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Sequence distribution and thermal behaviour of poly(ethylene 2,6-naphthalate-*co*-hexamethylene 2,6-naphthalate) copolyesters

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Binary copolymers of poly(ethylene 2,6-naphthalate) (PEN) and poly(hexamethylene 2,6-naphthalate) (PHN) were synthesized and their sequence distributions were investigated over the entire range of copolymer composition by ^{13}C nuclear magnetic resonance spectroscopy. The melting temperatures of these copolymers were depressed gradually with the increase of 1,6-hexanediol (HD) in the composition and eutectic behaviour appeared which depended only on the sequence propagation probability P, not directly on the composition, and showed a minimum at about 60 mol% HD content at which the average sequence length is the shortest. The copolymers rich in ethylene units formed only PEN crystals with complete rejection of the hexamethylene units. Also, the copolymers rich in hexamethylene units formed only PHN crystals excluding ethylene units. Copyright © 1996 Elsevier Science Ltd.

(Keywords: random copolyesters; poly(ethylene 2,6-naphthalate-*co*-hexamethylene 2,6-naphthalate); sequence distribution)

INTRODUCTION

Binary crystalline–crystalline random copolymers show some degree of isomorphism, owing to cocrystallization, when the two comonomer units have similar chemical structure, similar repeat-unit length, similar volume and compatible conformation[1–4]. The crystallizability of each comonomer unit may be a function of the crystallizable sequence distribution, the cohesive energy of molecules, the molecular mobility and the surface free energy of the crystal[5].

The crystallization behaviour in a random copolymer system is largely influenced by the copolymer sequence distribution. Zhu and Wegner[6] asserted that only sequences of the average length crystallize, with shorter and longer sequences being excluded from crystal formation. On the other hand, Briber and Thomas[7] have stated that all the sequences, including a minimum length and longer, participate in crystallization.

Copolyesters prepared by molten-state polycondensation are generally considered to have a random distribution of structural units along the polymer chain, because of the almost equal reactivities of the monomers and the random transesterification reaction during the polycondensation process. The structure of the resulting polycondensates can be studied by high-resolution nuclear magnetic resonance spectroscopy (n.m.r.). Several characterization studies of copolycondensates have been published[8–10]. Among these, Yamadera and Murano[8] were probably the first to evaluate the average sequence length and degree of randomness based on the determination of three types of triad.

In this paper, the crystallization behaviour of a random copolyester and the minimum melting temperature *versus* copolymer composition are discussed on the basis of the sequence distribution corresponding to each component polymer.

EXPERIMENTAL

Synthesis of PEN/PHN copolymers

Bis(2-hydroxyethyl)naphthalate/bis(6-hydroxyhexyl)-naphthalate (BHEN/BHHN) co-oligomers were synthesized from dimethyl 2,6-naphthalate (DMN), ethylene glycol (EG) and 1,6-hexanediol (HD) in an autoclave[11,12]. The starting materials were of commercial grade and were used without further purification.

In a first process, mixtures comprising various amounts (mol%) of DMN, EG, HD and zinc acetate (1.5×10^{-4} mol/mol DMN), as a catalyst, were charged into the reaction vessel, and the transesterification reaction was carried out with stirring at 240°C over a period of 2 h. After this time, methanol evolution ceased and BHEN/BHHN co-oligomers were obtained.

In a second process, BHEN/BHHN co-oligomers (200 g), antimony trioxide (1.5×10^{-6} mol/g co-oligomer), as a catalyst, and trimethyl phosphate (1.0×10^{-6} mol/g co-oligomer), as a stabilizer, were introduced into a 500 ml polymerization tube, and the polycondensation reaction was continued at 285°C for 2 h. Initially a low vacuum

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Table 1 Comparison of feed composition, ^{1}H n.m.r. and ^{13}C n.m.r. compositions of PEN/PHN copolymers

