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Degree of comonomer inclusion into lamella crystal for propylene/olefin copolymers

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Abstract

Copolymers of propylene with ethylene, butene-1, hexene-1, and octene-1 were synthesized with isospecific metallocene catalyst system. Crystalline structure of the melt-crystallized samples was investigated from the viewpoint of the comonomer location in a solid-state of the copolymers, using the fuming nitric acid (FNA) etching technique followed by ^{13}C NMR spectrum measurement. It was found that the copolymers were oxidatively degraded with FNA at 50 °C and the residue after etching was corresponding to the lamella crystal of the original state. ^{13}C NMR spectrum of the residue revealed that all kinds of comonomer used here were located not only in the amorphous phase but also in the crystalline core. Among comonomers, butene-1 is favorably incorporated in the crystalline phase with the expansion of the crystal lattice, and the amount of comonomer in the crystal is comparable with that in the amorphous phase. Ethylene, hexene-1 and octene-1 were also found to be included into the crystal, but the degree of inclusion in the crystal was much less than that of butene-1.

Considering both the continuous increase of the weight loss and the saturation of the molecular weight decrease of the residue during an etching time-course, a plausible mechanism for the FNA degradation of the propylene copolymers was proposed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Propylene–olefin copolymers; Crystalline structure; Comonomer inclusion

1. Introduction

It is needless to say that the structure–properties relationship of polyolefins is important to improve the product performances, and the authors found that the structural distribution on the crystalline level is the key factor governing the mechanical properties in case of linear low-density polyethylene (random copolymer of ethylene and α-olefin) [1–4]. On the other hand, random copolymers of propylene with ethylene and butene-1 have been commercially produced world widely and used mainly in the film applications, taking advantages of their good transparency, higher impact strength and lower heat-seal temperature compared with homopolypropylene. These advantages of propylene copolymers would be due to their unique crystalline structure, which is caused by molecular defects derived from comonomers in the polypropylene sequences. Thus it is significant to investigate the effect of comonomers on the crystalline structure. From this point of view, the location of the comonomer in the solid-state, which is still a subject of controversy for propylene copolymers, was focused here for the wide variety of copolymers.

As for the propylene/ethylene copolymer, there have been some precedent studies reported. Turner Jones [5], Busico et al. [6] and Avella et al. [7] found that γ-form crystal was formed in addition to α-form with increasing ethylene comonomer and they concluded that inclusion of ethylene units leads to less perfect crystal. Laihonen and Gedde [8] reported that the average length of 3/1 helices of the copolymer was shorter than that of homopolypropylene, and reached the conclusion that ethylene unit inclusion into the crystals occurs to some extent. On the contrary, Monasse and Haudin [9], Feng and Hay [10], and Pérez et al. [11] concluded that ethylene units are excluded from the crystal judging from the decrease of the crystallinity and of the melting temperature with increasing ethylene content. Zimmermann [12] also reached the same conclusion from the invariance of the heat of fusion reduced to 100% crystallinity with increasing ethylene content, and described the decrease of the crystallinity is due to the severe

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disturbance of helical regularity by the ethylene unit and not due to the inclusion of the ethylene unit into the crystal. As for the quantitative determination of the structural defects in polypropylene of solid-state, VanderHart et al. [13] developed the method using CP-MAS NMR spectroscopy and Alamo et al. [14] determined the concentration of ethylene units included into the crystal for propylene/ethylene copolymers by this method.

In the case of propylene/butene-1 copolymer, cocrystallization was found by Cimmino et al. [15] and Crispino et al. [16] to occur for all the comonomer compositions, which means a certain number of comonomers can be incorporated in the crystal lattice. The same conclusion was reported by Abiru et al. [17] for isotactic copolymer and Naga et al. [18] for syndiotactic copolymer from thermal analyses and the crystal lattice expansion measured by the wide angle X-ray diffraction (WAXD).

Recently various kinds of propylene copolymer with higher α-olefin (HAO) such as hexene-1, octene-1, have been increasingly reported [19–26] since new metallocene catalysts have been developed recently with which the copolymerization of propylene with HAO can proceed. But the papers on the crystalline structural investigation of the HAO copolymers are very few compared to those on the polymerization itself. Alamo et al. [25] found by analysis of CP-MAS NMR that hexene-1 and octene-1 units are rejected from the crystal. Lovisi et al. [26] reported that longer alkyl branch of HAO gives copolymers higher flexibility, that is, the lower storage modulus, the lower glass transition temperature and the increase of tan δ.

In many papers published so far, the subject on the comonomer inclusion into the crystal of the propylene/olefin copolymers has been discussed qualitatively, and the quantitative determination is a few case. Solid-state NMR spectroscopy is one of the possible methods to have a quantitative discussion on this matter [13,14], but its substantial limitation has been indicated because of the small differences in both the chemical shift and the relaxation time between the comonomer in the crystalline phase and that in the amorphous phase as suggested for ethylene/α-olefin copolymers [27,28].

On the other hand, degradation of polyethylene by fuming nitric acid (FNA) is a well known technique to remove the amorphous phase selectively [29–35] and we successfully measured the degree of comonomer inclusion into the crystalline phase of various kinds of ethylene/α-olefin copolymers by using FNA etching technique followed by high resolution ^{13}C NMR measurements in solution [36]. Compared to a great deal of works on FNA etching of polyethylene, papers of polypropylene are very few. Hock [37] investigated the structure of isothermally crystallized isotactic homopolypropylene treated by boiling 70% nitric acid (120 °C). It was reported the amorphous part was removed and the molecular weight after the treatment was that corresponding to the lamella crystal thickness, which varied according to the isothermal crystallization temperature. Proton spin–spin and spin–lattice relaxation times of the FNA etched isotactic polypropylene were measured by Tanaka [38], and the melting phenomena of the FNA etched syndiotactic polypropylene was reported by Uehara et al. [39].

