Microstructural Characterization of Propylene–Butene-1 Copolymer Using Temperature Rising Elution Fractionation

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ABSTRACT: Propylene–butene-1 copolymer (PBC) prepared with a titanium catalyst system was fractionated by temperature rising elution fractionation (TREF) over a temperature range of 5–80°C. PBC was shown to have a wide composition distribution ranging between 12–47 mol % of butene-1. Most of the fractions showed nearly the same crystallinity regardless of the butene-1 content. However, the solubility of the crystalline parts, which turned out to be the driving force for the fractionation, varied over the butene-1 content. Evidence that PBC shows isomorphism was obtained by the analysis of fractionated polymers, using ^{13}C nuclear magnetic resonance spectrometry, X-ray diffraction, differential scanning calorimetry, and gel permeation chromatography. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1493–1501, 1998

Key words: propylene–butene-1 copolymer; solubility; fractionation; isomorphism

INTRODUCTION

It is well known that some copolymers composed of two kinds of olefins exhibit semicrystalline properties like the polyolefins themselves. The crystalline form of the copolymer is usually determined by the predominant monomer unit, together with thermal and mechanical treatments. The minor comonomer unit disturbs the regular packing of the major comonomer sequence, resulting in a lowering of crystallinity. However, when two types of monomer units have similar chemical structures, a large amount of the minor comonomer unit can be included in the crystalline phase, inducing cocrystallization. Hence, the crystallinity may not be significantly changed. This phenomenon is called isomorphism.[1–5] Propyl-

ene–butene-1 copolymer (PBC), which is composed of two similar comonomers, is reported to show isomorphism.[1] It is therefore of great interest to investigate how much the crystalline packing is loosened by incorporation of the minor monomer unit (butene-1).

Recently, temperature rising elution fractionation (TREF) has been proved as a useful method to fractionate copolymers. A typical example is linear low-density polyethylene (LLDPE), which consists of ethylene and a small amount of α-olefin and is fractionated according to solubility of different polymer fractions.[6–13] In this sense, the application of TREF to PBC is very informative to understand the solubility of the crystalline parts over a wide range of copolymer composition. In this article, PBC is fully studied from this viewpoint through the analysis of the whole and fractionated polymers obtained by TREF.

EXPERIMENTAL

Preparation of MgCl₂-Supported TiCl₄ Catalyst

Twenty grams of $MgCl_2$ were milled with 6 mL of ethyl benzoate in a ball mill for 5 h under nitro-
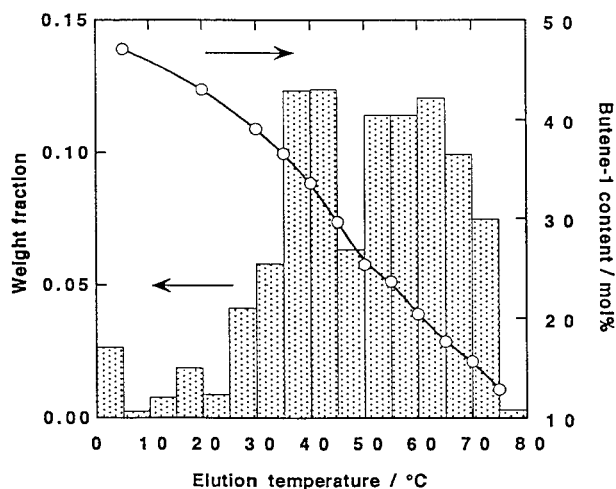
Figure 1 Histogram of fraction versus elution temperature and a plot of butene-1 content of fractions against elution temperature. Fraction 1 is assumed to have been eluted between 0 and 5°C.

gen. The milled product was heated with 200 mL of TiCl$_4$ at 80°C for 2 h in a 400-mL flask. Subsequently, the resulting solid product was separated by filtration and washed several times with n-decane. One gram of the MgCl$_2$-supported TiCl$_4$ catalyst contained 20 mg of Ti atoms.

