100 mL glass reactor equipped with a magnetic stirrer. Toluene was added to the reactor under nitrogen atmosphere. Ethylene or propylene was introduced into the reactor at 40°C under 1 atm until the solvent was saturated with ethylene or propylene, and a measured amount of comonomers such as HD and CPE was added. MAO or MMAO and a zirconocene catalyst were mixed in a 50 mL glass flask at 25°C for 5min. Polymerization was started by introducing the catalyst solution into the reactor. After a requisite time of reaction, the polymerization was terminated by adding a small amount of ethanol. The polymer was precipitated in a large excess of ethanol and recovered by filtration. The polymer obtained was extracted with boiling *o*-dichlorobenzene (ODCB) to fractionate into soluble and insoluble parts. The solution of extracted polymer was concentrated by evaporation and the polymer was precipitated in a large excess of ethanol. The precipitate was recovered by filtration and dried in vacuo at 60°C for 6h.

Analytical Procedures

Molecular weight and molecular weight distribution of the copolymer were measured at 140°C by means of gel-permeation chromatography (Toso HLC-8121 GPC/HT) using ODCB as a solvent and calibrated with standard polystyrene samples.

Glass-transition temperature (T_g) and melting temperature (T_m) of copolymers were measured by using Seiko Exstar 6000 (Seiko Instruments Inc.) at a heating rate of 10K/min after preheating to 200°C for ethylene copolymers or 250°C for propylene copolymers following precooling to – 150°C.

^{1}H NMR and ^{13}C NMR spectra of 5 wt-% trichlorobenzene/benzene-d_6 (9/1, v/v) solution were recorded at 130°C on a JEOL Lambda-400 Fourier transform NMR. FT-IR spectrum was measured under nitrogen at room temperature by using FT-730-IR spectrometer (Horiba Instruments Inc.) at a resolution of 1cm^{-1} and with 64-time integration. Samples for FT-IR measurement were prepared by annealing to room temperature after melting at 150–180°C. Wide-angle X-ray diffraction (WAXD) measurement was carried out by using M18XCE X-ray generator (Mac Science Inc.) under irradiation of Cu-Kα ray (λ=1.54 Å) at an acceleration voltage of 40 kV, electric current of 120 mA, and a scanning rate of 2°/min. Each WAXD sample was prepared by heating at requisite temperatures (180°C for ethylene copolymers and 250°C for propylene copolymers), compression moulding at 10Mpa and isothermal crystallization at 30°C for 1h.

Results and Discussion

Copolymerization of Ethylene and HD or CPE

Copolymerization of ethylene and HD with zirconocene catalysts **1** and **2** was carried out at 40°C using MMAO as a cocatalyst, and the results are shown in Table 1.

Table 1. Structure and properties of poly(ethylene-*co*-HD).

Run No.	Cat.	HD ^{a} (mol%)	*cis* ^{a} (%)	*trans* ^{a} (%)	M_n ^{b} ($\times10^{-4}$)	M_w/M_n ^{b}	T_m ^{c} (°C)	T_g ^{c} (°C)	X_c ^{d} (%)
1	**1**	0	-	-	10.6	3.6	129.8	n.d.	80.3
2	**2**	0	-	-	20.9	2.1	131.8	n.d.	85.5
3	**1**	1.8	20.1	79.9	7.4	2.6	120.3	n.d.	n.d.
4	**1**	3.1	19.2	80.8	9.3	2.5	114.3	n.d.	65.7
5	**1**	5.9	28.7	71.3	9.9	2.6	102.8 113.0	n.d.	64.7
6	**1**	6.6	25.8	74.8	7.4	3.4	112.6	n.d.	n.d.
7	**2**	8.1	31.0	69.0	12.4	2.9	100.9	n.d.	66.3
8	**1**	11.0	24.2	75.8	7.4	3.4	91.7	n.d.	49.6
9	**2**	14.8	29.6	70.4	9.1	2.7	89.6	n.d.	49.5
10	**1**	17.5	21.7	78.3	4.8	2.2	71.8	-26.3	n.d.

Table 1. (continued) Structure and properties of poly(ethylene-*co*-HD).