Polymer	Feed composition (mol%) EG	Feed composition (mol%) HD	^{1}H n.m.r. composition (mol%) EG	^{1}H n.m.r. composition (mol%) HD	^{13}C n.m.r. composition by diol group (mol%) EG	^{13}C n.m.r. composition by diol group (mol%) HD	^{13}C n.m.r. composition by naphthalene carbon (mol%) EG	^{13}C n.m.r. composition by naphthalene carbon (mol%) HD
PEN	100	0	100.0	0.0	100.0	0.0	100.0	0.0
EH1	95	5	92.3	7.7	90.6	9.4	90.6	9.4
EH2	90	10	84.3	15.7	82.0	18.0	81.0	19.0
EH3	80	20	59.8	40.2	62.0	38.0	62.8	37.2
EH4	60	40	22.0	78.0	29.1	70.9	29.8	70.2
EH5	40	60	5.2	94.8	6.3	93.7	7.6	92.4
EH6	20	80	1.4	98.6	–	–	–	–
PHN	0	100	0.0	100.0	0.0	100.0	0.0	100.0

(<760 mmHg) was applied to the system and after 30 min the vacuum was fully drawn (1.0–0.2 mmHg). Poly(ethylene 2,6-naphthalate-*co*-hexamethylene 2,6-naphthalate) (PEN/PHN) copolymers formed were quenched into cold water and dried *in vacuo*.

Measurements

The samples (50 mm × 50 mm × 0.02 mm) were made using a Carvers' Laboratory Press.

^{1}H n.m.r. spectra at 300 MHz were obtained on a Bruker AMX-300 FT-NMR spectrometer for copolymer composition determination; sequence distribution analysis was conducted on ^{13}C n.m.r. spectra recorded using a Bruker AMX-500 FT spectrometer at 500 MHz. The samples in both cases were dissolved in a mixture of $CF_3COOH/CDCl_3$ (7/3 v/v) solution employing tetramethylsilane (TMS) as an internal reference ($\delta = 0$ ppm). The concentration of the sample solutions was $0.1\ \mathrm{g\,ml^{-1}}$. The n.m.r. experiments were performed at room temperature and the conditions of ^{13}C n.m.r. data acquisition were as follows: pulse angle = 90° (4 μs); repetition time = 10 s; acquisition time = 2.1 s; sweep width = 31.25 kHz; number of scans = 4000–5000. Quantitative analysis of ^{13}C n.m.r. results necessitates special precautions as in such cases the peak intensities depend not only on the concentration of the species analysed but also on their relaxation time. Hence, we shall only compare peaks of the same ^{13}C chemical species and assume that substitution of diol with different methylene units produces only a slight modification of the motions of the nuclei to be studied. Therefore these changes have been ignored.

Thermal analyses (differential scanning calorimetry, d.s.c.) were carried out at a heating rate of $5^\circ\mathrm{C\,min^{-1}}$ using a Perkin–Elmer DSC-7. Wide-angle X-ray diffraction (WAXD) patterns were recorded on a Rigaku Denki diffractometer with Ni-filtered Cu *Kα* radiation.

RESULTS AND DISCUSSION

Copolymer composition and sequence analysis

The compositions of PEN, PHN and PEN/PHN copolymers determined from ^{13}C n.m.r. spectra are listed in *Table 1* and show good agreement with those determined from ^{1}H n.m.r. spectra[12]. The 500 MHz ^{13}C n.m.r. spectra of copolymer sample EH3 in $CF_3COOH/CDCl_3$ solution are shown in *Figure 1*. All the carbon resonances of PEN/PHN copolymers except for the methylene carbon are split into multiplets owing to three possible environments for naphthalate: E–N–E, E–N–H and H–N–H, where E, N and H represent ethylene, naphthalene and hexamethylene units, respectively. Indeed, we observed the presence of three types of naphthalene carbon nuclei (C_5, C_{11}, C_{17}, C_{22}) bearing respectively two ethylene groups ($C_5 = 129.6$ ppm), one ethylene and one hexamethylene ($C_{17} = 129.4$, $C_{22} = 130.2$ ppm) and two hexamethylene groups ($C_{11} = 130.0$ ppm). The assignments were made based on the comparison of spectra from different copolymer samples. The assignments for the naphthalene carbons are described elsewhere[13].

