

## Sequence Distribution and Thermal Property of PEN/PBN Copolymers

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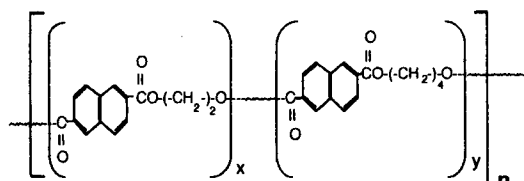
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Poly(ethylene 2,6-naphthalate-co-tetramethylene 2,6-naphthalate) (PEN/PBN) copolymers were synthesized and studied by  $^{13}\text{C}$  NMR spectroscopy, DSC analysis and X-ray diffraction. A minimum in the melting point vs. composition curve was found at approximately 60 mol% tetramethylene 2,6-naphthalate. The PEN/PBN copolymers were shown to be statistically random throughout the range of 1,4-butane diol compositions. The melting point depression behavior of annealed PEN/PBN copolymers depended upon the sequence propagation probability,  $P_s$ , which is suggested by individual crystal formation of two pure comonomers; that is, ethylene-naphthalate-ethylene, EE, and tetramethylene-naphthalate-tetramethylene, BB. However, it can be seen from the X-ray curve that the peaks of PEN/PBN copolymers appear from a crystal lattice which is governed only by the rich component between two different aliphatic units in the copolymer composition.

### Introduction

Many workers have investigated the sequence distribution obtained by NMR and the crystallization behavior by thermal analysis of binary A/B-type random copolymers.<sup>1-9</sup> They have suggested that the crystallization and the melting point depression behavior of the random copolymers are strongly influenced by local crystallization due to fractionation of the crystallizable sequences; however, no one has reported the relationship between sequence distribution and crystallization behavior in PEN/PBN copolymers. In a previous paper,<sup>10</sup> we reported the relationship between the thermal properties and sequence distribution in poly(ethylene 2,6-naphthalate-co-hexamethylene 2,6-naphthalate) (PEN/PHN) copolymer. The crystallization behavior of PEN/PHN random copolymers was strongly influenced by the sequence distribution which consists of both crystalline components. It can be seen that the variation of hexamethylene contents in the copolymers leads to meaningful changes in the molecular structure.

Accordingly, this study was undertaken to relate the sequence distribution with the thermal properties of poly(ethylene 2,6-naphthalate-co-tetramethylene 2,6-naphthalate) (PEN/PBN) copolymers.



Structure of PEN/PBN copolymers

### Experimental

**Synthesis of PEN/PBN Copolymers.** Bis(2-hydroxyethyl)naphthalate/bis(4-hydroxy butyl)naphthalate (BHEN/BHBN) co-oligoesters were synthesized from di-

methyl 2,6-naphthalate (DMN), ethylene glycol (EG) and 1,4-butane diol (BD) in an autoclave.<sup>10-11</sup>

The starting materials were commercial grade and used without further purification. In the oligomer forming process, a given mixture of EG, BD and DMN was charged into the reaction vessel, along with zinc acetate dihydride ( $1.5 \times 10^{-4}$  mol/mol DMN) as a catalyst. The transesterification reaction was carried out with stirring at 210 °C for 2 hrs. After 2 hrs, methanol evolution ceased and BHEN/BHBN co-oligomers were obtained.

In the second step, BHEN/BHBN co-oligomers (200 g), antimony trioxide ( $1.5 \times 10^{-6}$  mol/g co-oligomer), as a catalyst, and trimethyl phosphate ( $1.0 \times 10^{-6}$  mol/g co-oligomer), as a stabilizer, were introduced into a 500 mL polymerization tube, and the polycondensation reaction was carried out at 285 °C for 3 hrs. The vacuum was lowered from 760 mmHg to 1 mmHg over 30 minutes. Poly(ethylene 2,6-naphthalate-co-tetramethylene 2,6-naphthalate) (PEN/PBN) copolymers formed were quenched into cold water and dried in vacuum.