11	**1**	20.3	28.6	71.4	4.8	2.3	66.6	-26.8	n.d.
12	**1**	24.5	31.9	68.1	2.5	2.1	61.5	-22.5	n.d.
13	**1**	27.9	24.8	75.2	2.7	2.3	55.0	-23.4	n.d.
14	**1**	100	28.2	71.8	n.d.	n.d.	-	20.3	n.d.

[a] Determined by ^{13}C-NMR [b] Measured by GPC [c] Measured by DSC [d] Determined by WAXD.

^{1}H NMR and ^{13}C NMR spectra of boiling ODCB-soluble copolymer obtained with zirconocene catalyst **1** are shown in Figure 1.

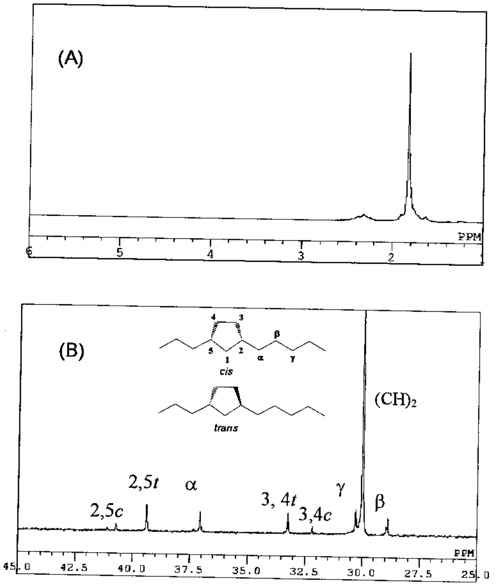


Figure 1. ^{1}H NMR(A) and ^{13}C NMR(B) spectra of poly(ethylene-*co*-HD).

No signals assignable to pendant double bonds were observed in the ^{1}H NMR spectrum of the copolymer. ^{13}C NMR spectrum of the copolymer proved clearly that HD was incorporated in copolymer as 1,3-cyclopentane unit *via* cyclization-addition mechanism. The cyclopentane unit assumes either *cis*- or *trans*-structure. According to the literatures[3a, b, c], the contents of *cis*- and *trans*-1, 3-cyclopentane units were determined and are presented in Table 1.

Copolymerization of ethylene and CPE was carried out with zirconocene catalysts **1** and **2** using MMAO as a cocatalyst at 40°C. Results of the copolymerization are summarized in Table 2.

Table 2. Structure and properties of poly(ethylene -*co*-CPE).

Run No.	Cat.	CPE[a] (mol%)	M_n[b] ($\times10^{-4}$)	M_w/M_n[b]	T_m[c] (°C)	T_g[c] (°C)	X_c[d] (%)
15	**2**	2.5	4.8	2.0	106.9	n.d	59.6
16	**1**	3.5	13.2	2.6	102.8	25.8	52.4
17	**1**	4.8	7.2	2.3	96.0	n.d.	48.3
18	**2**	6.1	7.3	1.9	90.6	43.2	42.6
19	**1**	12.9	5.8	1.9	66.0	40.5	19.9

[a] Determined by ^{13}C-NMR [b] Measured by GPC [c] Measured by DSC [d] Determined by WAXD.

The structure of inserted CPE units in the copolymers was investigated by ^{13}C NMR spectrum which is shown in Figure 2.

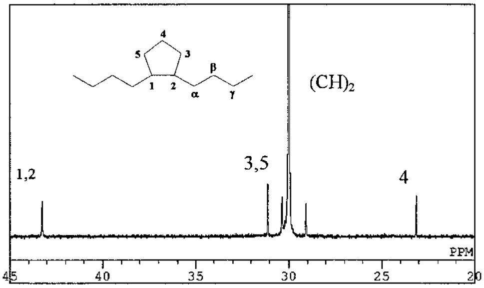


Figure 2. ^{13}C NMR spectra of poly(ethylene-*co*-CPE).

The signals at 43.3, 31.2 and 23.2 ppm are assigned to isolated *cis*-1,2-cyclopentane units in the ethylene sequence[2, 4, 5]. No signals assignable to isolated *cis*-1, 3-cyclopentane units were observed[5]. Copolymer obtained with isospecific catalyst **1** and syndiospecific catalyst **2** contained only *cis*-1, 2-cyclopentane structure. These results indicate that the preferential mode of

CPE polymerization is 1,2-type and that the stereospecificity of zirconocene catalysts does not affect the polymerization mode of CPE in the copolymerization.