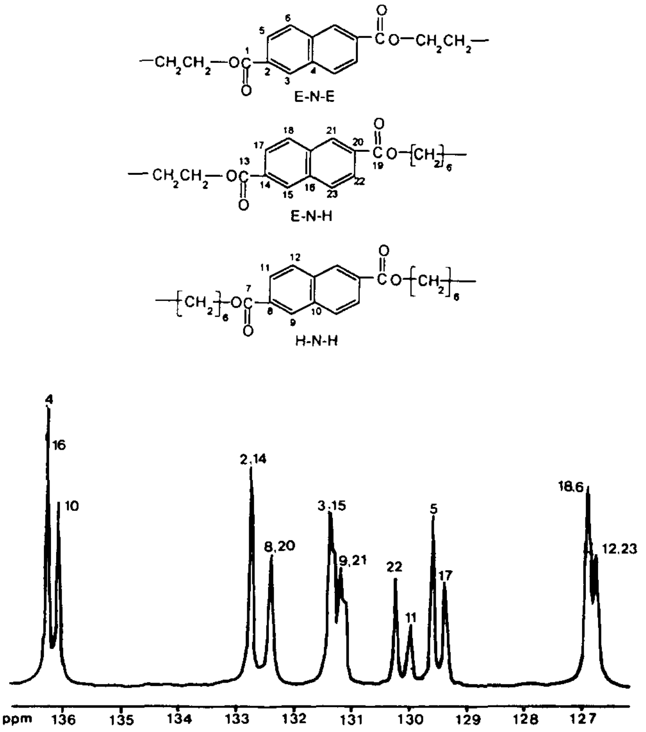

Figure 1 ^{13}C n.m.r. spectra of PEN/PHN copolymer EH3

Figure 2 represents the ^{13}C n.m.r. spectra of the homopolymers and PEN/PHN copolyesters as a function of copolymer composition. The new carbon signals appearing in the spectra are due to the substitution of an ethylene unit by a hexamethylene unit. As clearly shown in *Table 2*, the relative intensities of the C signals corresponding to PEN carbons decrease progressively whereas C signals of PHN increase. C_{17} and C_{22} were not observed in the spectra of the corresponding homopolyesters (PEN and PHN) and were assigned to naphthalene carbons placed between the different diol groups. Thus, the intensities of peaks C_{17} and C_{22} represent the amount of heterogeneity in the copolymers.

According to Yamadera and Murano[8], the relative content of H–N–H, E–N–H and E–N–E triads, as well as the number-average sequence lengths of the ethylene units (L_{nE}) and the hexamethylene units (L_{nH}), can be found from integral intensities of the corresponding triad signals. The probability (P_{EH}) of finding an H unit next to an E unit is:

$$P_{EH} = \frac{A_{17} + A_{22}}{A_5 + A_{17} + A_{22}} \tag{1}$$

Likewise:

$$P_{HE} = \frac{A_{17} + A_{22}}{A_{11} + A_{17} + A_{22}} \tag{2}$$

where A_5, A_{11}, A_{17} and A_{22} represent the relative integrated area for C_5, C_{11}, C_{17} and C_{22} peaks, respectively. Also, the number-average sequence length, L_{nE} and L_{nH}, of each unit are given by the terms:

$$L_{nE} = \frac{1}{P_{EH}} \tag{3}$$

$$L_{nH} = \frac{1}{P_{HE}} \tag{4}$$

Furthermore, the degree of randomness (B) is defined as the summation of the two probabilities:

$$B = P_{EH} + P_{HE} \tag{5}$$

For random copolyesters, B is unity. If $B < 1$, the units tend to cluster in blocks of each unit and finally $B = 0$ in a homopolymer mixture. On the other hand, if $B > 1$ the sequence length becomes shorter, and $B = 2$ in an alternating copolymer.