**Analysis of PEN/PBN Copolymers.**  $^1\text{H}$  NMR spectra was obtained on a Bruker AMX-300 FT-NMR spectrometer for copolymer composition determination. For sequence distribution analysis, integrated  $^{13}\text{C}$  NMR spectra were recorded using a Bruker AMX-500 FT-NMR spectrometer. The samples were dissolved in a mixture of trifluoroacetic acid-d and  $\text{CDCl}_3\text{-d}$  (7/3 (V/V)) solution employing TMS as an internal reference ( $\delta=0$  ppm). The NMR experiments were performed at room temperature and the conditions of  $^{13}\text{C}$  NMR data acquisition were the followings: pulse angle=90° (4 ms); repetition time=10 s; acquisition time=2.1 s; sweep width=31250 Hz; number of scans=4000~5000. Thermal analyses were carried out at a heating rate 5 °C/min using a Perkin Elmer DSC-7. Wide angle X-ray diffraction (WAXD) patterns were recorded on a Rigaku denki diffractometer with Ni-filtered  $\text{Cu-K}\alpha$  radiation.

### Results and Discussion

#### Copolymer Composition and Sequence Analysis.

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The 500-MHz  $^{13}\text{C}$  NMR spectrum obtained from EB5, the copolymer with 60.8 mol% BD content, is shown in Figure 1 together with the peak assignments. The composition data obtained by  $^1\text{H}$  and  $^{13}\text{C}$  NMR are shown in Table 1. It can be seen from these results that the molar composition determined by  $^{13}\text{C}$  NMR is very similar to those measured by  $^1\text{H}$  NMR. The peak assignments in the NMR spectra also were performed and listed in Table 2. The peaks at

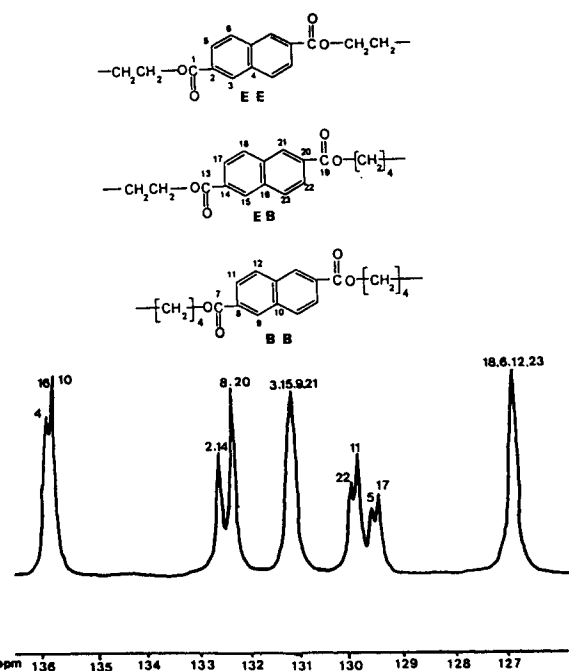


Figure 1.  $^{13}\text{C}$  NMR spectra of EB5 in the PEN/PBN copolymer.

126.8, 129.6, 132.4, 136.3 and 170.5 ppm were assigned to the EE signal of PEN polymer, and also the peaks at 126.8, 129.9, 131.3, 132.4, 136.1 and 171.0 ppm were assigned to the BB signal of PBN polymer. Figure 2 represents the NMR spectra of PEN/PBN copolymers with change of the copolymer compositions. With increasing BD contents of PEN/PBN copolymers, the intensities of the peaks at 129.9, 132.4, 136.1 and 171.0 ppm increased more strongly than the peaks at 131.3, 132.7, 136.3 and 170.5 ppm. The relative intensities of the carbon (C) signals corresponding to PEN carbons also decrease gradually, whereas carbon signals of PBN increase. The new carbon signals ( $\text{C}_{17}$ =129.4 ppm and  $\text{C}_{22}$ =130.0 ppm) were not observed in the spectra of the PEN and PBN homopolymers, so the two carbons of naphthalene bonded to the different aliphatic group at both sides of naphthalene unit were assigned. The chemical shifts of the 1- and 5-position carbons ( $\text{C}_5$ =129.6 ppm,  $\text{C}_{11}$ =129.9 ppm,  $\text{C}_{17}$ =129.4 and  $\text{C}_{22}$ =130.0 ppm) in the naphthalene ring are different from one another depending on the aliphatic units bonded to both sides of the naphthalene. These chemical shift differences were also big enough to resolve the peaks for quantification of peaks intensities. Thus, the sequence distribution of the copolymers can be deduced from these peak intensities. The carbon resonances were split into multiplets owing to three possible environments for naphthalate; EE ( $\text{C}_5$ ), EB ( $\text{C}_{17}$  and  $\text{C}_{22}$ ) and BB ( $\text{C}_{11}$ ) units which are comonomers. Three types of units also can be classified into two homogeneous signals (EE and BB) and one heterogeneous signal (EB).

