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Crystalline Structure of Polyethylene Containing 1,2- or 1,3-Disubstituted Cyclopentane Units in the Main Chain

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ABSTRACT: Polyethylene having 1,2- or 1,3-disubstituted cyclopentane structures was prepared by copolymerization of ethylene and cyclopentene (CPE) or 1,5-hexadiene (HD), and the crystalline structure was studied. Treatment with fuming nitric acid preferentially degraded the amorphous phase of the copolymers, and the structure of degraded samples indicated that 1,3-disubstituted cyclopentane units were taken in the crystalline phase of poly(ethylene-*co*-HD). Infrared spectra of the copolymers indicated the increase of hexagonal-phase character in poly(ethylene-*co*-HD) with increasing content of 1,3-disubstituted cyclopentane units. Wide-angle X-ray diffraction patterns of poly(ethylene-*co*-HD) showed a continuous transition from the orthorhombic phase to the hexagonal phase in the copolymer with HD content less than 15 mol %. On the other hand, 1,2-disubstituted cyclopentane structures were not taken in the crystalline phase, but in the amorphous phase.

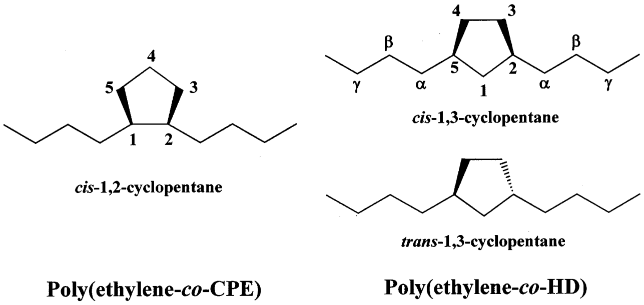
Introduction

Isomorphism of random copolymers is a unique phenomenon occurring in copolymers consisting of a certain pair of comonomers. Two different types of copolymer isomorphism can be defined. One of them is that the homopolymers of each component comonomer have a similar crystalline structure (type I). The other is that the two homopolymers have different crystalline structures, and each of them can accommodate a certain amount of the counterpart monomeric units (type II).[1]

Since the discovery of isomorphism in isotactic styrene-based copolymers by Natta,[2] the isomorphism has been found in olefin copolymers, such as copolymers of ethylene,[3] propylene,[4] 1-butene,[4b,5] and 4-methyl-1-pentene.[4c,6] Recent development in transition metal catalysts, such as metallocene catalysts, enables us to synthesize new olefin isomorphous copolymers. Highly syndiotactic poly(propylene-*co*-1-butene) was prepared by a C_s symmetrical zirconocene catalyst, and the crystalline structure of the copolymer was found to be isomorphous. Both syndiotactic polypropylene and poly(1-butene) form $(TTGG)_2$ conformation, and the copolymer formed the isomorphous phase of type I. Recently, we reported that, in the copolymerization of ethylene with cyclopentene (CPE)[7] or 1,5-hexadiene (HD)[8] using bridged zirconocene catalysts, the synthesized polyethylene contained cis-1,2- or cis,trans-1,3-disubstituted cyclopentane units in the main chain (Scheme 1), respectively. In the course of the investigation, we observed the isomorphous features of polyethylene having 1,3-disubstituted cyclopentane units in the main chain of poly(ethylene-*co*-HD).[9] The copolymer would be an isomorphous copolymer of type II.

In this study, we investigated in detail the crystalline structure of the polyethylenes with 1,2- and 1,3-disubstituted cyclopentane units by the oxidation degradation method, Fourier transform infrared(FT-IR) measurements, and wide-angle X-ray diffraction (WAXD).

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



Results and Discussion

The polyethylene samples subjected to the present investigation were prepared by using bridged zirconocene catalysts, dimethylsilylenebis(indenyl)zirconium dichloride (**1**) and diphenylmethylene(cyclopentadienyl)(9-fuluorenyl)zirconium dichloride (**2**). These catalysts were effective to take CPE and HD in the copolymer with ethylene and produced copolymers with narrow molecular-weight and composition distributions. The structure and properties of the ethylene copolymers are summarized in Table 1.