Copolymerization of Propylene with Butene-1

Into a 1-L autoclave were placed 600 mL of n-hexane and 360 mL of butene-1, and 60 mL of hydrogen at atmospheric pressure were introduced into the system. The system was raised to 70°C and kept thermostated at this temperature. Then, propylene was supplied to the system up to total pressure of approximately 5 kg/cm^2. Subsequently, 1.2 mmol of (i-C$_4$H$_9$)$_3$Al, 2.7 mmol of ethyl benzoate, and 0.2 mmol, as Ti atoms, of Ti catalyst (MgCl$_2$-supported TiCl$_4$ catalyst) were added to the autoclave in this order. Polymerization was carried out for 30 min, during which propylene was continuously supplied to the system to maintain the pressure at 10 kg/cm^2. After 30 min, a small amount of methanol was added into the system to terminate the polymerization, and the whole product was poured into a large amount of methanol. The resulting polymer was collected by filtration, washed with a mixed solution of hydrochloric acid and i-butanol, and then vacuum-dried for 24 h at 50°C.

Temperature–Rising–Elution–Fractionation (TREF)[14–16]

One gram of propylene–butene-1 copolymer (PBC) was dissolved in 150 mL of n-heptane with 0.1% of 2,6-di-$tert$-butyl-p-cresol as an antioxidant at 90°C in a 500-mL flask, and then 280 g of glass beads (a range of particle diameter of 75–125 μm) were added to the solution. The system was maintained at 90°C under rotation for 30 min and cooled to room temperature at 5°C/h. The n-heptane was then evaporated very slowly under reduced pressure. After complete removal of n-heptane, 200 mL of methanol was poured into the flask. Thus, methanol slurry, containing glass beads coated with the whole polymer, was obtained. The methanol slurry was packed into a double-walled glass column (30-mm internal diameter, 600-mm length) connected with a temperature-controlling unit described in our previous work.[17,18] The first fraction was obtained at 5°C by pouring approximately 400 mL of n-heptane into the column. In this procedure, about 150 mL of n-heptane was needed to flush out the methanol from the column. The temperature was then raised stepwise at an interval of 5°C from 5 to 80°C. A typical volume of 400 mL of each fraction was collected in a 1000-mL beaker for 2.5–3 h. The actual termination of each fraction was determined by confirmation that no turbidity appeared by the addition of several droplets of the eluate into cold acetone. The first polymer fraction was recovered by evaporating the solvent at reduced pressure. The polymers in the other fractions were precipitated by adding the eluate into 2.5 L of cold acetone, collected by filtration, and vacuum-dried. The recovery of polymer was 97.0%.

¹³C Nuclear Magnetic Resonance Aanlysis

¹³C nuclear magnetic resonance (¹³C-NMR) spectra were recorded at 120°C on a JEOL GX-270 spectrometer operating at 67.8 MHz with proton decoupling. The polymer solutions were prepared by dissolving 10–50 mg of polymers at 120°C in a mixture of 0.5 mL of hexachlorobutadiene and 0.05 mL of deuterobenzene. The adjusted pulse angle was 45° with a repetition time of 5.0 s in 10,000–50,000 scans. The spectral width was 7.5 kHz, and 32k data points were taken.