Thermal Properties of Poly(ethylene-co-HD) and Poly(ethylene-co-CPE)

T_m/copolymer composition relationship of poly(ethylene-*co*-HD) and poly(ethylene-*co*-CPE) is shown in Figure 3.

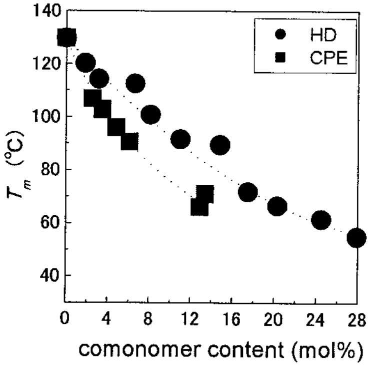


Figure 3. Relationship between comonome content and melting temperature of poly(ethylene-*co*-HD) and poly(ethylene-*co*-CPE).

It is clearly shown that T_m of polyethylene decreased with increasing content of HD or CPE, and that the T_m-lowering effect of CPE incorporation was greater than that of HD incorporation. A greater disturbance of the crystalline structure of polyethylene by CPE incorporation might be a reason for the difference.

T_g of ethylene copolymer increased with increasing content of CPE or HD as shown in Tables 1 and 2. The T_g-rising effect of CPE was much stronger than HD.

WAXD analysis of Crystalline Structure of Poly(ethylene-co-HD) and Poly(ethylene-co-CPE)

WAXD profiles of the ethylene copolymers are shown in Figure 4(A) and (B).

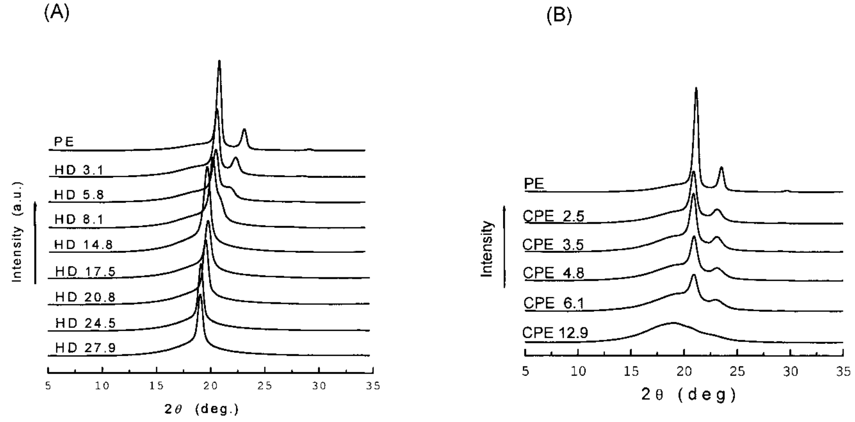


Figure 4. WAXD profiles of poly(ethylene-*co*-HD) (A) and poly(ethylene-*co*-CPE) (B).

With polyethylene, diffraction peaks appeared at 2θ = 21° and 24°, which are due to (110) plane and (200) plane of the orthorhombic crystal, respectively[6].

With poly(ethylene-*co*-HD), the diffraction intensity of the orthorhombic (200) plane decreased accompanying a peak shift toward low angle with increasing HD content. The diffraction peak was not observed in copolymers containing HD more than 14.8mol%. The diffraction intensity of the orthorhombic (110) plane also decreased with increasing HD content. However, the decrease of the (110) plane was much more gentle than the (200) plane. These results suggest that 1,3-cyclopentane structures are built in the planar zigzag chain of polyethylene to alter the packing of polyethylene chain.

In poly(ethylene-*co*-HD) containing HD more than 14.8mol%, a diffraction peak appeared at 2θ = 18°–20°. This peak could be ascribed to the (100) plane of hexagonal crystal of polyethylene[7]. It is considered that the crystalline structure of poly(ethylene-*co*-HD) containing

HD of 14.8mol% has changed to a pseudohexagonal crystal[8], which is similar to the hexagonal crystal of polyethylene. The rate of change of 2θ angle is notable in the range of HD content below 14.8 mol%, but neither 2θ angle nor the diffraction intensity changes with the HD content beyond 14.8 mol%. These observations suggest that the change of the crystalline structure of poly(ethylene-*co*-HD) to pseudohexagonal structure ultimately ceased at the HD content of 14.8 mol%.