Treatment of Poly(ethylene-*co*-CPE) and Poly(ethylene-*co*-HD) with FNA. As described above, we observed the isomorphous features of polyethylene having 1,3-disubstituted cyclopentane units in the main chain, poly(ethylene-*co*-HD).[9] We tried to elucidate the incorporation of 1,3-disubstituted cyclopentane units in the crystalline phase by treatment of fuming nitric acid (FNA).[10] The copolymers including a small amount of cyclopentane units, poly(ethylene-*co*-CPE) (samples 3

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Table 1. Samples of Polyethylene Containing Cyclopentane Units in the Main Chain

			cis-CP[a]					
sample	catalyst	comonomer	mol %	%	$M_n{}^b \times 10^{-4}$	$M_w/M_n{}^b$	T_m,[c] °C	X_c,[d] %
1	**1**		0		10.6	3.6	129.8	80.3
2	**2**		0		20.9	2.1	131.8	85.5
3	**2**	CPE	2.5	100	4.8	2.0	106.9	59.6
4	**1**	CPE	3.5	100	13.2	2.6	102.8	52.4
5	**1**	CPE	4.8	100	7.2	2.3	96.0	48.3
6	**2**	CPE	6.1	100	7.3	1.9	90.6	42.6
7	**1**	CPE	13.4	100	6.5	1.8	71.0	
8	**1**	HD	3.1	19.2	9.3	2.5	114.3	65.7
9	**1**	HD	5.8	28.7	9.9	2.6	102.8, 113.0	64.7
10	**2**	HD	8.1	31.0	12.4	2.9	100.9	66.3
11	**1**	HD	9.7	25.0	3.5	3.2	84.5, 115.1	
12	**1**	HD	11.0	24.2	7.4	3.4	91.7	49.6
13	**2**	HD	14.8	29.6	9.1	2.7	89.6	
14	**1**	HD	17.5	21.7	4.8	2.2	71.8	
15	**1**	HD	20.3	28.6	4.8	2.3	66.6	
16	**1**	HD	21.8	26.6	4.8	2.3	70.1	
17	**1**	HD	24.5	31.9	2.5	2.1	61.5	
18	**1**	HD	27.9	24.8	2.7	2.3	55.0	
19	**1**	HD	100	28.2				
20	**2**	HD	100	19.2			79.7	

[a] Content of *cis*-cyclopentane units determined by ^{13}C NMR spectroscopy. [b] Number-average molecular weight and poly dispersity index determined by GPC using polystyrene standard. [c] Melting temperature determined by DSC. [d] Crystallinity calculated from WAXD pattern.

Table 2. Results of FNA Treatment of Poly(ethylene-*co*-CPE) and Poly(ethylene-*co*-HD)

	before FNA treatment					after FNA treatment			
sample	comonomer	mol %	cis-1,3-CP,[a] %	trans-1,3-CP,[a] %	X_c,[b] %	residual amount, wt %	comonomer content, mol %	cis-1,3-CP,[a] %	trans-1,3-CP,[a] %
3	CPE	2.5	100	0	59.6	8.1	0		
4	CPE	3.5	100	0	52.4	6.5	0		
8	HD	3.1	19.2	80.8	65.7	16.9	1.2	42.4	57.6
9	HD	5.8	28.7	71.3	64.7	16.0	1.3	36.0	64.0

[a] Content of cis- and trans-1,3-disubstituted cyclopentane units determined by ^{13}C NMR spectroscopy. [b] Crystallinity calculated from WAXD pattern.

and 4) and poly(ethylene-*co*-HD) (samples 8 and 9), were treated with FNA at 50 °C for 160 h to remove the amorphous phase, and the structure of the residual crystal part was studied by ^{13}C NMR spectroscopy. The composition and structure of the copolymers before and after the FNA treatment are summarized in Table 2. A large proportion of copolymers were removed by the FNA treatment. It is seen that not only the amorphous phase but also the crystalline phase of the copolymers was removed by the FNA treatment. However, the lower the crystallinity of the original copolymers, the lower the residual amount of copolymers after the FNA treatment. The residual amount of poly(ethylene-*co*-HD) after the FNA treatment was larger than that of poly(ethylene-*co*-CPE). These results indicate that poly(ethylene-*co*-HD) possesses better stability against the oxidative degradation with FNA than poly(ethylene-*co*-CPE). Figure 1 shows the WAXD patterns of poly(ethylene-*co*-HD) (sample 9) before and after the FNA treatment. The broad diffraction peak due to the amorphous phase in the range of $2\theta = 15°-23°$ almost completely disappeared, and sharp diffraction peaks due to (110) and (200) crystal planes of polyethylene are observed at $2\theta = 21°$ and 23.5°, respectively. These results indicate that the amorphous region of the copolymer was preferentially removed by the FNA treatment.