The parameters P_{EH}, P_{HE}, L_{nE}, L_{nH} and B shown in *Table 3* were calculated with equations (1)–(5). For sample EH6, it was difficult to estimate the sequence distributions accurately from ^{13}C n.m.r. spectra because the resonances of the less abundant unit were too small to be analysed. Among the values of B, which are somewhat greater than unity, the B-value of 1.320 points to a greater contribution of E–N–H triads than required by a statistical unit distribution. Thus the average sequence length of EH3 is the shortest of all.

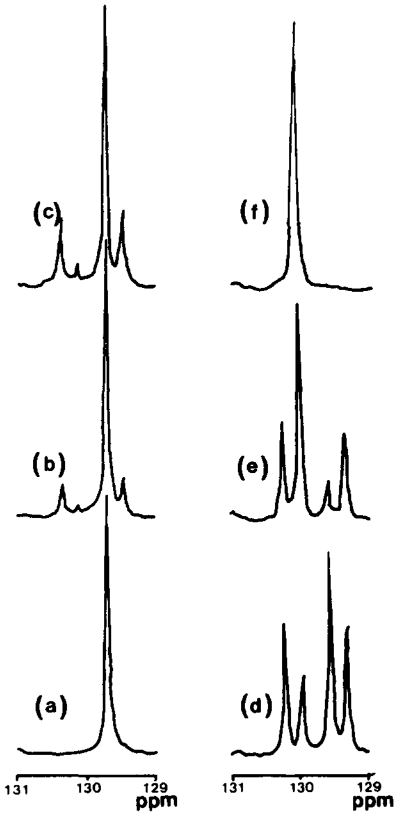

Figure 2 ^{13}C n.m.r. spectra of homopolymers and PEN/PHN copolyesters: (a) PEN; (b) EH2; (c) EH3; (d) EH4; (e) EH5; (f) PHN

Table 2 Evaluation of PEN/PHN ^{13}C peaks and relative intensities with composition (chemical shifts relative to TMS)

Assignment	Chemical shift (ppm)	Relative intensity (arbitrary units)							
		PEN	EH1	EH2	EH3	EH4	EH5	EH6	PHN
$C_{7,19}$	171.0	–	1.5	3.0	6.3	11.6	14.7	15.6	15.7
$C_{1,13}$	170.5	15.7	14.4	13.3	10.1	4.9	1.3	n.m.[b]	–
$C_{4,16}$[a]	136.3	17.4	15.1	13.6	10.8	6.1	2.1	n.m.	–
$C_{10,16}$[a]	136.1	–	2.5	3.7	6.6	11.6	15.3	16.9	17.1
$C_{2,14}$	132.7	16.2	15.2	13.2	10.6	4.8	1.3	n.m.	–
$C_{8,20}$	132.4	–	1.7	3.2	6.3	11.5	15.1	16.8	17.1
$C_{3,15}$	131.4	16.8	14.2	12.9	10.4	5.0	1.7	n.m.	–
$C_{9,21}$	131.2	–	2.6	3.9	6.5	11.4	15.3	17.0	17.2
C_{22}	130.2	–	1.5	2.4	3.7	3.6	1.7	n.m.	–
C_{11}	130.0	–	0.1	0.6	2.2	7.7	13.6	16.2	16.3
C_5	129.6	16.8	12.5	10.3	6.1	1.5	0.1	n.m.	–
C_{17}	129.4	–	2.0	2.8	3.7	3.3	1.1	n.m.	–
$C_{18,6}$	126.9	17.0	14.0	12.7	10.0	5.6	1.8	n.m.	–
$C_{12,23}$	126.8	–	2.6	4.2	6.6	11.4	14.9	16.5	16.9

[a] C_{16} peak is not split accurately
[b] Not measurable

Table 3 Effect of composition on the sequence distribution of PEN/PHN copolymers

		Fraction of triads centred on naphthalene (N)[a]			Probability of finding of unit		Block length		
Sample	HD unit (mol%)	f_{ENE}	f_{ENH}	f_{HNH}	P_{EH}	P_{HE}	L_{nE}	L_{nH}	Degree of randomness B
PEN	0.0	1.000	0.000	0.000	0.000	0.000	–	–	0.000
EH1	7.7	0.781	0.218	0.001	0.222	0.997	4.505	1.003	1.219
EH2	15.7	0.637	0.323	0.040	0.337	0.890	2.967	1.124	1.227
EH3	40.2	0.391	0.471	0.138	0.547	0.773	1.828	1.294	1.320
EH4	78.0	0.089	0.424	0.487	0.826	0.465	1.211	2.151	1.291
EH5	94.8	0.009	0.168	0.823	0.951	0.167	1.052	5.988	1.118
EH6	98.6	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
PHN	100.0	0.000	0.000	1.000	0.000	0.000	–	–	0.000