From these results, the sequence distributions for the randomized PEN/PBN copolymers were determined from the area of NMR spectra on the basis of the peaks ( $\text{C}_5$ ,  $\text{C}_{11}$ ,  $\text{C}_{17}$  and  $\text{C}_{22}$ ) discussed above and expressed as follows; that is,

Table 1. Comparison of feed composition,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR composition of PEN/PBN copolymers

Polymer	Feed composition (mol%)		$^1\text{H}$ NMR composition (mol%)		$^{13}\text{C}$ NMR composition by diol group		$^{13}\text{C}$ NMR composition by naphthalene carbon (mol%)	
	EG	BD	EG	BD	EG	BD	EG	BD
PEN	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
EB1	95.0	5.0	94.9	5.1	-	-	-	-
EB2	90.0	10.0	90.0	10.0	-	-	-	-
EB3	80.0	20.0	79.0	21.0	77.9	22.1	75.1	24.9
EB4	60.0	40.0	63.1	36.9	65.3	34.7	61.4	38.6
EB5	40.0	60.0	39.2	60.8	40.5	59.5	40.1	59.9
EB6	20.0	80.0	20.0	80.0	20.0	80.0	23.1	76.9
PEN	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0

Table 2. Assignment of PEN/PBN  $^{13}\text{C}$  NMR peaks and relative intensities with the composition

Attribution	$\text{C}_{7,19}$	$\text{C}_{1,13}$	$\text{C}_{4,16}^a$	$\text{C}_{10,16}^a$	$\text{C}_{2,14}$	$\text{C}_{8,20}$	$\text{C}_{3,15,9,21}$	$\text{C}_{22}$	$\text{C}_{11}$	$\text{C}_5$	$\text{C}_{17}$	$\text{C}_{18,6,12,23}$	Sample
Chemical shift (ppm)	171.0	170.5	136.3	136.1	132.7	132.4	131.3	130.0	129.9	129.6	129.4	126.8	
Relative intensities (arbitrary unit)	-	15.7	17.4	-	16.2	-	16.8	-	-	16.8	-	17.0	PEN
	3.0	10.1	13.6	3.4	13.3	4.1	17.3	3.2	1.1	9.7	3.3	16.9	EB3
	4.5	8.1	10.6	7.0	10.9	6.7	17.2	4.1	2.6	6.4	4.3	17.7	EB4
	9.0	6.7	6.4	10.0	6.4	10.6	17.1	4.0	5.8	2.5	4.1	17.4	EB5
	12.5	3.6	3.5	13.8	3.8	12.7	16.3	3.4	9.5	1.3	2.5	17.1	EB6
	10.1	-	-	18.1	-	17.6	18.8	-	17.1	-	-	18.3	PBN

<sup>a</sup> $\text{C}_{16}$  peak is not split accurately.

the dyad fractions ( $f_{EE}$ ,  $f_{EB}$  and  $f_{BB}$ ) were represented as the proportion of the integrated intensities of EE, EB and BB signals.

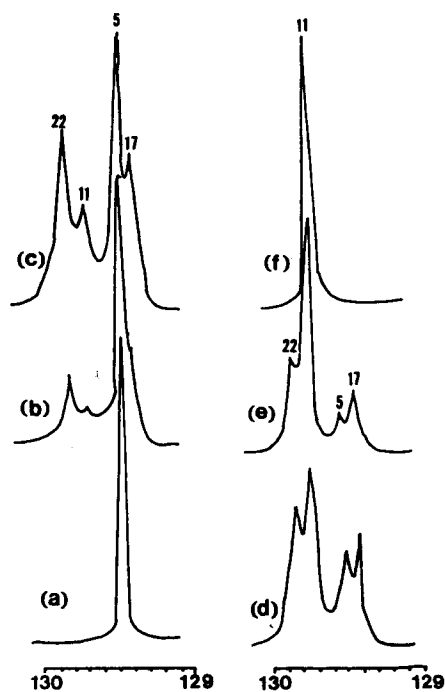
$$f_{EE} = \frac{A_5}{A_5 + A_{11} + A_{17} + A_{22}} \quad (1)$$