With regard to poly(ethylene-*co*-CPE), the diffraction intensity of the orthorhombic (110) plane and (200) plane equally decreased with increasing CPE content without changing 2θ angle. When the CPE content of the ethylene copolymer reached 12.9 mol%, no diffraction peak due to crystallinity was observed. The copolymer film was transparent and amorphous. These results suggest that 1,2-cyclopentane structure is not taken in the planar zigzag polyethylene chain.

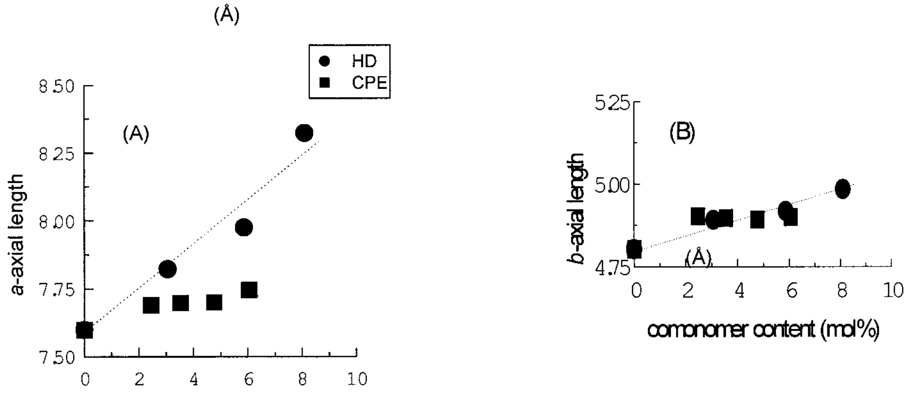


Figure 5. Relationship between comonomer content and unit-cell parameter of poly(ethylene-*co*-HD)(●) and poly(ethylene-*co*-CPE)(■).

In Figure 5, the unit-cell parameters, *i.e.*, *a*-axial length and *b*-axial length, which are determined by WAXD measurement, are correlated with the copolymer compositions. With poly(ethylene-*co*-CPE), both lengths were almost unchanged by the change of copolymer composition. On the other hand, with poly(ethylene-*co*-HD), the *a*-axial length only increased with increasing HD content. These results suggest that the 1,3-cyclopentane structure can be accommodated in the crystalline structure of polyethylene by extending the *a*-axis. After extention of the unit cell toward *a*-axis, the relationship $a = b\sqrt{3}$ nearly holds[9]. This relationship suggests that the crystalline structure of poly(ethylene-*co*-HD) becomes similar to pseudohexagonal structure with increasing HD content[10].

In Figure 6, the crystallinity of poly(ethylene-*co*-HD or CPE), which was calculated from the WAXD profile, is correlated with the comonomer content. The crystallinity of copolymer was found to decrease with increasing content of comonomers. The extent of decreased crystallinity due to copolymerization was more significant in poly(ethylene-*co*-CPE) than in poly(ethylene-*co*-HD) for copolymers containing similar amount of HD or CPE. These results suggest that 1,3-cyclopentane units due to HD insertion are incorporated in the crystalline structure of polyethylene.

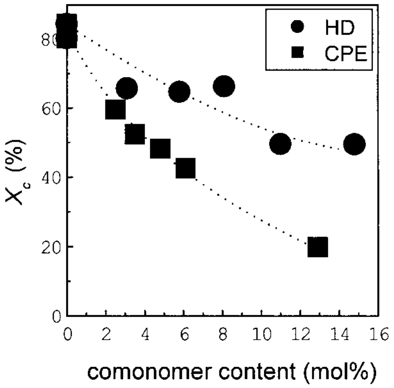


Figure 6. Relationship between crystallinity and comonomer content of poly(ethylene-*co*-HD) and poly(ethylene-*co*-CPE).