Then in this paper, we tried to determine the degree of comonomer inclusion in the perfect crystalline phase for copolymers of propylene with various kinds of olefin comonomers with this conventional straightforward method followed by the solution ^{13}C NMR measurement.

2. Experimental

2.1. Materials

The copolymer samples of propylene with various kinds of olefin were synthesized in our laboratory with isospecific metallocene catalyst system; dimethylsilyl bis(2-methyl-4-naphtylindenyl) zirconium dichloride and methyl aluminoxane in toluene solvent at 40 °C (Table 1). Propylene homopolymer was also prepared with the same metallocene catalyst system (P-1 in Table 1) and with a conventional Ziegler–Natta catalyst system (P-2 in Table 1) at the same condition as that of copolymers. Polymer flake obtained was kneaded with some antioxidants at 190 °C using counter-rotating mixing roll.

2.2. Characterization

The molecular weight and molecular weight distribution of the original samples and of the FNA-treated samples were measured in *ortho*-dichlorobenzene at 145 °C using Waters 150C GPC equipped with a refractometer. The melting and crystallization curves of the as polymerized samples were measured with a Perkin–Elmer DSC-7 differential calorimeter. Polymer sample was heated to 220 °C, maintained for 5 min, cooled at 5 °C/min to 50 °C to obtain an exothermic curve, and endothermic curve was recorded by heating from 50 to 180 °C at 5 °C/min. T_m and ΔH_m were calibrated with indium standard (156.6 °C and 28.4 J/g, respectively). WAXD was measured with a Rigaku RU-200B X-ray diffractometer to obtain the X-ray crystallinity of the sample (X_c) and some crystal lattice dimensions. Small angle X-ray scattering (SAXS) was also measured to determine the long period (L). The thickness of the lamella crystal (l_c) was calculated from the following relationship by assuming that the X-ray crystallinity is proportional to the total number of electrons in the crystalline region or (surface area) × (crystal thickness) × (density) for a two phase model of the solid-state of polypropylene

$$l_c = 0.85X_cL/(0.936 - 0.086X_c) \tag{1}$$

where the densities of crystalline and amorphous phases of polypropylene were taken to be 0.936 and 0.850 g/cm^3, respectively [40,41].

Table 1
Samples of propylene homopolymer and propylene/olefin copolymers

Sample	Comonomer	Comonomer content[a] (mol%)	$M_n/10^3$	M_w/M_n	C.I.[b] (mol%)	Crystallinity[c] (%)	Density (g/cm^3)	T_m (°C)	ΔH_m (J/g)	Lattice dimension[c]		
										(110)	(040)	(130)
P-1	–	0	131	2.1	0.32	62.0	0.9064	159.8	109.7	6.3386	5.2948	4.8126
P-2	–	0	90	4.0	–	64.9	0.9045	165.1	119.1	6.3205	5.2917	4.2586
PE-1	Ethylene	4.6	191	1.8	0.15	57.7	0.8993	136.3	87.5	6.3431	5.3074	4.8178
PE-2		7.2	118	1.7	0.24	52.3	0.8952	121.1	71.3	6.3431	5.3106	4.8101
PE-3		10.3	117	1.8	0.22	48.3	0.8930	109.4	40.8	6.3386	5.3074	4.8230
PB-1	Butene-1	1.6	143	1.8	0.35	61.7	0.9024	152.6	105.3	6.3522	5.3296	4.8361
PB-2		2.7	134	1.7	0.36	58.4	0.9018	148.1	100.5	6.3704	5.3488	4.8545
PB-3		7.9	73	1.8	0.40	57.9	0.8995	133.0	87.1	6.4025	5.4335	4.9051
PB-4		11.7	84	1.7	0.39	55.5	0.8988	132.4	87.2	6.4442	5.4668	4.9403
PH-1	Hexene-1	1.2	138	1.6	0.26	58.9	0.9000	142.7	94.9	6.3476	5.3169	4.8230
PH-2		2.0	142	1.7	0.29	54.0	0.8976	132.5	82.4	6.3476	5.3201	4.8413
PH-3		3.5	99	1.8	0.37	46.5	0.8936	123.2	67.2	6.3422	5.3182	4.8376
PH-4		7.1	73	1.9	0.49	42.1	0.8878	105.0	43.3	6.3841	5.2529	4.8587
PH-5		9.5	70	1.8	–	–	0.8820	97.9	–	6.3795	5.3552	4.8783
PH-6		12.3	70	1.8	0	–	0.8757	83.6	–	–	–	–
PO-1	Octene-1	1.7	118	2.1	0.24	50.9	0.8967	134.8	73.5	6.3386	5.3137	4.8308
PO-2		2.5	116	2.0	0.25	45.9	0.8934	127.1	64.7	6.3522	5.3264	4.8413
PO-3		4.2	107	2.0	0.40	43.6	0.8861	115.3	55.0	6.3522	5.3296	4.8466

[a] Determined by ^{13}C NMR.
[b] Concentration of chemical inversion (2,1-insertion) determined by ^{13}C NMR.
[c] Determined by WAXD.

2.3. NMR measurements

^{13}C NMR spectra were obtained on a Bruker AVACAS 600 spectrometer with a ^{13}C resonance frequency of 150 MHz at 135 °C. Sample solutions for NMR measurements were prepared in *ortho*-dichlorobenzene with concentration maintained at 10 wt%.

2.4. Fuming nitric acid treatment

The sample specimen of $30 \times 10 \times 0.3$ mm^3 was compression-molded at 230 °C and quenched in a water-cooled press. After dipping in FNA at 50 °C for a definite period, the sample specimen was washed in pure water for 3 h at room temperature and in acetone for 6 h at the boiling temperature of acetone, and then dried in vacuo for 24 h.

For the characterization of the samples before and after FNA etching, the endothermic curve was recorded by heating sample specimen from 20 to 210 °C at 10 °C/min with SEIKO DSC220. Then melting temperature and heat of fusion of the samples before FNA treatment were thus substantially different from those obtained under the conditions described above with Perkin–Elmer DSC 7.