X-ray Diffraction Analysis

Samples of 0.1-mm sheets of the whole and fractionated polymers were prepared between heated
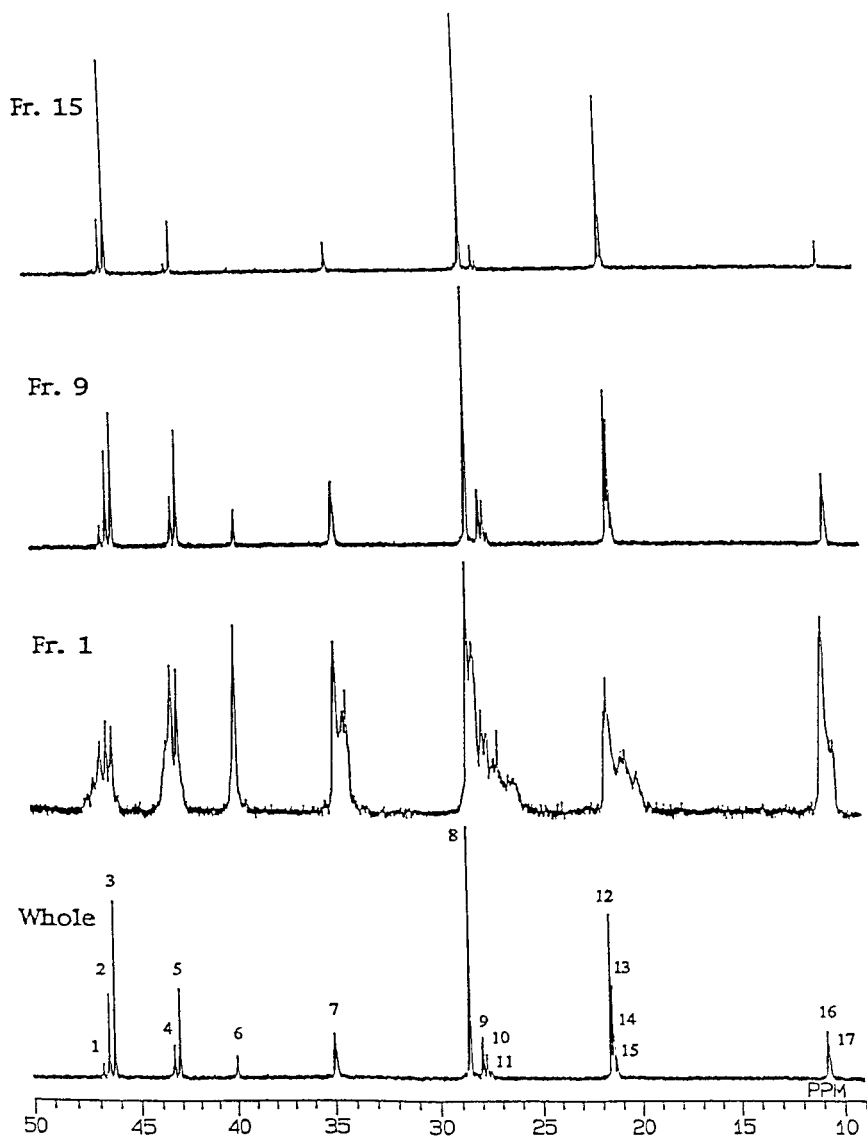
Figure 2 ^{13}C-NMR spectra of the whole PBC and its fractions 1, 9, and 15.

plates in a moulding press at 150°C. The X-ray diffraction (XRD) patterns of the sample sheets were obtained with a Rigaku RU-300 X-ray diffractometer. The instrumental conditions were as follows: Ni-filtered CuK$_\alpha$ radiation, 50 kV, 200 mA; collimator slit diameter, 1 mm, receiving slit, 0.3 mm; scatter slit, 1°; scanning speed, 2°/min; measurement angle, 5–32°.

Differential Scanning Calorimetric Analysis

The melting temperature was measured in an atmosphere of nitrogen on a Perkin–Elmer DSC-7 differential scanning calorimeter (DSC) in the fol-

lowing manner. First, the sample was heated to 200°C and maintained at this temperature for 10 min in order to fully melt the polymer, then cooled to −50°C at 10°C/min to crystallize and kept at −50°C for 10 min, followed by reheating at the same constant rate. The thermogram of each sample was recorded in the second heating run in order to remove the thermal history. Temperature was calibrated by the melting points of indium and lead, and the heat of fusion was by that of indium.

Gel Permeation Chromatographic Analysis

The molecular weight of the samples were measured by a Millipore Waters 150C gel permeation

Table I ^{13}C-NMR Peak Assignments of PBC

Peak No.	Carbon	δ (TMS)/ppm	Assignment
1	$\alpha\alpha$-CH$_2$	46.79	B**PP**B
2	$\alpha\alpha$-CH$_2$	46.49	P**PP**B
3	$\alpha\alpha$-CH$_2$	46.22	P**PP**P
4	$\alpha\alpha$-CH$_2$	43.35	B**PB**P + P**PB**B
5	$\alpha\alpha$-CH$_2$	43.07	P**PB**P + B**PB**B
6	$\alpha\alpha$-CH$_2$	39.96	**BB**
7	CH	34.90	B
8	CH	28.56	P
9	2-CH$_2$	27.97	PBP
10	2-CH$_2$	27.76	PBB
11	2-CH$_2$	27.53	BBB
12	CH$_3$	21.57	PPP
13	CH$_3$	21.46	PPB
14	CH$_3$	21.44	PPB
15	CH$_3$	21.30	BPB
16	CH$_3$	10.80	PBP
17	CH$_3$	10.73	PBB + BBB