$$f_{EB} = \frac{A_{17} + A_{22}}{A_5 + A_{11} + A_{17} + A_{22}} \quad (2)$$

$$f_{BB} = \frac{A_{11}}{A_5 + A_{11} + A_{17} + A_{22}} \quad (3)$$

where  $A_5$ ,  $A_{11}$ ,  $A_{17}$  and  $A_{22}$  represented as the relative area integrated for carbon peaks,  $C_5$ ,  $C_{11}$ ,  $C_{17}$  and  $C_{22}$ . The relative contents of EE, EB and BB dyads as well as the number-average sequence lengths,  $L_{nE}$  and  $L_{nB}$ , of the ethylene unit and tetramethylene unit, were calculated from integral intensities of the signals corresponding to dyads suggested by Yamadera and Murano.<sup>1</sup>

In several studies<sup>1,4,6</sup> a high-resolution NMR spectra were successfully used to determine the quantitative ratio of



**Figure 2.**  $^{13}\text{C}$  NMR spectra of PEN/PBN copolymers; (a) PEN, (b) EB2, (c) EB3, (d) EB4, (e) EB5 and (f) PBN.

dyads,  $f_{EE}$  and  $f_{BB}$ . From the sequence distribution of dyad-system, the molar fractions,  $P_E$  and  $P_B$ , of ethylene and tetramethylene unit can be calculated as follows;

$$P_E = \frac{1}{2} f_{EB} + f_{EE}, \quad P_B = \frac{1}{2} f_{EB} + f_{BB} \quad (4)$$

The probability,  $P_{EB}$ , of finding a B (or E) unit next to an E (or B) unit may be written as the following equations (5) and (6);

$$P_{EB} = \frac{1}{2} \times \frac{f_{EB}}{P_E} = \frac{f_{EB}}{f_{EB} + 2f_{EE}} \quad (5)$$

$$P_{EB} = \frac{1}{2} \times \frac{f_{EB}}{P_B} = \frac{f_{EB}}{f_{EB} + 2f_{BB}} \quad (6)$$

From the dyad fractions and PEN/PBN copolymer composition, we also can readily calculate the number average sequence lengths ( $L_{nE}$  and  $L_{nB}$ ) of each of the homo-unit blocks by equation (7)<sup>1</sup>;

$$L_{nE} = \frac{1}{P_{EB}}, \quad L_{nB} = \frac{1}{P_{BE}} \quad (7)$$

By definition, the summation of both  $P_{EB}$  and  $P_{BE}$  also was expressed as the degree of randomness ( $R_D$ );

$$R_D = P_{EB} + P_{BE} \quad (8)$$

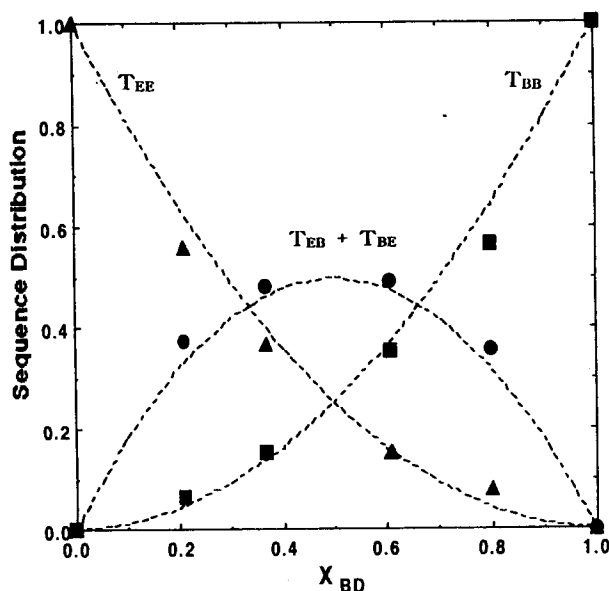
Various values of the dyad fractions and parameters ( $P_E$ ,  $P_B$ ,  $P_{EB}$ ,  $P_{BE}$ ,  $L_{nE}$  and  $L_{nB}$ ) were listed in the Table 3. In the study of PEN/PBN copolymers, the minimum sequence length of PEN crystal may be close to 2.523 and to 2.429 of PBN crystal.