The structure of the copolymer samples before and after the FNA treatment was studied by ^{13}C NMR. Figures 2 and 3 show the ^{13}C NMR spectra of poly(ethylene-*co*-CPE) and poly(ethylene-*co*-HD), respectively. For the signal assignment, refer to Scheme 1. In the case of poly(ethylene-*co*-CPE), signals due to 1,2-disubstituted cyclopentane units disappeared completely in the spectrum of FNA-treated sample. This result indicates that the 1,2-disubstituted cyclopentane units are not included in the crystalline phase of the copolymer and completely degraded by FNA. On the other hand, in the case of poly(ethylene-*co*-HD) with a small amount of HD, 22−33% of 1,3-disubstituted cyclopentane units remained in the sample after the FNA treatment.[11] The cis/trans ratios of the 1,3-disubstituted cyclopentane units of the FNA-treated samples are higher than these of the original samples. These results indicate that 1,3-disubstituted cyclopentane

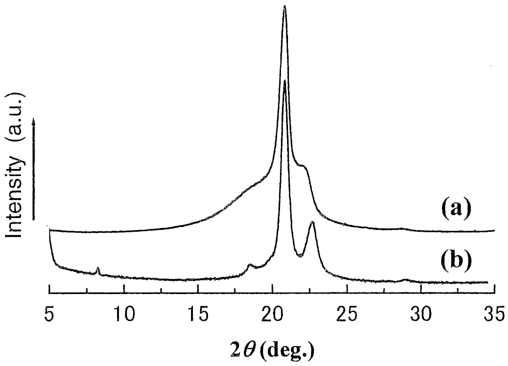

Figure 1. WAXD patterns of poly(ethylene-*co*-HD) (sample 9): (a) before and (b) after FNA treatment. A weak reflection at $2\theta = 18°$ in WAXD pattern (b) would be derived from impurities mingled during FNA treatment.

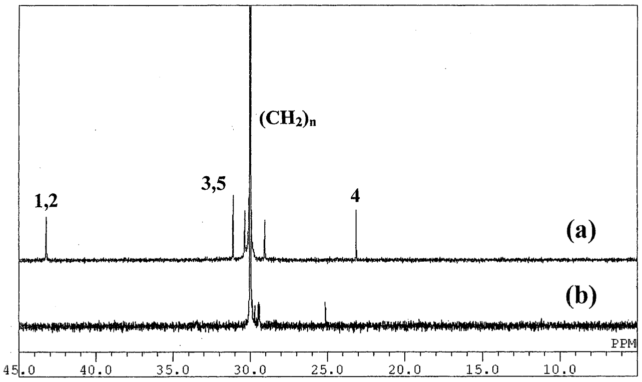

Figure 2. ^{13}C NMR spectra of poly(ethylene-*co*-CPE) (sample 3): (a) before and (b) after FNA treatment.

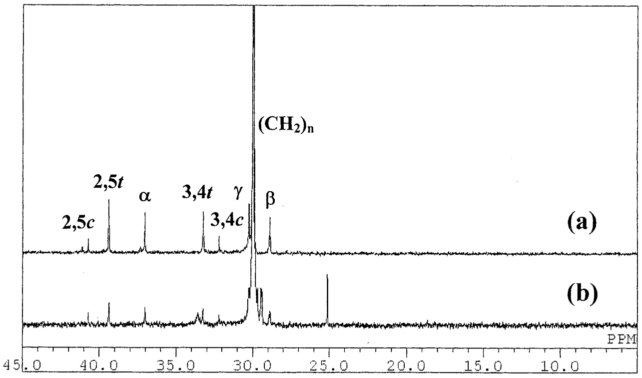

Figure 3. ^{13}C NMR spectra of poly(ethylene-*co*-HD) (sample 9): (a) before and (b) after FNA treatment; c = cis, t = trans.

units, especially cis-units, are taken in the crystalline phase of the poly(ethylene-*co*-HD).