3. Results and discussion

3.1. Qualitative investigation on the comonomer inclusion into the crystal

The structural characteristics of the propylene copolymers and homopolypropylene are shown in Table 1. Molecular weight distribution of samples obtained here is narrow ($M_w/M_n =$ ca. 2) and indicates that the most probable polymerization occurs in this catalyst system. DSC endothermic curve of the copolymer sample exhibits a sharp single peak, indicating a narrow chemical composition distribution. Therefore the effect of the molecular structural distribution on the crystalline structure is considered small for samples used in this study. Crystallinity, density, T_m and ΔH_m of the copolymers with various comonomer contents were measured. The relationships between comonomer content with T_m, and with density are shown in Figs. 1 and 2, respectively. It is noted that both T_m and density decrease with increasing comonomer content, but the degree of change with comonomer content is different among samples; i.e. octene-1 $\fallingdotseq$ hexene-1 $>$ ethylene $>$ butene-1. Lamella thickness, l_c, also shows the same tendency as shown in Fig. 3. Thus we can understand that all kinds of olefin comonomer have the crystallization hindrance effect for propylene copolymers and the higher α-olefin such as hexene-1, octene-1 exhibits larger effect than smaller comonomers similarly to the case of ethylene/α-olefin copolymers [1,36]. But these data do not give any information of the location of the comonomer, i.e. whether the comonomer is included into the crystal or not.

On the other hand, as shown in Fig. 4, lattice spacing of (110) and (040) for butene-1 copolymer was found to increase largely with increasing butene-1 content as reported by Cavallo et al. [42] and Abiru et al. [17], while that of ethylene copolymer did not show any remarkable change in lattice spacing. Hexene-1 and octene-1 comonomers also expanded the crystal lattice to some extent.

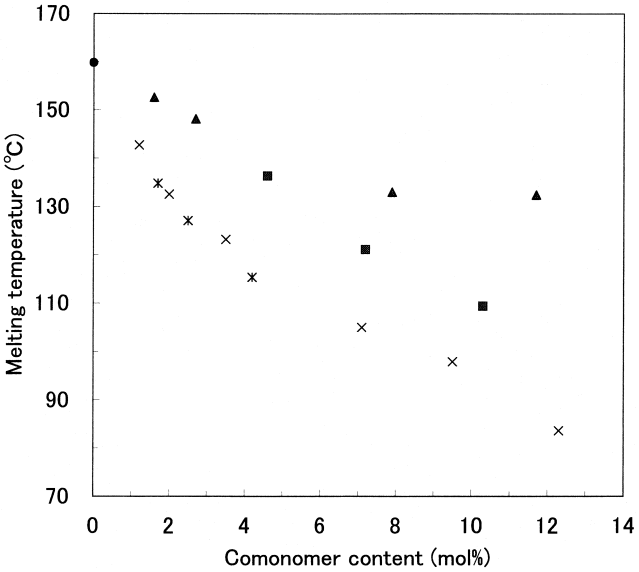

Fig. 1. Changes of melting temperature as a function of comonomer content (●; homo, ■; C′2, ▲; C′4, ×; C′6, ∗; C′8).

Expansion of the lattice spacing for propylene/α-olefin copolymers strongly suggests the inclusion of comonomer into the crystal, but there have been many indications that the distortion near the surface of the crystal which is caused by the comonomer might affect the inner part of lamella especially in the case of thin lamella, resulting in the slight change in the lattice spacing. Then it is considered difficult only from the results in Fig. 4 to conclude the inclusion of α-olefin comonomer into the crystal and the exclusion of ethylene unit from the crystal.

Next ΔH_m reduced to a 100% crystalline sample was calculated as the ratio of $\Delta H_m/X_c$, which is considered as a measure of the crystalline perfection [6,7] of the crystal part. In other words, it indicates the crystallographical similarity

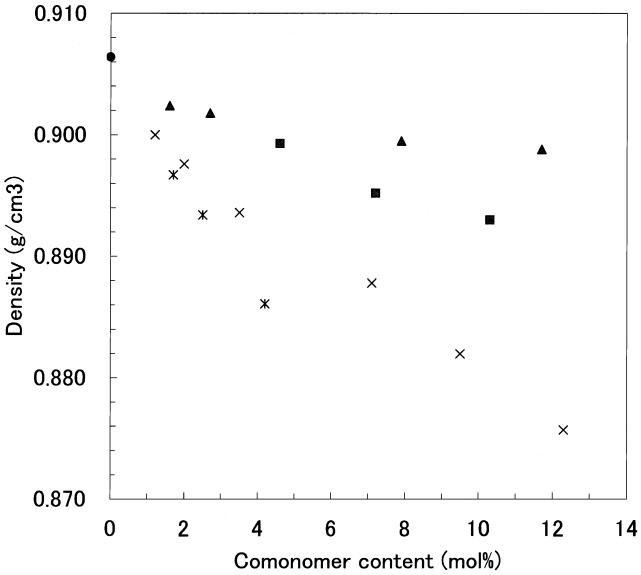

Fig. 2. Changes of density as a function of comonomer content (●; homo, ■; C′2, ▲; C′4, ×; C′6, ∗; C′8).

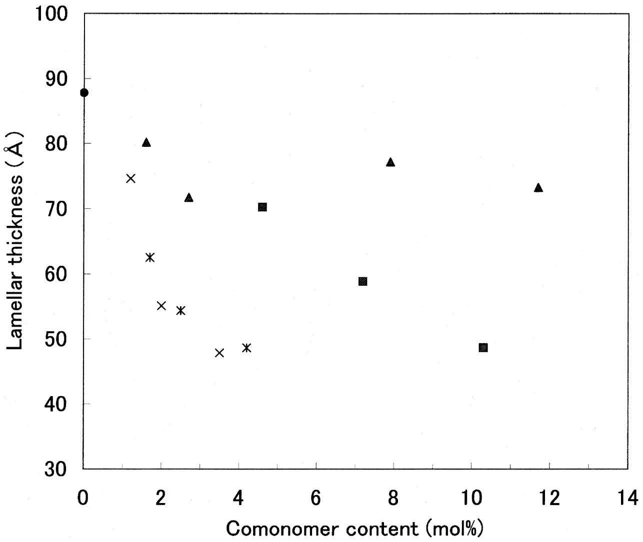

Fig. 3. Changes of lamellar thickness as a function of comonomer content (●; homo, ■; C′2, ▲; C′4, ×; C′6, ∗; C′8).