It can be seen that the incorporations of PEN with PBN in the copolymers result in weaknesses of the crystalline intensities of the copolymers. Values of the degree of randomness ( $R_D$ ) were also listed in Table 3. The  $R_D$  is equal to 0.0 for a mixture of homopolymer, 1.0 for a random distribution of units in a copolymer chain, and 2.0 for an alternating copolymer.<sup>15</sup> Also, if  $R_D < 1$ , these units tend to cluster in blocks of each units, whereas if  $R_D > 1$ , the sequence length becomes shorter. From the result of  $R_D$  value, the PEN/PBN copolymers were shown to be random copolymer.

In the dyad-system study of poly(ethylene terephthalate-co-1,4-cyclohexene dimethylene terephthalate) copolymers, Yoshie *et al.*<sup>4</sup> also have suggested the sequence distribution can be described by Bernoullian statistics.<sup>1</sup> Accordingly, if the sequence of PEN/PBN copolymer is statistically random,

**Table 3.** Effect of composition on the sequence distribution of PEN/PBN copolymers

Polymer	BD unit mol%	Fraction of dyads centered on naphthalene (N)			Mole fraction of alkylene unit		Probability of finding of unit		Block length		Degree of randomness $R_D$
		$f_{EE}$	$f_{EB}$	$f_{BB}$	$P_E$	$P_B$	$P_{EB}$	$P_{BE}$	$L_{nE}$	$L_{nB}$	
PEN	0.0	1.000	0.000	0.000	1.000	0.000	0.000	0.000	-	-	-
EB3	21.0	0.560	0.375	0.065	0.748	0.253	0.251	0.743	3.987	1.347	0.993
EB4	36.9	0.367	0.482	0.151	0.608	0.392	0.396	0.615	2.523	1.627	1.011
EB5	60.8	0.153	0.494	0.353	0.400	0.600	0.618	0.412	1.619	2.429	1.029
EB6	80.0	0.079	0.355	0.566	0.257	0.744	0.692	0.239	1.445	4.189	0.931
PBN	100.0	0.000	0.000	0.000	0.000	1.000	0.000	0.000	-	-	-



**Figure 3.** Curves of Bernoulli statistics by the fractions of dyads centered on naphthalene.

the sequence distribution also can be represented as a dyad-system defined by Bernoullian statistics and calculated from the following equations (9)-(11);

$$F_{EE} = f_{EE}^2 \quad (9)$$

$$F_{EB} = F_{BE} = f_{EE}(1-f_{EE}) \quad (10)$$

$$F_{BB} = (1-f_{EE})^2 \quad (11)$$

The probabilities ( $T_{EE}$ ,  $T_{BB}$  and  $T_{EB}+T_{BE}$ ) of EE, BB and (EB+BE) were obtained from the dyad fraction defined by equations (9)-(11) and calculated from the equations (12)-(14);

$$T_{EE} = \frac{F_{EE}}{F_{EE} + F_{EB} + F_{BE} + F_{BB}} = \frac{f_{EE}^2}{f_{EE}^2 + 2f_{EE}(1-f_{EE}) + (1-f_{EE})^2} = f_{EE}^2 \quad (12)$$

$$T_{EB} + T_{BE} = 2f_{EE}(1-f_{EE}) \quad (13)$$

$$T_{BB} = (1-f_{EE})^2 \quad (14)$$

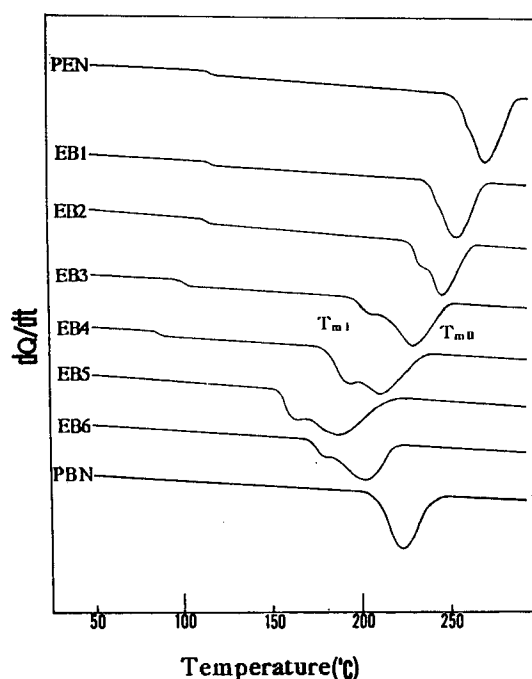
The sequence distributions of PEN/PBN copolymers represented by Bernoullian statistics are also shown in Figure 3. The dotted lines in this diagram represent theoretical curves based on Bernoulli statistics. All  $f_{EB}$  dyad points fall on the theoretical curves obtained by Bernoulli statistics. Accordingly, the PEN/PBN are shown to be statistically random copolymers.