FT-IR Measurement of Poly(ethylene-*co*-CPE) and Poly(ethylene-*co*-HD). FT-IR measurement of polyethylene gives us useful information about the structural transformation from orthorhombic to - pseudohexagonal cell. Figures 4 and 5 show the FT-IR spectra in the frequency region of the methylene rocking vibration (710−740 cm^{-1}) and the methylene wagging vibration (1320−1390 cm^{-1}) of poly(ethylene-*co*-CPE) and poly(ethylene-*co*-HD), respectively.[12] In the case of poly(ethylene-*co*-CPE), the absorption bands (719 and 730 cm^{-1}) of the methylene rocking vibration due to orthorhombic cell did not change, and the absorption intensity at 730 cm^{-1} due to crystalline phase decreased with increasing CPE content. On the other hand, in the poly(ethylene-*co*-HD), the absorption intensity of methylene rocking vibration at 719 and 730 cm^{-1} decreased with increasing HD content, and new absorption due to the pseudohexagonal cell appeared at 723 cm^{-1}. The absorption due to wagging vibration at 1352 and 1366 cm^{-1} can be assigned to a double gauche conformation (TTGGTT) and kink structure (TTGTTT), respectively, due to the conformationally disordered hexagonal-type structure of polyethylene. The intensity of these absorptions is independent of CPE content in the poly(ethylene-*co*-CPE). However, it increased remarkably with increasing HD content in the poly(ethylene-*co*-HD). These results indicate that 1,3-cyclopentane units in poly(ethylene-*co*-HD) generates gauche conformation (G) in the main chain of the copolymer. In other words, the polymer chains are conformationally disordered in the crystal lattice of poly(ethylene-*co*-HD)s.

WAXD Patterns of Poly(ethylene-*co*-HD). In our previous report,[9] we studied the crystalline structure of polyethylene containing cyclopentane units less than 15 mol % by WAXD. 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. On the other hand, in the case of poly(ethylene-*co*-HD), the intensity of reflection peak due to the (200) plane remarkably decreased with increasing HD content, and 2θ values of both reflections shifted to lower angles, indicating a continuous transition of the orthorhombic cell to the hexagonal cell. In the present investigation, we synthesized poly(ethylene-*co*-HD) with higher HD content by using bridged zirconocene catalysts and investigated the crystalline structure of the copolymer. The WAXD patterns and crystalline structure of poly(ethylene-*co*-HD)s are summarized in Figure 6 and Table 3. A reflection was observed at $2\theta = 19−20°$ in the copolymers with HD content higher than 15 mol %. This reflection should be due to the (100) plane of hexagonal cell, indicating that transition from the orthorhombic cell to the hexagonal cell completes in the copolymer containing HD more than 15 mol %. The Bragg distance of (100) reflections (d_{100}) and interchain distance (a) slightly increased with increasing HD content in the copolymer. The result indicates that HD can be incorporated in the crystalline phase of the hexagonal-type chain packing mode under expansion of the unit cell. The coherent length of the crystallites in a direction perpendicular to the chain axis (D) is also summarized in Table 3. The D values of the copolymers ranged from about 110 to 130 Å, and any clear relation was not observed between X_c and D of the copolymers.

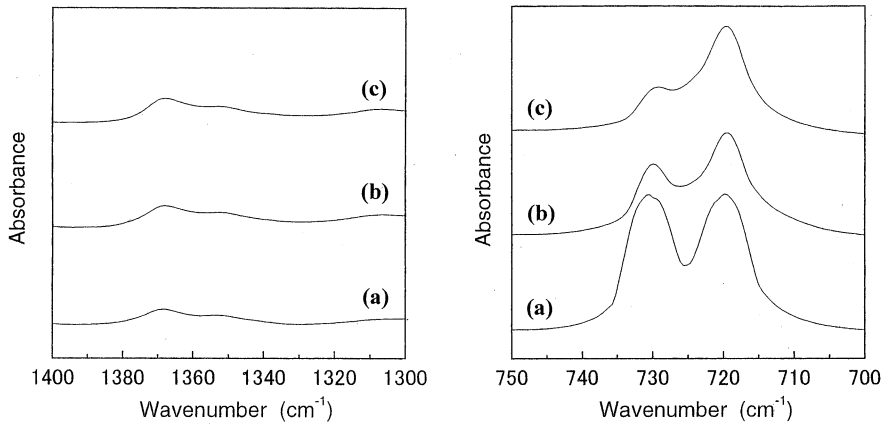

Figure 4. FT-IR spectra of poly(ethylene-*co*-CPE): (a) CPE, 0 mol %; (b) CPE, 4.8 mol %; (c) CPE, 13.4 mol %.