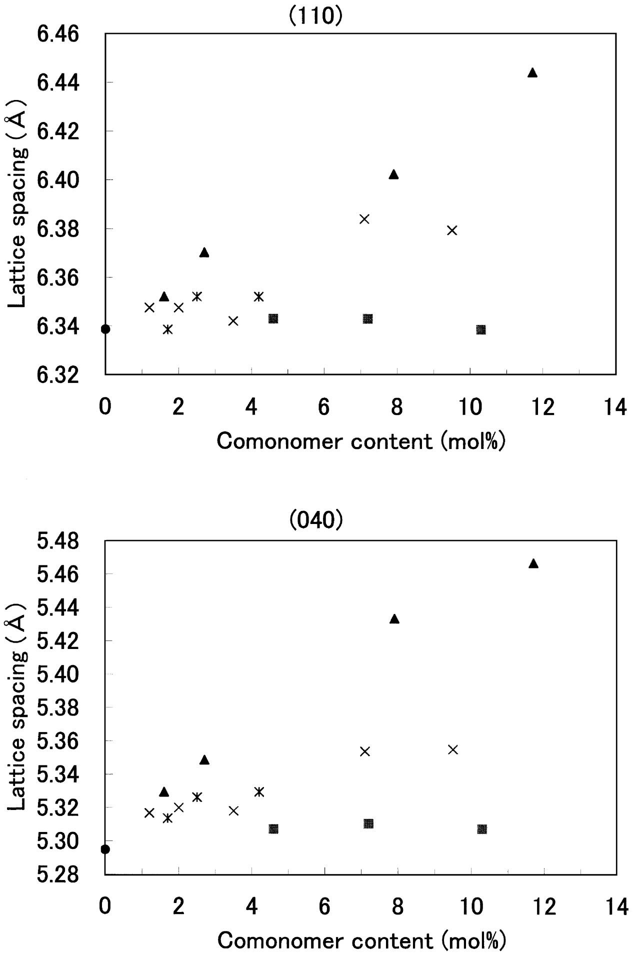

Fig. 4. Changes of lattice spacing of (110) and (040) planes as a function of comonomer content (●; homo, ■; C′2, ▲; C′4, ×; C′6, ∗; C′8).

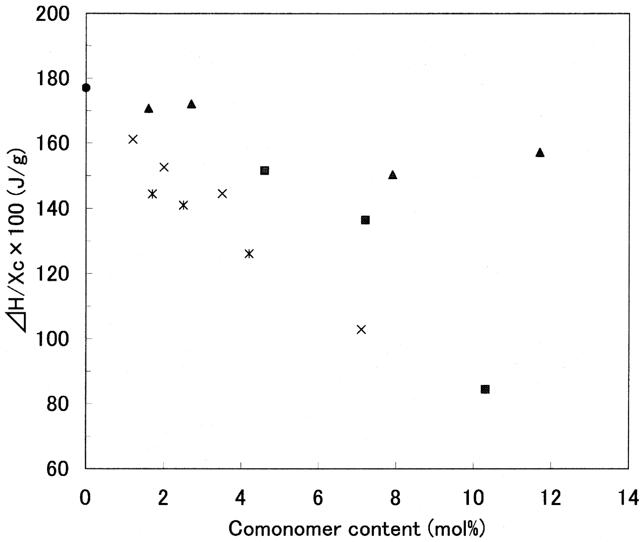

Fig. 5. Changes of melting enthalpy reduced to 100% crystallinity as a function of comonomer content (●; homo, ■; C′2, ▲; C′4, ×; C′6, ∗; C′8).

of the copolymers with the 3/1 helical isotactic polypropylene crystals. If the comonomer is included into the crystal part and decreases the structural perfection, this value should decrease with comonomer content. As shown in Fig. 5, the degree of change in $\Delta H_m/X_c$ is in order; octene-1 > hexene-1 > ethylene > butene-1.

Taking the changes in the physical values shown in Figs. 1–5 with comonomer content into consideration, we can say that all kinds of comonomer studied here have the possibility of inclusion into the crystalline phase of the copolymer though the effect of and the degree of inclusion are not quantitatively clear at this stage. Ethylene can be included but does not largely affect the *a*–*b* plane dimension of the crystal lattice because of its small bulkiness. But the crystal perfection along the *c*-axis would be distorted by the inclusion of ethylene sequence in propylene molecular chain as Laihonen and Gedde [8] pointed out using IR spectrum of the copolymer. Butene-1 can be also included with the expansion of the crystal lattice, but the *c*-axis distortion would be small because of the small steric hindrance of butene-1 unit which is based on the similarity of the crystal chain conformation between isotactic polypropylene and isotactic polybutene-1 (3/1 helices, (TG$_3$) and $c = 6.5$ Å for both polymers) [43]. When the sequence containing bulkier HAO comonomers is included into the crystal, it may largely distort the crystal perfection. Therefore it becomes necessary to decrease the mutual repulsive energy between branches derived from comonomers and other main chains in the crystal. Thus the bulky branches from hexene-1 and octene-1 comonomers may have disadvantage based on the steric hindrance, and then the exclusion from the crystalline stem may be dominant.

As described, we can discuss the inclusion of the comonomer into the crystal qualitatively from the changes of the structural parameters and the physical properties of the copolymers, but the quantitative determination of the included comonomer still remains.