Peak numbers are used in Figure 2.

chromatograph (GPC), using a commercially available mixed polystyrene gel column [Tosoh Co. Ltd., Sin-nanyou-si, Yamaguchi-ken, 746-8501, Japan; G3000–G7000, trade names; exclusion limits, $4*10^8$ (estimate) for polystyrene molecular weight (MW)] and o-dichlorobenzene as solvent at 140°C. The molecular weight was calibrated on the basis of polystyrene standard samples.

RESULTS AND DISCUSSION

Figure 1 shows the histogram of weight fraction versus elution temperature of our PBC sample obtained by TREF. This figure clearly shows that this PBC is eluted over a wide temperature range, suggesting a wide composition distribution. The whole polymer and some key fractions were analyzed by ^{13}C-NMR, XRD, DSC, and GPC to evaluate polymer compositions, crystallinity and lattice lengths of the unit cell, thermal properties, molecular weight (MW), and MW distributions.

Figure 2 shows ^{13}C-NMR spectra of the whole PBC and fractions 1, 9, and 15. The peak assignments were taken from the literature[19,20] and are listed in Table I. The butene-1 content (B : mol %) is calculated from eq. (1), using the main chain methylene peaks resonating between 39–48 ppm (see bold letters in Table I and Figure 2, respectively), as follows:

$$B = 100*(BB + 0.5*PB)/(BB + PB + PP) \quad (1)$$

where BB, PB, and PP denote the areas of the methylene peaks based on butene-1–butene-1, propylene–butene-1, and propylene–propylene dyad sequences, respectively. The contents of BB, PB, and PP dyad sequences show that the whole and fractionated polymers are statistically random copolymers because these dyad contents are in good agreement with the values calculated from
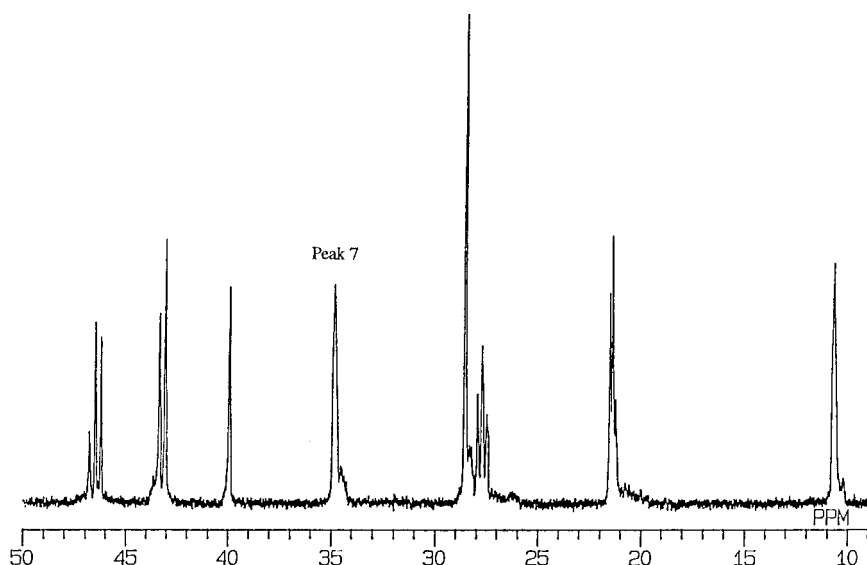

Figure 3 ^{13}C-NMR spectrum of fraction 4.