FT-IR Analysis of Crystalline Structure of Poly(ethylene-co-HD) and Poly(ethylene-co-CPE)

It has been reported on IR spectra of polyethylene that the doublet absorption due to methylene rocking mode appearing at around 725 cm^{-1} and the absorption due to methylene deformation mode appearing at around 1460cm^{-1} change significantly upon changing crystalline structure[11]. With regard to the doublet absorption in the 725cm^{-1} region, the absorption at 720 cm^{-1} involves contribution from either crystalline or amorphous region, but the absorption at 730 cm^{-1} is solely due to crystalline part[11, 12]. These phenomena, however, occur only with orthorhombic crystal of polyethylene, in the unit cell of which two polymer chains are involved. The absorption splittings do not occur with monoclinic or hexagonal crystal or amorphous polyethylene.

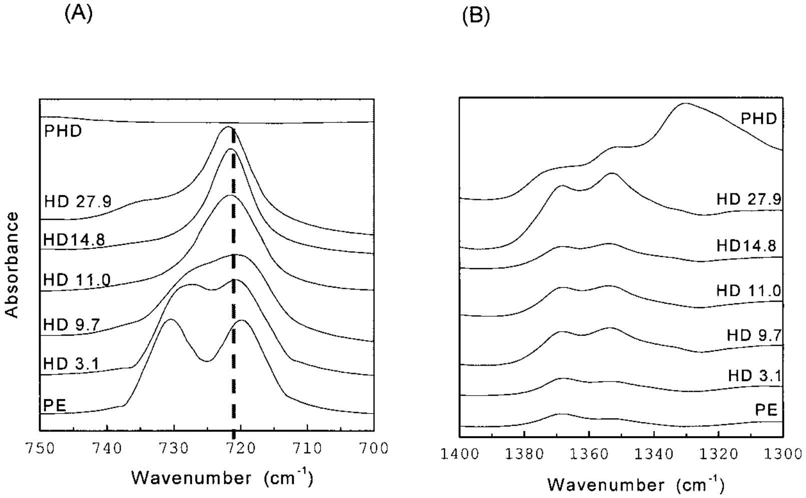


Figure 7. IR spectra of unoriented poly(ethylene-*co*-HD) with 0, 3.1, 9.7, 11.0, 14.8, 27.9, 100 mol% of HD content. (A) 700—750 cm^{-1} region and (B) 1300—1400 cm^{-1} region.

In FT-IR spectrum of polyethylene, methylene rocking absorptions appear at 720cm^{-1} and 730cm^{-1}, which are the results of splitting due to interactions of polyethylene chains in the unit cell. With increasing content of HD, the splitting width decreases to merge into a broad absorption at around 720cm^{-1}. These behaviors are similar to those observed on the transformation from orthorhombic to hexagonal crystal of polyethylene under stretching[13].

In 1350cm^{-1}–1370cm^{-1} region, absorptions appear, which are due neither to polyethylene nor to polyhexadiene. These absorptions are ascribed to polyethylene chain having *gauche* conformation[14]. It is considered that taking 1,3-cyclopentane structure in the crystalline region consisting of all-*trans* zigzag chain of polyethylene disturbs the crystalline structure to generate *gauche* conformation.

IR absorptions in 1470cm^{-1}–1480cm^{-1} region could not be discussed in detail because of overlapping of PHD absorptions.

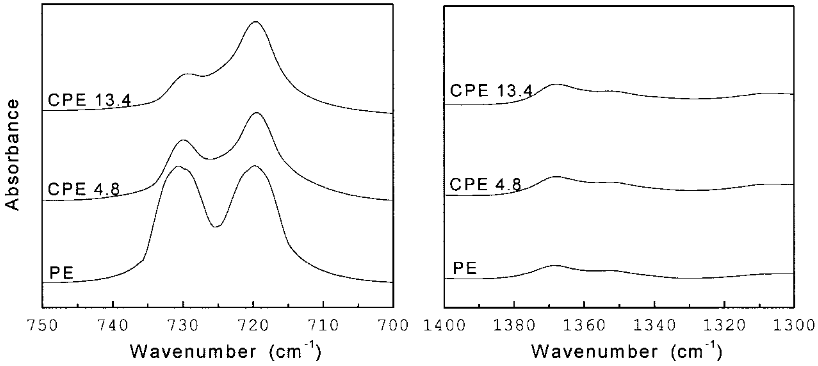


Figure 8. IR spectra of unoriented poly(ethylene-*co*-CPE) with 0, 4.8, 13.4 mol% of CPE content. (A) 700—750 cm^{-1} region and (B) 1300—1400 cm^{-1} region.