[a] f_{ENE}—molar fraction of ENE unit; f_{ENH}—molar fraction of ENH unit; f_{HNH}—molar fraction of HNH unit

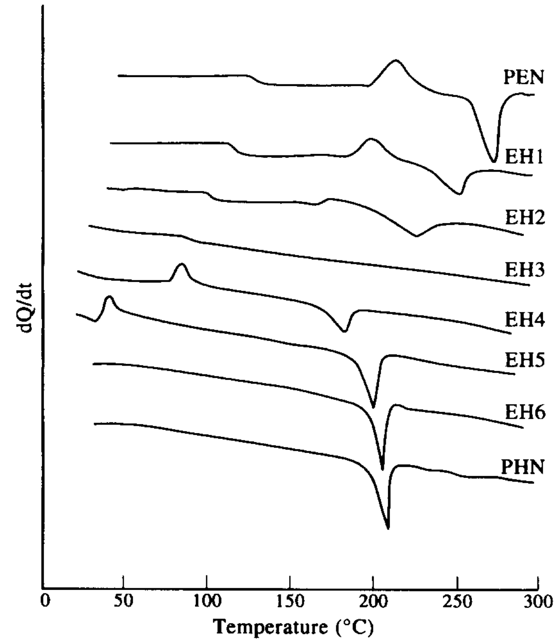

Figure 3 D.s.c. curves of the quenched PEN/PHN copolymers

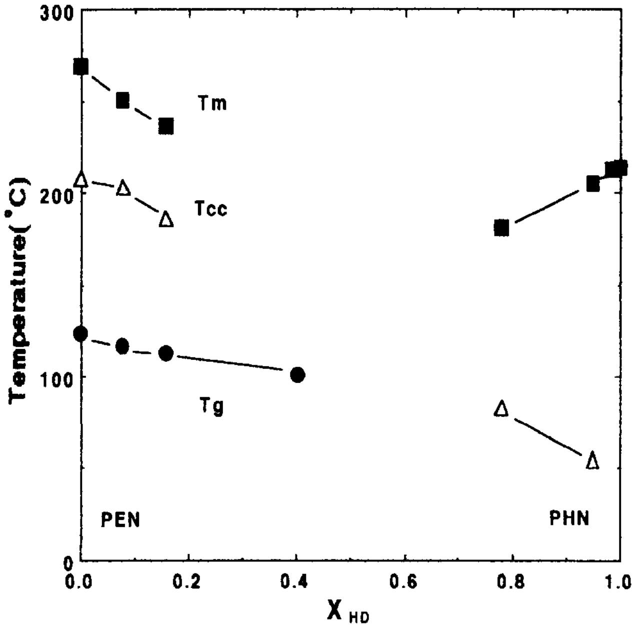

Figure 4 Melting temperature (T_m), crystallization temperature (T_{cc}) and glass transition temperature (T_g) as a function of copolymer composition expressed as HD molar fraction (X_{HD})

In the present work, we are focusing on the relationship between the sequence length (degree of randomness) of the copolyester and the thermal properties. In particular, the melting temperature depression and crystal lattice transition phenomenon may be explained by the crystallizable-sequence length and will be compared with the cohesive energy concept.