Table II Characterization of Whole and Fractionated PBC

Fraction	Elution Temperature (°C)	Weight Fraction (wt %)	Butene-1 Content (mol %)	P_{av}	Crystallinity (%)	Lattice Length from XRD (110) (Å)	(040) (Å)	T_m (°C)	T_c (°C)	ΔH (J g^{-1})	M_n (×10^{-5})	M_w (×10^{-5})	M_w/M_n
1	5	2.66	47.1	—	0	—	—	—	—	—	—	—	—
2	10	0.25	—	—	—	—	—	—	—	—	—	—	—
3	15	0.77	—	—	—	—	—	—	—	—	—	—	—
4	20	1.88	43.0	2.52	39	6.810	5.701	68.1	28.5	21.78	—	—	—
5	25	0.90	—	—	—	—	—	—	—	—	—	—	—
6	30	4.12	39.1	2.77	51	6.743	5.681	77.9	34.9	35.63	0.56	1.84	3.29
7	35	5.80	36.6	2.91	52	6.705	5.654	—	—	—	0.79	2.38	3.01
8	40	12.34	33.6	3.08	50	6.655	5.635	87.0	45.9	42.64	—	—	—
9	45	12.37	29.7	3.56	52	6.610	5.608	92.6	—	—	1.14	3.04	2.67
10	50	6.33	25.4	3.95	52	6.548	5.576	97.8	60.5	50.76	1.10	2.87	2.61
11	55	11.41	23.7	4.23	51	6.503	5.562	—	—	—	—	—	—
12	60	11.41	20.4	4.82	51	6.451	5.540	108.0	70.7	57.75	—	—	—
13	65	12.06	17.7	5.64	54	6.422	5.504	—	—	—	1.46	3.68	2.52
14	70	9.93	15.7	6.29	53	6.362	5.457	120.4	83.2	64.70	—	—	—
15	75	7.47	12.9	7.94	53	6.345	5.422	128.1	91.5	70.51	1.78	4.13	2.32
16	80	0.30	—	—	—	—	—	—	—	—	—	—	—
Whole PBC	—	—	25.9	4.08	49	6.496	5.550	109.3	61.3	47.31	1.16	3.47	2.99
HomoPP	—	—	0	—	—	6.234	5.258	—	—	—	—	—	—

T_c is the crystallization from temperature observed in the cooling process of the DSC measurement.
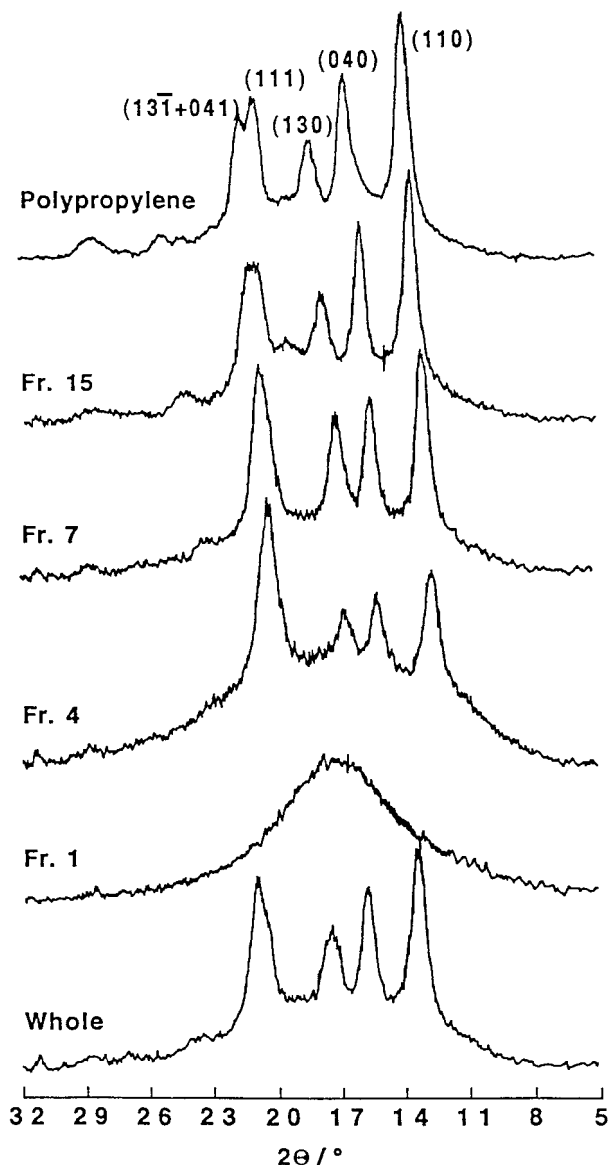
Figure 4 XRD patterns of the whole PBC and its fractions 1, 4, 7, and 15 in comparison with polypropylene.