In FT-IR spectra of poly(ethylene-*co*-CPE), the absorption peak at 730cm^{-1} decreased its intensity with increasing content of CPE, keeping the absorption wavelength unchanged. In the 1300–1400cm^{-1} region, no absorption due to *gauche* polyethylene was observed. These phenomena are in sharp contrast to those in poly(ethylene-*co*-HD). It is therefore concluded with poly(ethylene-*co*-CPE) that the 1,2-cyclopentane units cannot be taken in the crystalline structure of polyethylene.

Copolymerization of Propylene and HD or CPE

Copolymerization of propylene with HD or CPE was carried out with isospecific zirconocene catalyst **3** using MAO as a cocatalyst at 40°C. The results are summarized in Tables 3 and 4, respectively.

Table 3. Structure and properties of poly(propylene-*co*-HD).

Run No.	Cat.	HD [a] (mol%)	*cis* [a] (%)	*trans* [a] (%)	M_n [b] ($\times 10^{-4}$)	M_w/M_n [b]	T_m [c] (°C)	X_c [d] (%)
29	**3**	0	-	-	6.74	1.68	147.7	69.1
30	**3**	2.5	n.d	n.d	4.81	1.73	134.3	59.0
31	**3**	3.0	n.d	n.d	5.54	1.71	127.7	54.1
32	**3**	3.5	28.8	71.2	6.10	1.88	115.3	41.1
33	**3**	6.1	29.7	70.3	9.77	2.06	98.1	35.1

[a] Determined by ^{13}C-NMR [b] Measured by GPC [c] Measured by DSC [d] Determined by WAXD.

Table 4. Structure and properties of poly(propylene-*co*-CPE).

Sample No.	Cat.	CPE [a] (mol%)	M_n [b] ($\times 10^{-4}$)	M_w/M_n [b]	T_m [c] (°C)	X_c [d] (%)
34	**3**	1.7	3.0	1.84	132.1	58.8
35	**3**	2.3	2.7	1.89	123.2	54.2
36	**3**	4.3	1.8	2.07	108.1	45.3
37	**3**	6.1	0.84	2.04	89.6	34.1

[a] Determined by ^{13}C-NMR [b] Measured by GPC [c] Measured by DSC [d] Determined by WAXD.

^{13}C NMR spectrum of poly(propylene-*co*-HD) showed that the 1,3-cyclopentane units in the copolymer take either *cis*- or *trans*-structure. For the *cis*-1,3-cyclopentane units, the stereochemistry of cyclopentane-propylene diad sequence was *cis-meso* form exclusively. On the other hand, for the *trans*-1,3-cyclopentane units, the diad sequence was either *trans-meso* or *trans-rac*.

With poly(propylene-*co*-CPE) obtained with the catalyst **3**, ^{13}C NMR spectroscopy showed that only 1,2-insertion occurred.

Thermal Properties of Poly(propylene-co-HD or CPE)

The relationship between T_m and composition of propylene copolymer is shown in Figure 9.

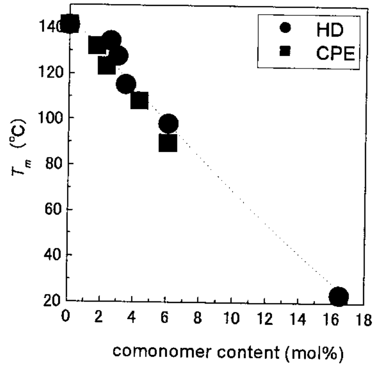


Figure 9. Relationship between comonomer content and melting temperature of poly(propylene-*co*-HD or CPE).

It is found in Figure 9 that T_m of the copolymer decreases with increasing content of HD or CPE, as was found with the ethylene copolymers (Figure 3). However, the extent of T_m decrease is the same for two kinds of propylene copolymers. This result is in contrast to the ethylene copolymers, in which CPE incorporation was more effective to decrease T_m of polyethylene (Figure 3). These results show that copolymerization of HD or CPE equally affects the crystalline structure of isotactic polypropylene.

WAXD Analysis of Crystalline Structure of Poly(propylene-co-HD or CPE)

WAXD profiles of poly(propylene-*co*-HD) and poly(propylene-*co*-CPE) are shown in Figures 10 and 11, respectively.