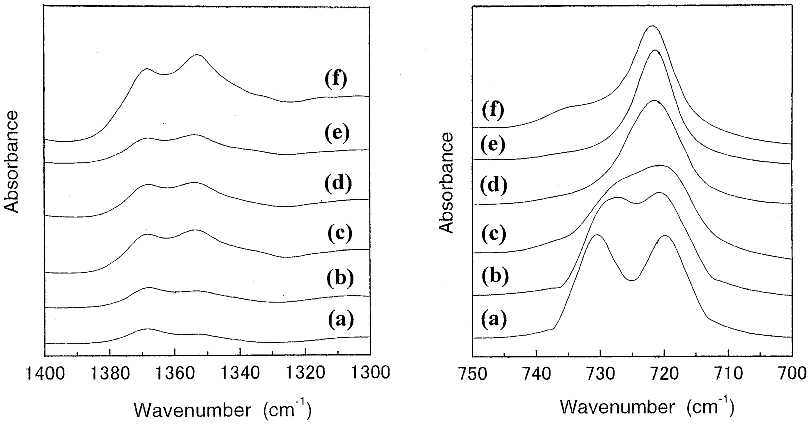

Figure 5. FT-IR spectra of poly(ethylene-*co*-HD): (a) HD, 0 mol %; (b) HD, 3.1 mol %; (c) HD, 9.7 mol %; (d) HD, 11.0 mol %; (e) HD, 14.8 mol %; (f) HD, 27.9 mol %.

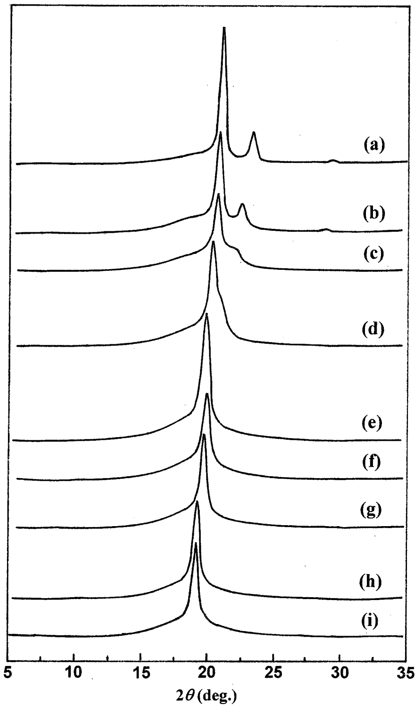

Figure 6. WAXD patterns of poly(ethylene-*co*-HD): (a) HD, 0 mol %; (b) HD, 3.1 mol %; (c) HD, 5.8 mol %; (d) HD, 8.1 mol %; (e) HD, 14.8 mol %; (f) HD, 17.5 mol %; (g) HD, 20.8 mol %; (h) HD, 24.5 mol %; (i) HD, 27.9 mol %.

Table 3. Crystalline Structure of Poly(ethylene-*co*-HD) Containing Higher Content of HD and Poly(methylene-1,3-cyclopentane)

sample	HD, mol %	d_{100},[a] Å	a,[b] Å	X_c,[c] %	D,[d] Å
13	14.8	4.44	5.13	42.1	107
14	17.5	4.46	5.15	35.5	110
15	20.3	4.53	5.23	34.2	118
17	24.5	4.62	5.33	31.6	129
18	27.9	4.64	5.36	30.5	115
19	100	4.84	5.59	33.3	73
20	100	4.87	5.62	40.0	173

[a] Bragg distance of (100) reflections. [b] Interchain distance. [c] Crystallinity calculated from the WAXD pattern. [d] Coherent length of the crystallites in the (100) direction.

An X-ray fiber diagram of oriented poly(ethylene-*co*-HD) (sample 16) was acquired.[13] No reflection peak due to orthorhombic crystalline phase was detected. A sharp reflection at $2\theta = 18.8°$ due to (100) planes and a weak reflection at $2\theta = 33.4°$ were observed. The lattice spacing of the each reflection is estimated as 4.7 and 2.7 Å, respectively. They are in the ratio of $\sqrt{3}$:1, indicating that the latter reflection is due to (110) planes of the hexagonal structure.

Auriemma and co-workers investigated the crystalline structure of poly(methylene-1,3-cyclopentane), a homopolymer of HD synthesized by various zirconocene catalysts.[14] The WAXD pattern of poly(methylene-1,3-cyclopentane) showed reflections at 2θ about 18° and 32°, which are due to (100) and (110) planes of the hexagonal crystalline phase, respectively. From the coincidence of reflection angles, it seems that the hexagonal crystalline structure of poly(ethylene-*co*-HD) is similar to that of poly(methylene-1,3-cyclopentane), namely homopolymer of HD.