Bernoullian statistics (for example, the observed value of BB–PB–PP of the whole polymer is 1.0/6.0/8.5, while the calculated value 1.0/5.7/8.2). Taking these into consideration, the ^{13}C-NMR. spectral patterns in Figure 2 reflect in detail both the copolymer composition and the stereoregularity. Particularly, the NMR spectrum of fraction 1 demonstrates the atactic structure indicated by broad peaks and the higher butene-1 content, while the spectrum of fraction 15 is featured by sharp peaks due to the isotactic structure and smaller butene-1-associated signals. As the elu-

tion temperature increases, the butene-1 content decreases from 47.1 to 12.9 mol % (see Fig. 1). All the fractions show high isotacticity, except for fraction 1, as discussed above. Fraction 4 also has a portion of atactic structure, which is, for example, shown by a small shoulder on the high field side of peak 7 in the ^{13}C-NMR spectrum (Fig. 3). Furthermore, the number-averaged propylene sequence lengths (P_{av}) can be determined from the dyad distributions using the formula proposed by Randall,[19] as follows:

$$P_{av} = (PP + 0.5*PB)/(0.5*PB) \qquad (2)$$

We have found P_{av} values between 2.35 for fraction 1 and 7.94 for fraction 15 (see Table II).

Typical XRD patterns of the whole PBC and fractions 1, 4, 7, and 15 are presented together with a commercially available isotactic homopolypropylene in Figure 4. While fraction 1 shows only a halo peak due to the amorphous structure, the patterns of the whole and other fractionated samples are similar to that of homopolypropylene, suggesting that the unit cell structure is dominated by the isotactic propylene sequences. The crystallinity, which is derived from the ratio of the diffraction peak areas to the whole peak areas, including broad amorphous parts, is nearly constant (50–54%) for fractions eluted at 30°C and above. Fraction 4 eluted at 20°C shows a considerably lower crystallinity of 39%. This lower crys-
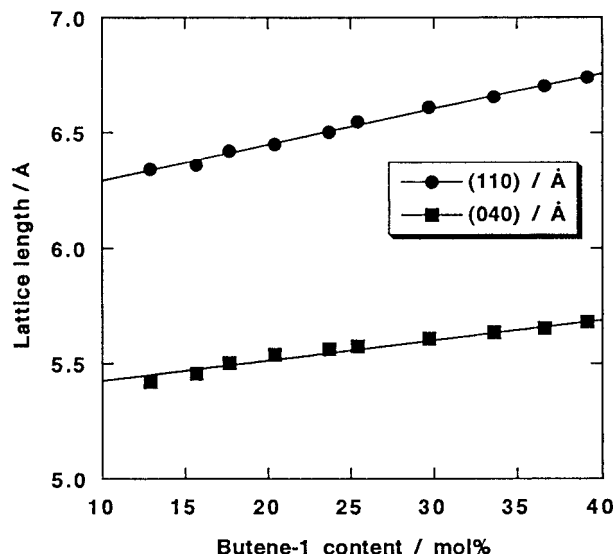