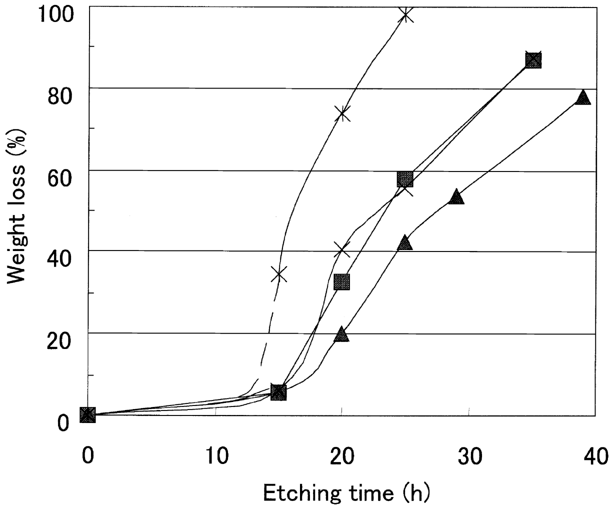

Fig. 6. Weight loss as a function of FNA etching time (etching temperature; 50 °C, ■; PE-1, ▲; PB-2, ×; PH-2, ∗; PO-3).

3.2. FNA etching and determination of the comonomer included into the crystal

First the etching temperature was surveyed. Degradation of the sample of propylene/ethylene copolymer at room temperature was very slow (20% weight loss after two months), and the degree of degradation increased with increasing temperature between 20 and 80 °C. Finally 50 °C was selected as an adequate temperature considering an experimental convenience. Fig. 6 shows a typical weight loss curve during immersion in FNA for some samples. For the copolymers with the crystallinity of more than 50% (PE-1, PB-2, and PH-2), weight loss clearly exhibited induction for about 15 h and increased rapidly during next 10 h. Though the degradation seems to become comparatively slow after that, saturation phenomenon was not observed. On the other hand, in FNA etching of ethylene/α-olefin copolymers [36] at the same temperature, the saturation was explicitly observed at the time that the etched residue reaches the amount corresponding to the crystallinity of the original sample. Comparing the copolymer pairs containing the same level of comonomer in the figure, the degradation rate of butene-1 copolymer PB-2 is slower than that of hexene-1 copolymer PH-2, and octene-1 copolymer PO-3 degrades faster than ethylene copolymer PE-1. It was found that the time at which the weight loss reaches 50% as a measure of the degradation rate exhibits a good correlation with T_m and ΔH_m as shown in Figs. 7 and 8, respectively. This suggests that the thicker the lamella and the higher the crystallinity of the original sample, the slower the FNA degradation rate.

A typical example of molecular weight change during FNA etching is shown in Fig. 9. Molecular weight of the

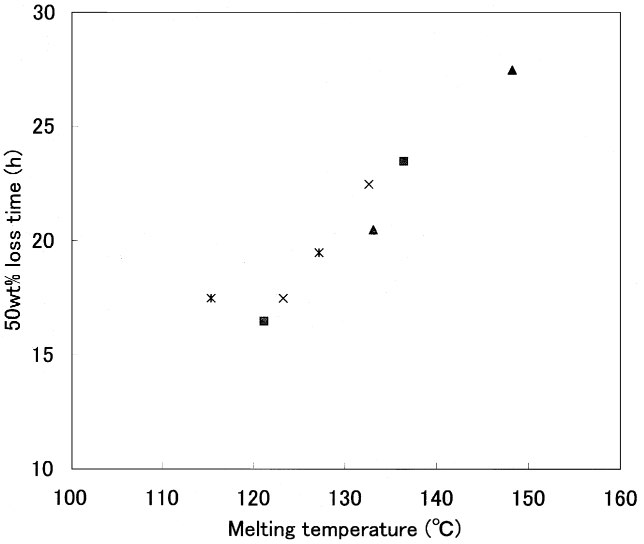

Fig. 7. Relationship between melting temperature of propylene copolymers before etching and 50 wt% loss time (■; C′2, ▲; C′4, ×; C′6, ∗; C′8).

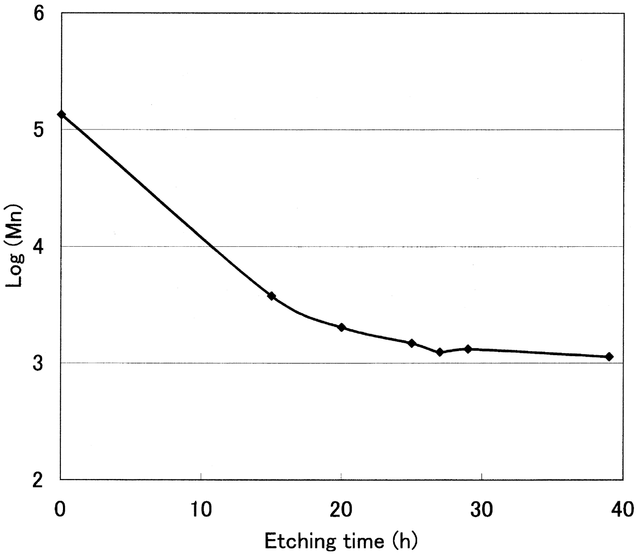

Fig. 9. Molecular weight change with FNA etching for propylene/butene-1 copolymer (PB-2).

residue decreased monotonously with etching time until the weight loss becomes about 50% (around 25 h) and keeps some steady value after that though the weight loss still continues to increase as shown in Fig. 6. Considering both the results of weight loss time-course and the molecular weight change during FNA etching, the degradation mechanism can be estimated as shown in Fig. 10. The apparent induction period is necessary for FNA to interpenetrate into the sample, which should be dependent on the temperature, the shape of sample specimen and the crystallinity. Enough amount of FNA interpenetrating in the amorphous phase decomposes amorphous chains selectively, resulting both in the molecular weight decrease and the weight loss increase at the first step. After the first step of FNA etching, the residue is considered to be the crystal blocks composed of the lamella stems of the original sample. The block would be fragile against continuous FNA attack because of the lack of bonding among crystalline stems, and they could be scraped off mainly from the edge of the block, which leads the successive weight loss but no change in molecular weight. As described above there seems to be a difference in the weight loss time-course between propylene copolymers here and ethylene/α-olefin copolymers [36]. That is, the latter exhibited the weight loss saturation but the former continues to lose weight at the same temperature. This may be because of the difference in the molecular packing density in the crystalline part between propylene copolymers and ethylene copolymers, which might govern the easiness of FNA interpenetration and of the collapse of crystalline stems without a mutual bonding.