**Melting Depression and Sequence Propagation Probability.** The PEN/PBN copolymers were isothermally annealed and crystallized at different temperatures in order to get the highest degree of crystallinity, as listed in Table 4. It can be seen from Table 4 that the degree of crystallinity ( $X_c$ ) of the PEN/PBN copolymer increases after the isothermal heat treatment. DSC curves of the annealed PEN/PBN copolymers are shown in Figure 4. When the

**Table 4.** Annealing conditions (heating temperature; 120 min), degree of crystallinity ( $X_c$ ) and melting temperatures ( $T_m$  at heating rate 5 °C/min) of PEN/PBN copolymers

Polymer	Annealing temperature	Annealed sample			
	(°C)	$T_m$ , °C	$X_c$ , %	$T_{mI}$ , °C	$T_{mII}$ , °C
PEN	210	270	63.7	-	270
EB1	210	253	58.5	-	254
EB2	210	244	58.5	235	246
EB3	180	228	62.7	207	230
EB4	150	210	56.0	198	210
EB5	140	187	75.8	165	187
EB6	150	202	82.6	182	202
PBN	170	228	87.0	-	228

<sup>a</sup> Degree of crystallinity ( $X_c$ ) were measured by density gradient method



**Figure 4.** DSC curves of the annealed PEN/PBN copolymers.

PEN/PBN copolymers were annealed, two melting endothermic peaks,  $T_{mI}$  and  $T_{mII}$ , each of which includes a shoulder were observed on DSC thermograms. For these phenomena, Yoo *et al.*<sup>6</sup> have suggested that the higher melting peak,  $T_{mII}$ , is attributed to the crystals formed by isothermal crystallization but the lower melting peak,  $T_{mI}$ , may be associated with the crystals formed during the cooling process after isothermal crystallization. It can be seen from Table 4 that the PEN/PBN copolymers have exactly the same endothermic melting peak regardless of their thermal history. Accordingly, the  $T_{mII}$  peak of annealed PEN/PBN copolymers was taken as the  $T_m$  peak. Up to about 60 mol% of tetramethylene content, melting depression was observed. The molar fraction which exhibits the minimum in the melting point, so called a eutetic point, was predicted; that point was about 60 mol% tetramethylene unit. After passing through the eutetic point, the  $T_m$  increased with the

increase of BD content. The  $T_m$  depression with the increase of BD content also can be represented by the theory of equilibrium melting of PEN/PBN copolymers.

We related the sequence length of each of PEN/PBN copolymers investigated by  $^{13}\text{C}$  NMR spectra with Flory's equation<sup>13</sup> to explain this phenomenon. Flory proposed that the melting temperature depression could be expressed by equation (15)

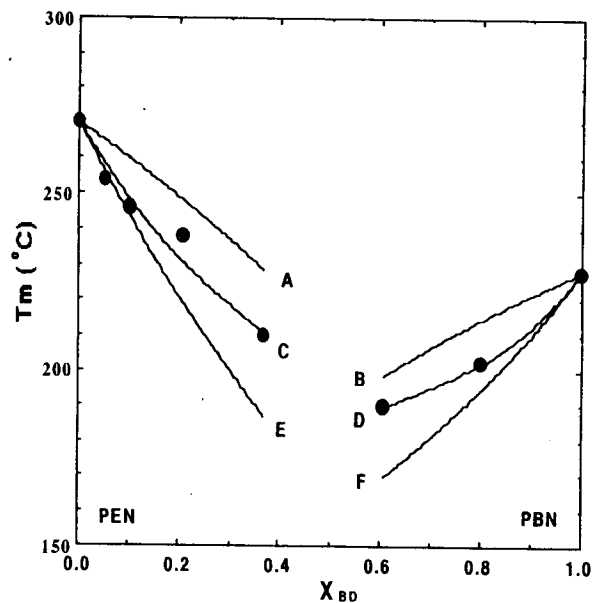
$$\frac{1}{T_m} - \frac{1}{T_m^0} = - \left( \frac{R}{\Delta H_u} \right) \ln X_a \quad (15)$$