Figure 5 Plots of lattice lengths of (110) and (040) against butene-1 content.
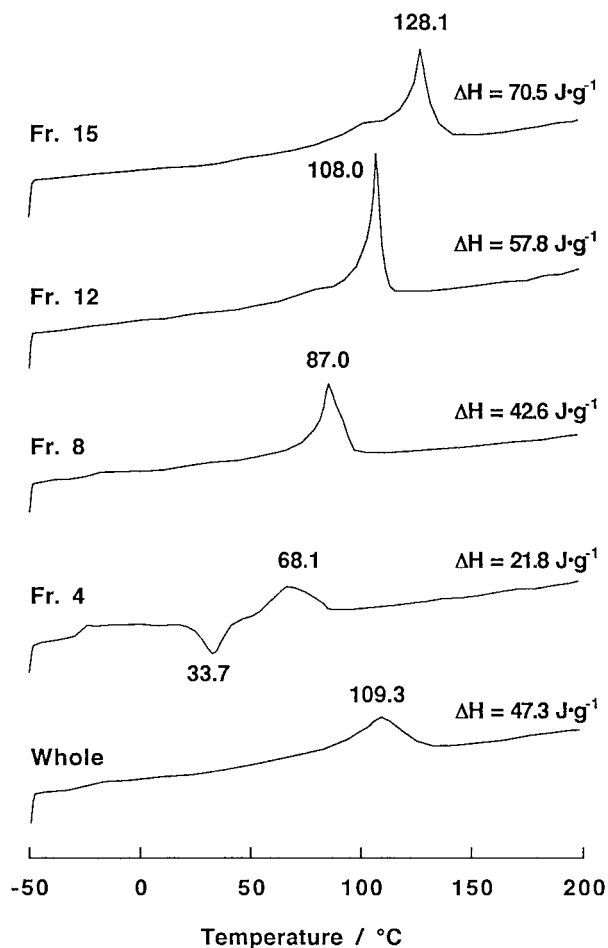
Figure 6 DSC thermograms of the whole PBC and its fractions 4, 8, 12, and 15.

tallinity is mainly induced by its partial atactic structure discussed above in the NMR results. Accordingly, as long as the tacticity is sufficiently high (in other words, no shoulder on the high field side of peak 7 appears in the ^{13}C-NMR spectrum), the crystallinity is independent of the butene-1 content at least in the range of 12–40 mol %. If only propylene sequences form the crystalline phase, the crystallinity must increase as the butene-1 content decreases, contrary to the experimental results. Moreover, the number-averaged propylene sequence lengths (P_{av}) of the fractionated polymers are too short to form a crystalline phase. These findings indicate that the butene-1 unit is incorporated into the crystalline phase mainly formed by the isotactic propylene sequences. Compared with the XRD pattern of homopolypropylene, the diffraction peaks of PBC are shifted to smaller angles proportional to the

butene-1 content, which means a swelling of the unit cell, resulting in a looser packing. This can be directly derived from Bragg's law since 1 is constant, as follows:

$$2d * \sin \Theta = 1 \qquad (3)$$

The looser the packing becomes, the more easily the polymer can be dissolved in a solvent. From the (040) and (110) peak positions, lattice distances were calculated. In both directions, an increasing butene-1 content slightly enlarges the distances (see Fig. 5). This looser packing, as well as the constant crystallinity, is considered to be a proof that PBC shows isomorphism.

DSC thermograms of the whole sample and fractions 4, 8, 12, and 15 are shown over a wide temperature range from -50 to 200°C in Figure 6. The melting temperature (T_m) and the heat of fusion (ΔH) were measured from the peak top and the peak area, respectively. Both T_m and ΔH, which is the energy required to melt the crystalline parts, are good measures for the rigidity of the crystalline phase. Both of these increase from 68.1 to 128.1°C and from 21.78 to 70.51 J/g, respectively, as the butene-1 contents of the fractionated polymers decrease from 43.1 mol % (fraction 4) to 12.9 mol % (fraction 15). The thermogram of fraction 4 is of particular interest, since the crystallization peak appears in the reheating process. This indicates that the crystallization rate of this fractionated polymer is too slow to sufficiently crystallize during the cooling process
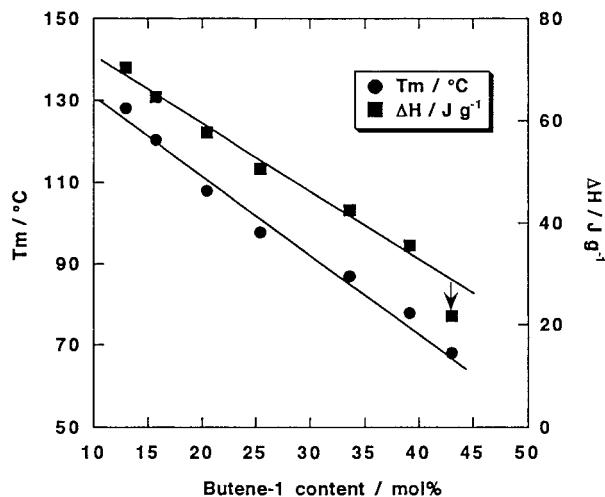