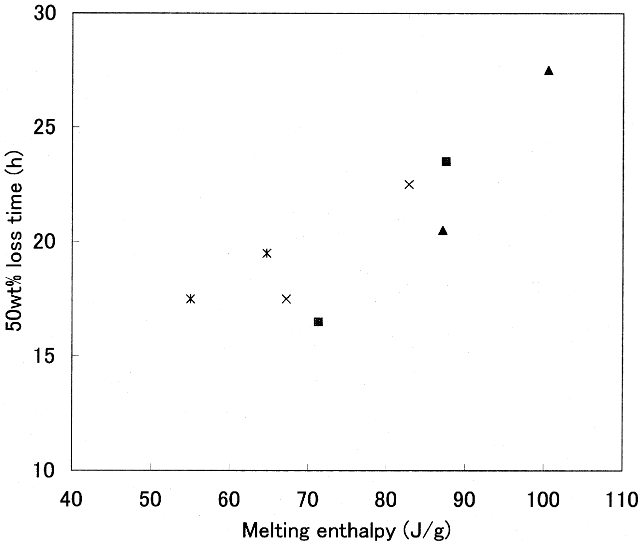

Fig. 8. Relationship between melting enthalpy of propylene copolymers before etching and 50 wt% loss time (■; C′2, ▲; C′4, ×; C′6, ∗; C′8).

As for the chemical structural change on the surface of the crystal caused by FNA etching, nitration and carboxylation are considered to occur judging from the new absorptions around at 1560 and 1710 cm^{-1} in FT-IR spectra of the copolymer after the treatment (Fig. 11).

Molecular weight and thermal properties before and after FNA etching are shown in Table 2. The molecular weight of lamella stem of the original sample is calculated from the lamella thickness obtained with SAXS and WAXD according to Eq. (2), letting the c-axis length be 6.5 Å (for three units in 3/1 helices):

$$M_n = 42 l_c / 2.17 \qquad (2)$$

The molecular weight level of the residue after FNA etching is in good agreement with that of the original crystalline stem. ΔH_m increased remarkably (140% increase for ethylene and 70–90% increase for α-olefin copolymers) by FNA etching as Hocks reported [37]. ΔH_m of homopolypropylene after etching obtained in this study is 163 J/g,

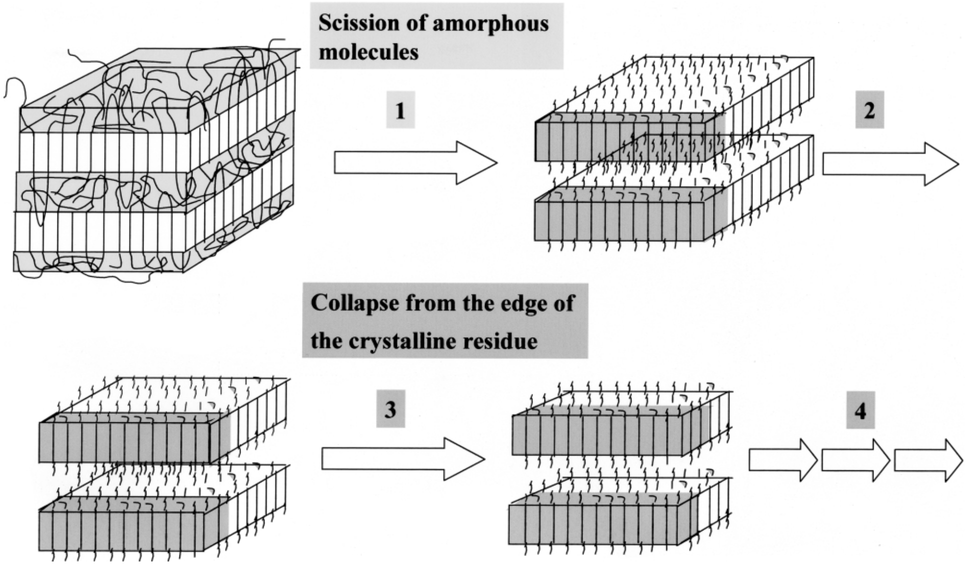

Fig. 10. Schematic representation of FNA etching of propylene copolymer.

which is very close to the average value (165 J/g) for homopolypropylene with the equilibrium melting point [44] (whole polymer). On the contrary, ΔH_m of the copolymers after FNA etching is rather smaller than that of homopolypropylene. This might be mainly due to the effects of the comonomer inclusion into the crystalline phase.