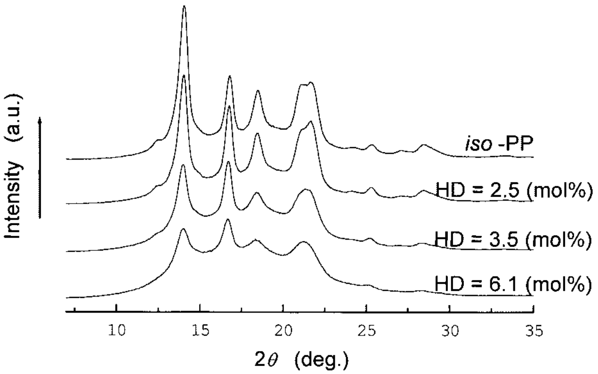


Figure 10. WAXD profiles of poly(propylene-*co*-HD).

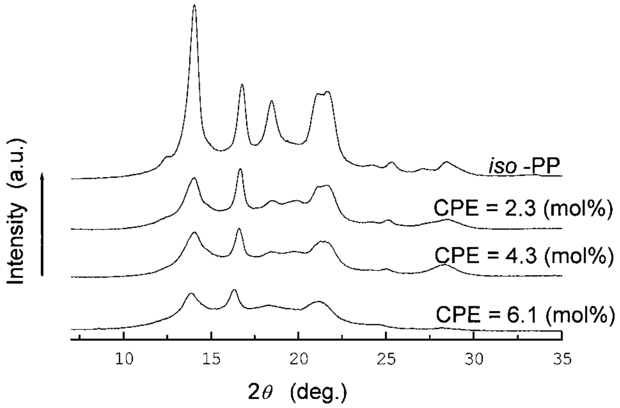


Figure 11. WAXD profiles of poly(propylene-*co*-CPE).

With poly(propylene-*c*o-HD), diffraction peaks characteristic of α-type crystal are seen[15, 16]. With increasing content of HD, the intensity of diffraction peaks decreased without changing 2θ angles.

With poly(propylene-*co*-CPE), α-type crystal is dominating with weak diffraction of (117) plane of γ-type crystal[15]. The presence of γ-type crystal should be due to low molecular weight fractions of poly(propylene-*co*-CPE). With increasing content of CPE, the intensity of diffraction peak decreased without changing 2θ angles.

The crystal lattice constants of the propylene copolymers are related with copolymer compositions in Figure 12.

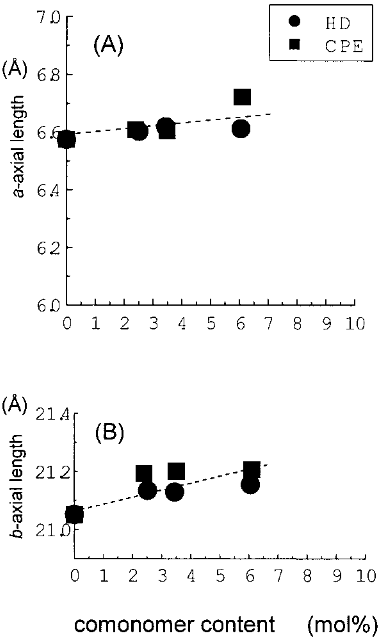


Figure 12. Relationship between unitcell parameter and comonomer content of poly(propylene-*co*-HD) and poly(propylene-*co*-CPE).

For either HD or CPE as a comonomer of propylene, the lattice constants such as *a*-axial length and *b*-axial length were almost unchanged with increasing content of comonomer, indicating that the crystalline structure of polypropylene (3_1-helix) does not change by copolymerization. These results show that 1,3-cyclopentane structure originating from either HD or CPE copolymerization is not taken in the 3_1-helical structure of polypropylene and therefore does not form isomorphism. The crystallinity of the propylene copolymers, which was determined from WAXD profile, is correlated with the copolymer composition in Figure 13.