where  $T_m$  and  $T_m^0$  are the melting temperatures at the molar fractions ( $X_a$ ) corresponding to the copolymers and the homopolymer, respectively, and  $R$  is the gas constant (8.314 J/mol) and  $\Delta H_u$  is the heat of fusion per repeating unit of the homopolymer; Here, the theoretical values of  $\Delta H_u$  were calculated as about 25 kJ/mol for PEN and 41 kJ/mol for PBN by the group contribution method.<sup>14</sup> Ponnusamy *et al.*<sup>8</sup> have suggested that the  $T_m$  depression depends not only on the  $\Delta H_u$  but also on the sequence propagation probability ( $P_s$ ), which, in random copolymers, can be identified with  $X_a$ . Thus, it can be substituted by the  $P_s$  in equation (16) for the  $X_a$  in equation (15)

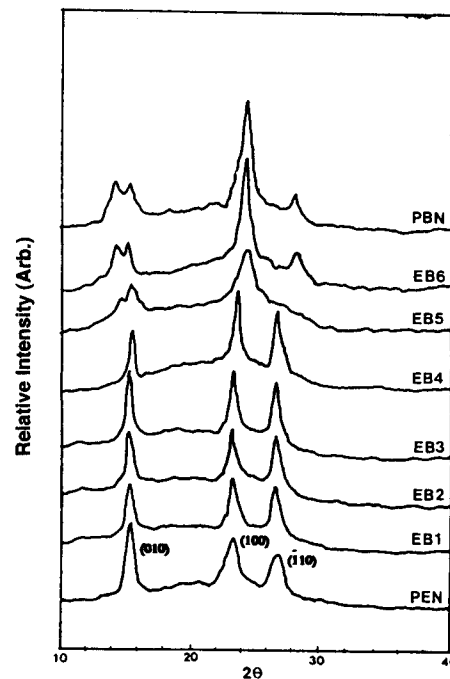
$$\frac{1}{T_m} - \frac{1}{T_m^0} = - \left( \frac{R}{\Delta H_u} \right) \ln P_s \quad (16)$$

The  $P_s$  can be represented as the  $f_{EE}$  in PEN polymer and the  $f_{BB}$  in PBN polymer given by the fraction of dyads centered on naphthalene, as listed in Table 3. Here, the  $f_{EE}$  can be used when the crystalline units are only PEN polymer, whereas the  $f_{BB}$  is applied when the crystalline units are PBN. If the sequences of ethylene unit and tetramethylene unit were co-crystallized, then  $P_s$  could be represented as the summation of the  $f_{EE}+f_{BB}$ . Accordingly, we distinguished the  $P_s$  obtained by the  $f_{EE}+f_{BB}$  and the  $P_s$  calculated by the each  $f_{EE}$  or  $f_{BB}$ . Figure 5 shows graphically the higher  $T_m$  trends of the annealed PEN/PBN copolymer composition, and those predicted theoretically by Flory theory (curves A and B derived from  $X_a$ , curves C and D derived from the summation of  $f_{EE}$  and  $f_{BB}$  and curves E and F derived from each  $f_{EE}$  and  $f_{BB}$ ). The melting temperatures of copolymers appear an eutectic-like behavior from those of homopolymers, PEN and PBN. The experimental data of curves C and D derived from the  $f_{EE}+f_{BB}$  are fitted better by the equation (16) than those of curves E and F from each  $f_{EE}$  and  $f_{BB}$ . Curves A and B derived from  $X_a$  considering only a copolymer composition give a smaller melting temperature depression than that from the experimental data. Considering the relatively good fit of the experimental values to the curves C and D derived from the  $f_{EE}+f_{BB}$ , it can be seen that the  $T_m$  depression was influenced by the result of each crystal formation including PEN and PBN polymer.