Conclusion

Crystalline structures of polyethylene containing 1,3-cyclopentane units, poly(ethylene-*co*-HD), were studied in comparison with the structures of polyethylene containing 1,2-cyclopentane structure, poly(ethylene-*co*-CPE), by the oxidation−degradation method, FT-IR spectroscopy, and WAXD. A certain amount of the 1,3-cyclopentane structure in the poly(ethylene-*co*-HD) was taken in the crystalline phase of the copolymer. The transition from the orthorhombic- to the hexagonal-type chain packing was observed in poly(ethylene-*co*-HD) by IR and WAXD. The gauche conformation of the main chain increased with increasing content of 1,3-cyclopentane units, which were taken in the crystalline phase accompanying expansion of the unit cell. The reflections due to (100) and (110) planes of pseudohexagonal lattice were observed in the X-ray fiber diagram of oriented poly(ethylene-*co*-HD) sample, allowing us to confirm the hexagonal packing structure.

Polyethylene with 1,3-cyclopentane units, poly(ethylene-*co*-HD), showed isomorphous behavior accompanying a transition of crystalline phase. A similar isomorphism has been reported for poly(ethylene-*co*-propylene).[15] The present copolymer is the first example of isomorphism of olefin copolymer containing a cyclic structure in the main chain.

Experimental Part

Materials. Copolymers were prepared by zirconocene catalysts (*rac*-dimethylsilylenebis(indenyl)zirconium dichloride, diphenylmethylene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride), using MAO as a cocatalyst (molar ratio of MAO-[Al]/[Zr] = 1000) according to the literature.[7,8] Copolymerizations were conducted in toluene at 40 °C under 1 atm of ethylene. The copolymers produced were extracted with boiling *o*-dichlorobenzene (ODCB) to remove catalyst residues and cross-linked fraction in the poly(ethylene-*co*-HD).[8]

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.[7,8] 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.

Treatment of polyethylene by FNA was conducted at 50 °C for 160 h. The treated samples were washed with boiling acetone and water to remove degraded fractions of the copolymer.

Samples for FT-IR spectroscopy were melted at 180 °C and gradually cooled to room temperature. Infrared spectra were measured using Horiba FT-730 IR spectrometer. The rapid scan mode was employed at 32 times scan with a spectral resolution of 1 cm^{-1}.

Samples of WAXD measurement were melted at 180 °C and pressed under 10 MPa pressure, followed by quenching in 30 °C water and kept for 1 h. WAXD patterns of the copolymers were acquired on a MAC Science M18XCE using Cu Kα radiation. The approximate evaluation of the crystallinity was obtained by resolving the WAXD patterns between 2θ values of 10° and 25° into a crystalline peak and an amorphous halo and by comparing the areas of the peak and halo.[14] The amorphous halo was taken from the WAXD patterns of the melt samples.[16] The coherent length of the crystallites in a direction perpendicular to the chain axis (D) was evaluated for the (100) reflection using the Scherrer equation:

$$D = K\gamma(\beta \cos \theta)$$

where β is the angular (2θ) width of the half-maximum intensity and K was taken to be 0.9. An oriented sample of poly(ethylene-*co*-HD) was obtained by 4-fold stretching in water bath at 40 °C. An X-ray fiber diagram of a copolymer was taken on a Rigaku R-AXIS using Cu Kα radiation.

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Supporting Information Available: X-ray fiber diagram and WAXD patterns of poly(ethylene-*co*-HD). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) The content of HD (cyclopentane) units in poly(ethylene-*co*-HD) was determined by ^{13}C NMR spectra using integrals ratio of secondary carbons signals using following equation: $[\text{HD}] = I_{\alpha}/(I_{\text{CH}_2} + I_{\alpha})$ where I_{α} and I_{CH_2} are integral of signals derived from α carbons at 37 ppm and methylene sequence of the main chain (CH_2, β, γ) at 29−30.5 ppm, as shown in Scheme 1 and Figure 1.

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(13) An X-ray fiber diagram of oriented poly(ethylene-*co*-HD) (sample 16) is available in the Supporting Information.

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(16) The WAXD pattern of amorphous halo of poly(ethylene-*co*-HD) was acquired at 149−151 °C on a RINT Ultima^{+}-DSC (Rigaku) using Cu Kα radiation. The WAXD patterns of crystalline and amorphous sample 10 are available in the Supporting Information.

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