Minimum points in thermal properties and cohesive energy

D.s.c. thermograms of the quenched PEN/PHN copolymers[12] are shown in *Figure 3*. For all compositions except EH3, it was observed that a single melting temperature (T_m) occurred at 180–270°C depending upon the EG and HD contents; EH3 showed only a glass transition temperature (T_g) without a cold crystallization temperature (T_{cc}) and T_m. Both T_g and T_{cc} decreased with increasing content of the flexible methylene unit (HD) in the copolymer, as shown in *Figure 4*. The increased HD content of PEN/PHN copolymers will result in a reduced packing density. Thus the PEN/PHN copolymers, which are believed to have very long flexible methylene units, have lower T_g and T_{cc}. On increasing the HD content from EH3 to copolymer homopolymer to PHN the T_g and T_{cc} peaks disappeared, although the peaks may appear below room temperature.

Also, the T_m peak decreased at first and then disappeared for EH3. In order to investigate this problem, the samples of PEN/PHN copolymers were isothermally annealed and crystallized at different temperatures to attain the highest possible degree of crystallinity, as listed in *Table 4*. D.s.c. curves of the annealed PEN/PHN copolymers are shown in *Figure 5*. For all compositions including EH3, a T_m peak was observed. It can be seen that the quenched EH3 could not be crystallized at all from the molten state, but the annealed EH3 could be easily crystallized. Moreover, the T_g and T_m values of the quenched PEN/PHN copolymers were very similar to those of the annealed PEN/PHN samples.

To compare the relationship between the eutectic point revealed by the thermal treatment and a thermodynamic parameter, we investigated the cohesive energy

Table 4 Annealing temperature and degree of crystallinity for PEN/PHN copolymers (annealing time = 2 h)

Polymer	Annealing temperature (°C)	Degree of crystallinity, X_c[a] (%)
PEN	210	63.7
EH1	200	60.4
EH2	200	57.9
EH3	150	47.3
EH4	140	72.7
EH5	150	77.2
EH6	160	74.8
PHN	160	78.0

[a] All X_c values were measured by the density method

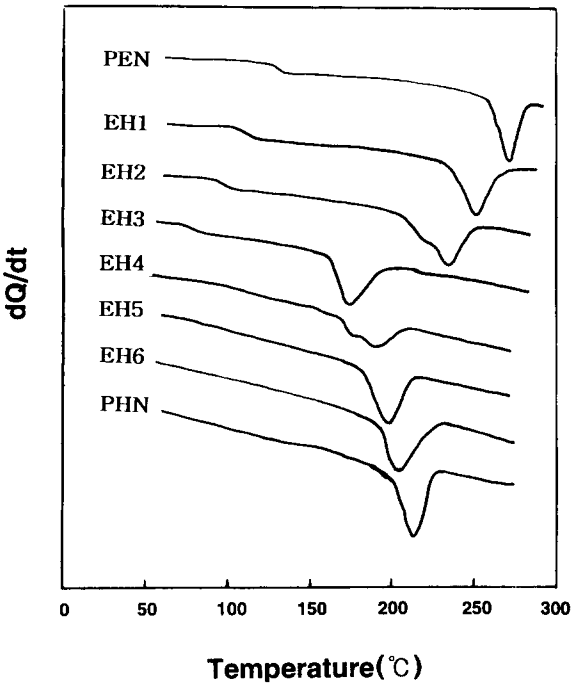

Figure 5 D.s.c. curves of the annealed PEN/PHN copolymers

which expresses the energetic interaction in the molten state prior to crystallization. The cohesive energies of the A and B sequence units for the random copolymer are assumed to be proportional to the copolymer composition. If the cohesive energy of the A (or B) sequence unit is larger than that of the B (or A) sequence unit, only A (or B) sequence units can crystallize, driving the B (or A) sequence units into a non-crystallized region. Also, when the cohesive energies for both the A and B sequence units are equal, $E_A V_A = E_B V_B$, the two units can crystallize separately into each crystal lattice or cocrystallize into a crystal lattice at the composition expressed by:

$$V_A = \frac{E_B}{E_A + E_B} \tag{6}$$

where E_A and E_B are the cohesive energies of A and B sequence units determined by group contribution methods, and V_A and V_B are the volume fractions of A and B sequence units, respectively.