**X-ray Measurement and Crystallizable Sequence Length.** Figure 6 shows the WAXD diffractograms of the PEN/PBN copolymers annealed by isothermal crystallization for 2 hrs after quenching. In the PEN polymer, the peak at the diffraction angle of  $15.5^\circ$  is assigned for 010 plane and the peaks at the diffraction angle of  $23.4^\circ$  and  $26.8^\circ$  are assigned for 100 and 110 plane, respectively. The PEN polymer annealed at  $210^\circ\text{C}$  also shows the crystal re-

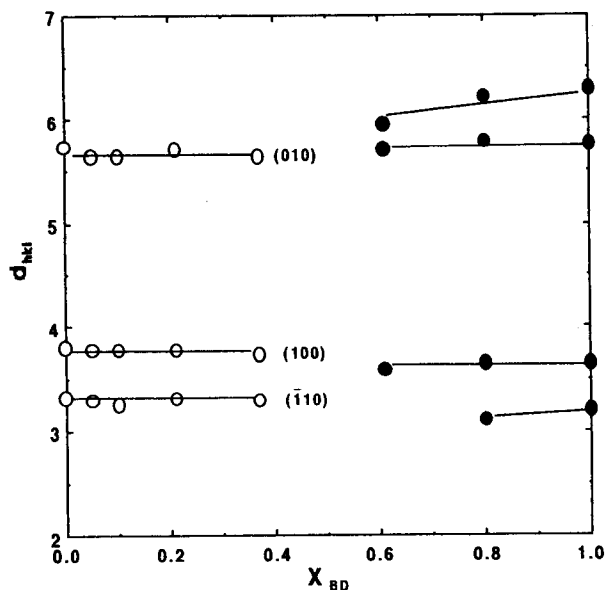


**Figure 5.** Maximum melting temperatures of PEN/PBN copolymers versus copolymer composition ( $X_{BD}$ ); experimental data ( $\bullet$ ); (curves A and B derived from  $X_a$ , curves C and D derived from the summation of  $f_{EE}$  and  $f_{BB}$  and curves E and F derived from each  $f_{EE}$  and  $f_{BB}$ ).



**Figure 6.** Wide angle X-ray diffraction pattern of PEN/PBN copolymers.

flections reported by Mencik,<sup>9</sup> which are consistent with the unit cell ( $a=0.651$  nm,  $b=0.575$  nm,  $c=1.32$  nm,  $\alpha=81.33^\circ$ ,  $\beta=144^\circ$ ,  $\gamma=100^\circ$ ) of the  $\alpha$ -modification type. These peaks are observed in the PEN/PBN copolymers (EB1, EB2, EB3 and EB4). Consequently, the copolymers in the range from PEN to EB4 are made up of only PEN crystal. The copolymers in the range from PBN to EB5 are also formed only PBN crystal. The crystal lattice transitions in the in-



**Figure 7.** Changes in crystal lattice spacing ( $d_{hkl}$ ) with PEN/PBN copolymer composition ( $X_{BD}$ );  $\circ$ =PEN peak and  $\bullet$ =PBN peak.

tervals of EB4 and EB5 were also observed. This fact implies that the sequences participating in the crystal formation have close relationship with the transition of unit cell by the incorporation of copolymers. From the result of Figure 6, the crystal lattice spacings ( $d_{hkl}$ ) of the annealed PEN/PBN copolymers were calculated, as shown in Figure 7. With the increase of BD content, the tendencies of  $d_{hkl}$ -spacings were certainly divided into two classes. It can be proved that when EE sequence unit is crystallized, BB sequence unit is not included in the crystal formation.

In the study of sequence distribution, the result of melting depression corresponds well to the actual melting behavior under the assumption that the EE and the BB sequence units in the PEN/PBN copolymer were crystallized respectively. But the result of WAXD pattern shows the formation of the crystal in which the poor component was excluded completely, and was different from the result of melting behavior. The phenomenon can be explained by an imperfect crystal having lattice defect, and it is not detected in the X-ray diffraction pattern but can have an effect on the melting behavior. The poor component with the sequence length shorter than the critical sequence length in which the chain is able to crystallize completely seems to be excluded in the crystal formation but can form an imperfect crystal

which is difficult to be detected in the X-ray diffraction pattern.

## Conclusions

The crystallization behaviors of PEN/PBN random copolymers were investigated by means of DSC analyses and X-ray diffraction, and discussed in terms of sequence distribution theories for copolymers. From the X-ray curve, the PEN/PBN copolymer seems to form the crystal composed of only the rich component in the copolymer. On the other hand, the melting point depression behavior of annealed PEN/PBN copolymers depended upon two component; EE and BB dyads. The melting depression curve is affected by the  $f_{EE}$  and  $f_{BB}$  because of an imperfect crystal affecting the melting behavior. But such an imperfect crystal peak is difficult to be detected in the X-ray diffraction pattern.

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