Figure 7 Plots of melting temperature (T_m) and the heat of fusion (ΔH) against butene-1 content.
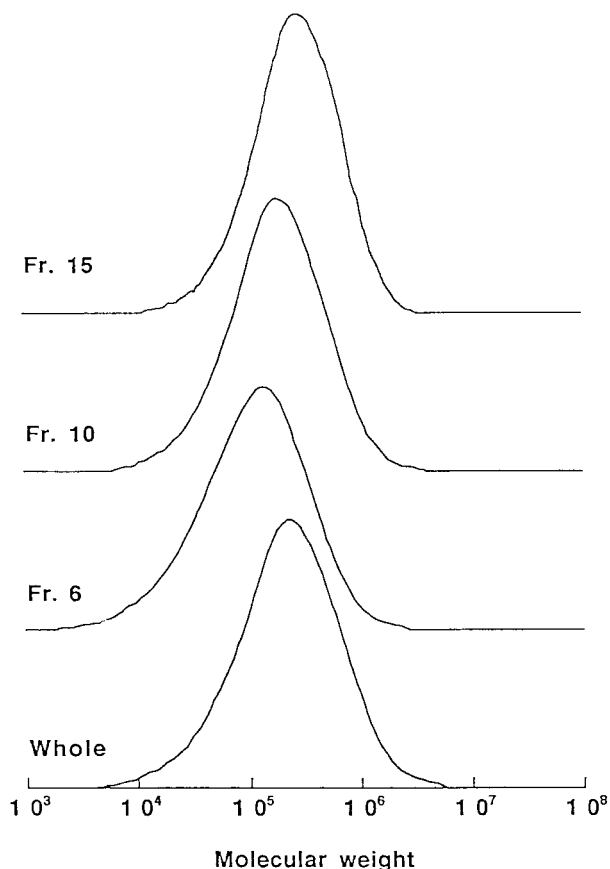
Figure 8 GPC curves of the whole PBC and its fractions 6, 10, and 15.

on account of its lower isotacticity. In order to examine the rigidity of the crystalline parts of the fractions, both T_m and ΔH are plotted against the butene-1 content in Figure 7. This figure shows that a fraction with a higher content of butene-1 is subject to melting with lower thermal energy. The lowering of the melting temperature and the heat of fusion as the butene-1 content increases can be attributed to the looser packing of the crystalline parts due to replacement of propylene unit by butene-1 unit. The reason why the heat of fusion of fraction 4 deviates from the trend in other fractions may be explained by both its lower crystallinity and the influence of the crystallization peak appearing in the opposite direction in the thermogram (see Fig. 6).

Figure 8 presents MW distribution curves by GPC of the whole sample and some fractionated polymers. There is no significant MW change, so TREF has not separated the polymer according to MW.

All the analytical data are summarized in Ta-

ble II. Some fractions could not be analyzed because of the small amount of collected polymer. PBC was fractionated according to the solubility of the crystalline parts dominated by the composition. The polymer fraction having a higher butene-1 content was eluted at lower temperature than that with a lower butene-1 content.

CONCLUSION

PBC showing isomorphism was fractionated using TREF. As the elution temperature increases, the content of the butene-1 unit in the fraction decreased. The data showed that there was some incorporation of the butene-1 unit into the polypropylene lattice, which caused a swelling of the lattice dimensions. This resulted in a lower T_m and ΔH. However, the crystallinity in itself is not influenced by the butene-1 content in the range of 12–40 mol %. The solubility of polymer fractions is regarded as the main mechanism for separating polymer fractions using TREF. TREF can be used to separate polymers into fractions, which have different compositions. As a result, a PBC sample used was shown to have a wide butene-1 composition distribution from 12 to 47 mol %.

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