Taking the results obtained so far into consideration, it is judged that amorphous chains are completely removed by FNA etching and the residue after the treatment is the blocks of the crystalline stems of the original sample. Thus it is possible to determine the comonomer included into the crystal by the ^{13}C NMR spectrum of the residue after FNA etching. An example of the spectrum of the residue is shown in Fig. 12 (PB-3). Peaks assigned to the butene-1 sequences can be clearly observed, suggesting the inclusion of butene-1 unit into the crystalline core. Then the amount of comonomer included in the crystalline phase was measured by NMR spectra for various kinds of copolymers degraded by FNA until the weight percent residue is substantially corresponding to the crystallinity of the original sample, and the results are shown in Table 3. The comonomer content in the amorphous phase was calculated from Eq. (3), where N_t stands for the total amount of comonomer of the original sample, and N_c and N_a the amount of comonomer in the

$$N_t = N_c X_c + N_a(1 - X_c) \qquad (3)$$

crystalline phase and in the amorphous phase, respectively. It was proved by this method that a considerable amount of butene-1 comonomer could be included into the polypropylene crystal. For the sample with lower comonomer content (PB-2), butene-1 concentration in the amorphous phase and that in the crystalline phase are equivalent, indicating that butene-1 location does not seem to be selective when molten polymer chains containing butene-1 units crystallize. It is noteworthy that clear evidence of ethylene unit inclusion into the crystal was obtained by this method. N_c/N_a values of 0.24 and 0.31 mean that three to four times larger amount of ethylene unit is included in the amorphous phase than in the crystal under the crystallization

Table 2
Characterization of propylene homopolymer and propylene/olefin copolymers before and after FNA etching

Sample	T_m (°C)[a]		ΔH (J/g)[a]		$>M_n$[b]		$M_{n\,(\mathrm{calcd})}$[c]
	Before	After	Before	After	Before	After	
P-2	166.3	150.3	110.9	163.5	90,300	1450	1640
PE-1	132.1	131.1	51.7	122.1	191,000	1240	1360
PB-2	147.4	137.1	87.0	145.1	134,000	1320	1388
PH-1	133.8	130.6	71.9	122.7	142,000	1270	1067
PO-3	113.3	121.1	47.6	90.0	107,000	1290	942

[a] Determined by DSC.
[b] Determined by GPC.
[c] See text.

Table 3
Comonomer content in the crystalline and in the amorphous phases for propylene/olefin copolymers

Sample	Comonomer	Comonomer content (mol%)			N_c/N_a	N_c/N_t	N_a/N_t
		N_t	N_c	N_a			
PE-1	Ethylene	4.6	2.3	9.4	0.24	0.50	2.00
PE-2		7.2	3.8	12.2	0.31	0.52	1.70
PB-2	Butene-1	2.7	2.7	2.7	1.00	1.00	1.00
PB-3		7.9	6.9	9.4	0.73	0.87	1.19
PH-3	Hexene-1	2.0	0.9	3.5	0.26	0.45	1.75
PH-4		3.5	2.2	5.0	0.44	0.63	1.43
PO-2	Octene-1	2.5	1.5	3.6	0.42	0.60	1.44
PO-3		4.2	2.2	5.8	0.38	0.52	1.38

N_t: comonomer content of the whole polymer, N_c: comonomer content in the crystalline phase, N_a: comonomer content in the amorphous phase.

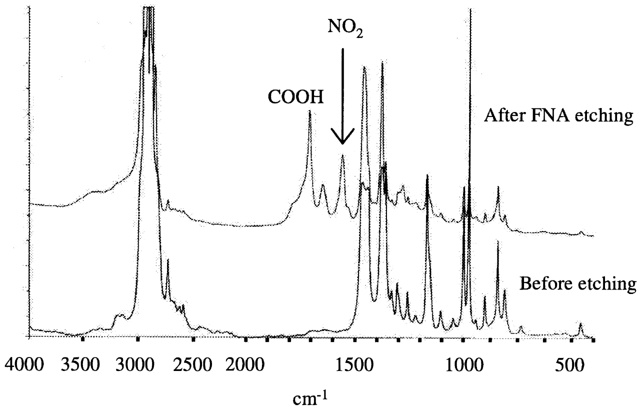

Fig. 11. IR spectra of propylene/ethylene copolymer (PE-1) before and after FNA etching.

condition in this study. Values of N_c/N_t and N_a/N_t, which may be corresponding to the crystalline partitioning coefficient ($P_{\mathrm{CR(eth)}}$) and the amorphous partitioning coefficient ($P_{\mathrm{NC(eth)}}$) proposed by VanderHart et al. [13], are comparable to the results reported by Alamo et al. [14] though N_c/N_t values here are somewhat larger; 0.50 and 0.52 in this study vs. 0.44 and 0.42 in Ref. [14] for the samples of the same level of ethylene content. If the targeted part in the solid-state sample is morphologically same between CP-MAS NMR spectroscopy and FNA etching, the small differences in the relative concentration of ethylene in the crystal might be due to the difference in the crystallization condition, i.e. the rapid quench from 230 °C in this study and slow cooling from 190 °C at the rate of 1 °C/min in Ref. [14]. Furthermore, it is interesting that inclusion of ethylene, which has smaller excluded volume than butene-1, occurs to the less extent than butene-1. This may be because existence of ethylene units causes the interruption of 3/1 helices of polypropylene sequences and thus exclusion of ethylene unit to the amorphous phase is likely to occur. It was also found that not only a small size comonomer but also bulky HAO comonomers could be included into the crystal though the amount of the comonomer included in the crystal is much less than that in the amorphous phase. The effect of the crystallization condition such as the degree of supercooling in the isothermal crystallization and the rate of cooling in the melt crystallization on the content of comonomer included in the crystal is of great interest and is a next subject matter in the series of this work.

On the other hand, comparing the results of ethylene/α-olefin copolymers [36], it is clear that in the case of propylene copolymers much higher extent of comonomers can be included into the polypropylene crystal. For example, N_c/N_a value of butene-1 comonomer is 1.0 and 0.74 for propylene/butene-1 copolymers in this study, but 0.10 is the average value for ethylene/butene-1 copolymers. For hexene-1 and octene-1, 0.35 and 0.40, respectively, on the average for propylene copolymers, and 0.06 each for ethylene copolymers. These considerably large differences in the comonomer inclusion between propylene copolymers and ethylene copolymers would be due to the difference in the molecular packing density of the crystal between isotactic polypropylene and polyethylene.