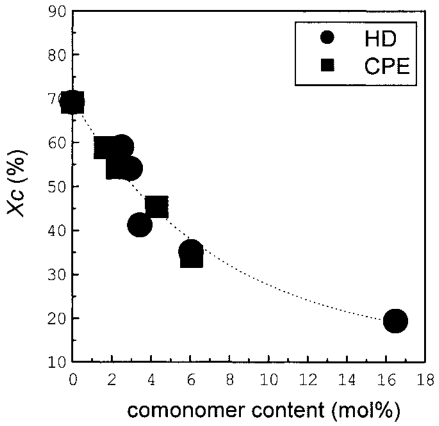


Figure 13. Relationship between comonomer content and crystallinity of poly(propylene-*co*-HD or CPE).

For both kinds of copolymers, the crystallinity decreased with increasing content of comonomers. The extent of crystallinity decrease was not influenced by the nature of comonomer. These comonomers do not seem to be taken in 3_1-helix of polypropylene, thus decreasing the crystallinity of isotactic polypropylene.

Conclusion

1,3-Cyclopentane structure of poly(ethylene-*co*-HD), which was formed by cyclization-addition polymerization of HD, is taken in the crystalline structure of polyethylene by partially changing the *trans* zigzag chain into *gauche* conformation, thereby inducing a transformation of orthorhombic crystal to pseudohexagonal crystal. This is a scarce example of polyolefin isomorphism.

1,2-Cyclopentane structure of poly(ethylene-*co*-CPE) is not taken in the crystalline structure of polyethylene. Therefore, CPE decreases the crystallinity and T_m of polyethylene more strongly than HD.

Neither 1,3-cyclopentane structure of poly(propylene-*co*-HD) nor 1,2-cyclopentane structure of poly(propylene-*co*-CPE) was taken in 3_1-helix of isotactic polypropylene. Without the formation of isomorphism, the extent of the decrease of crystallinity and T_m was independent of the nature of comonomers.

Acknowledgement: The present authors are very grateful to Professor Kohji Tashiro of Osaka University for discussions on FT-IR investigation on the crystallinity of poly(ethylene-*co*-HD).

[1] L. Resconi, R. M. Waymouth, *J. Am. Chem. Soc.* **1990**, *112* 4953.
[2]W. Kaminisky, R. Spiehl, *Macromol. Chem.*, **1989**, *190*, 515.
[3][3a]Ch. Bergemann, R. Corpp, G. Luft, *J. Mol. Catl. A: Chem.*, **1997**, *116*, 317;
[3b] F. G. Sernetz, R. Mülhaupt, R. M. Waymouth, *Polym. Bull. (Berlin)*, **1997**, *38*, 141;
[3c]P. Pietikäinen, T. Vänänäne, J. V. Seppälä, *Eur. Polym. J.*, **1999**, *35*, 1047.
[4] A. Jerscow, E. Ernst, W. Hermann, N. Müller, *Macromolecules*, **1995**, *28*, 7095.
[5] M. Galimberti, E. Albizzati, L. Abis, G. Bacchilega, *Makromol.Chem.*, **1991**, *192*, 2591.
[6] S. Krimm, A. V. Tobolsky, *J. Polym. Sci.*, **1951**, *7*, 57.
[7] B.Wunderlich, T. Arakawa, *J. Polym Sci. Part A*, **1964**, *2*, 3697.
[8] M. Takahashi, K. Tashiro, S. Amiya, *Macromolecules*, **1999**, *32*, 5860.
[9] I. W. Bassi, P. Corradini, A. Fagherazzi, *Eur. Polym. J.*, **1970**, *6*, 709.
[10]H. Uehara, T. Kamamoto, A. Kawaguchi, S. Murakami, *Macromolecules*, **1996**, *29*, 1540.
[11] R. S. Stein, G. B. B. M. Sutherland, *J. Chem. Phys.*, **1954**, *22*, 1993.
[12] A. Keller, I. Sandeman, *J. Polym. Sci.*, **1955**, *15*, 133.
[13] K. Tashiro, S. Sasaki, M. Kobayashi, *Macromolecules*, **1996**, *29*, 7460.
[14] S. Krimm, C. Y. Liang, G. B. B. M. Sutherland, *J. Chem. Phys.*, **1956**, *25*, 549.
[15] G. Natta, P. Corradini, *Nuovo Cimento, XV*, **1960**, 40.
[16] A. Turner-ones, J. M. Aizlewood, D.B. Beckett, *Maktomol. Chem.*, **1964**, *75*, 134.