3.3. Energy calculation with molecular dynamics

Packing energy calculation for each kind of copolymer was conducted with molecular dynamics method using a commercial computer-aided chemistry system 'Polymer 4.0.0'; crystal cell module (Accelrys Co. Ltd). In the calculations, four crystalline stems (a left spiral upward, a left spiral downward, a right spiral upward, and a right spiral downward) composed of 12 monomer units for each stem are aligned in the crystal cell (initial condition; $a = 6.5$ Å, $b = 20.5$ Å, $\beta = 100°$, $\alpha = \gamma = 90°$). Calculations for three cases of different comonomer content; 8.3, 4.2 and 2.1 mol% were tried. In the case of 8.3 mol% comonomer content, one comonomer was placed at the center of all four

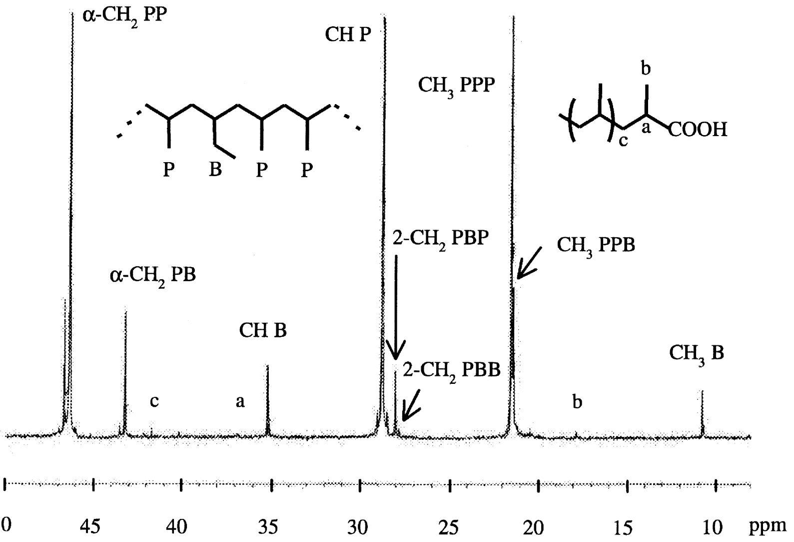

Fig. 12. ^{13}C NMR spectrum of FNA etched propylene/butene-1 copolymer (PB-3, etching time: 20 h).

Table 4
Packing energy (kcal/RU) of crystalline phase of propylene/olefin copolymers

Comonomer content (mol%)	Comonomer			
	Ethylene	Butene-1	Hexene-1	Octene-1
0	− 177.7	− 177.7	− 177.7	− 177.7
2.1	− 175.5	− 174.8	− 157.9	− 147.8
4.2	− 174.7	− 176.0	− 155.2	− 129.0
8.3	− 173.2	− 173.8	− 135.1	− 128.2

stems. One comonomer was placed for two stems in the case of 4.2 mol%, and one comonomer for only one stem in the case of 2.1 mol%. Packing energy of the crystal is defined as the energy difference between the potential energy of the whole crystal system and the summation of the potential energy for each four stem, and then the lower the value, the more stable the crystalline structure is. As shown in Table 4, the estimated stability of the crystal is in order of ethylene copolymer ≒ butene-1 copolymer > hexene-1 copolymer > octene-1 copolymer. Especially, the packing energies of the copolymers of propylene with ethylene and butene-1 are close to that of homopolypropylene, indicating that the stability of the polypropylene crystal is not significantly affected by these kinds of comonomers.

On the contrary, Table 4 also suggests that the inclusion of hexene-1 or octene-1 into the crystal affects largely the stability of the crystal. In case of propylene/α-olefin copolymers, mutual repulsive energy between branching and main chains would be an important factor governing the total packing energy of the crystalline core in addition to the stability of a helical stem containing α-olefin. Then we can easily understand that the bulky branching derived from HAO largely influences the packing energy, and the bulkier the branching, the lower the stability. Here it is recognized again from the energy calculation that less bulkiness of butene-1 is of great advantage for the formation of the stable crystal of propylene/butene-1 copolymer, and as a result, the large degree of the comonomer inclusion into the crystal is estimated to occur. As for the copolymer of propylene with ethylene, small excluded volume of ethylene unit does not affect the lateral spacing of the crystal as shown in Fig. 4 and thus does not increase the energy level of the crystal, but it causes a considerable distortion with propylene sequences through the interruption of 3/1 helices, which may lead the exclusion of the distorted sequences from the crystal.

4. Conclusion

How much degree of comonomer can be included into the crystalline core for melt-crystallized ethylene copolymers and propylene copolymers is a very significant issue from the viewpoint of the lamella thickness distribution which is considered to be a key factor governing the mechanical properties, especially the impact strength. For ethylene/α-olefin copolymer (linear low-density polyethylene), we have found that fuming nitric acid (FNA) etching followed by ^{13}C NMR spectrum measurement is the useful technique to determine the degree of comonomer inclusion into the lamella crystal and concluded that less inclusion of higher α-olefin (HAO) results in a narrower distribution of lamella thickness.

Here we tried the same technique to distinguish the comonomer inclusion into the crystal for propylene/olefin copolymers. As a result, it was proved that butene-1 is favorably incorporated into the crystalline core comparably to the inclusion into the amorphous phase. This may be because of the similarity of the crystal chain conformation between isotactic polypropylene and isotactic polybutene-1. In case of the copolymers of propylene with HAO, comonomer inclusion into the crystal is much less than the case of butene-1 copolymer, which is due to the low stability of the crystal composed of polypropylene stems containing bulky branches derived from HAO.

Clear evidence of ethylene unit inclusion into the crystal was obtained by this technique. However, the inclusion of ethylene, which has smaller excluded volume than butene-1, occurs to the remarkably less extent than butene-1. Interruption of 3/1 helices of polypropylene sequences by ethylene unit and the exclusion of the resulting distorted sequences into the amorphous phase would be the reason.

On the other hand, comonomer inclusion into the crystal of propylene/olefin copolymers is higher about one order of magnitude than ethylene/α-olefin copolymers crystallized under the same condition. This would be due to the difference in the molecular packing density of the crystal between isotactic polypropylene and polyethylene.

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