The relationship between the molar fraction at the eutectic point given by experiment and that at which the cohesive energies for A and B sequence units are the same, is shown in *Figure 6*. It is interesting to note that the PEN/PHN copolymer (number 5) deviates a little from the linear relation. Thus, other factors in addition to cohesive energy might play an important role in the T_m depression causing a minimum point in the melting temperature–composition relation. Hence we correlated the sequence length of each of the PEN/PHN copolyesters, determined from ^{13}C n.m.r. spectra, with Flory's equation to explain the above phenomenon.

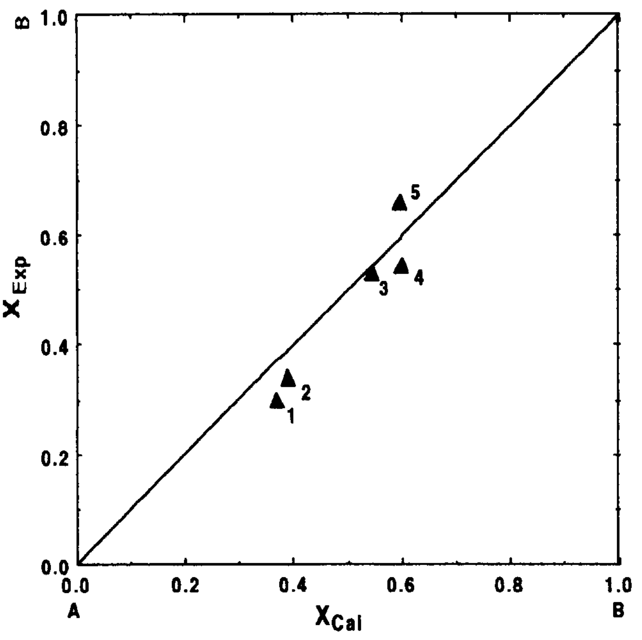

Figure 6 Relationship between the compositions (X_{exp}) at which the melting point shows a minimum experimentally in various random copolymers and those (X_{cal}) at which the cohesive energies for the two components estimated by group contribution methods[14] are identical: (1) poly(ethylene terephthalate-*co*-*p*-oxybenzoate); (2) poly(ethylene terephthalate-*co*-1,4-cyclohexylene dimethylene terephthalate); (3) poly(ethylene terephthalate-*co*-tetramethylene terephthalate); (4) poly(ethylene terephthalate-*co*-trimethylene terephthalate); (5) poly(ethylene 2,6-naphthalate-*co*-hexamethylene 2,6-naphthalate)

Relationship between sequence length and melting temperature depression

From the results of the thermodynamic parameter (cohesive energy), we can conclude that both A and B sequence units cannot crystallize individually or cannot cocrystallize together. If so, when the A sequence units in the random copolymer crystallize but the B sequence units are exactly excluded from crystal formation, the melting behaviour can be expressed as a function of composition. Flory[15] proposed that the melting temperature depression can be expressed by:

$$\frac{1}{T_m} - \frac{1}{T_m^o} = -\left(\frac{R}{\Delta H_u}\right) \ln X_a \tag{7}$$

where T_m and T_m^o are the melting temperatures at the molar fractions (X_a) corresponding to random copolymers and the homopolymer, respectively; R is the gas constant (8.314 J mol^{-1}) and ΔH_u is the enthalpy of fusion per repeating unit: here, ΔH_u was taken as 25 kJ mol^{-1} for PEN and 41 kJ mol^{-1} for PHN. The molar fraction (X_a) also equals the sequence propagation probability (P), thus converting equation (7) into[16]:

$$\frac{1}{T_m} = \frac{1}{T_m^o} = -\left(\frac{R}{\Delta H_u}\right) \ln P \tag{8}$$

For a block copolymer, $P \gg X_a$; but for an alternating copolymer, $P \ll X_a$. The most significant consequence (prediction) of equation (8) is that the melting temperature of a copolymer, in which crystallization of A or B sequence units takes place either in an A polymer or a B polymer crystal with complete rejection of the comonomer units from the crystals, depends only on P and not directly on composition X_a.

The sequence propagation probability (P) can be represented by f_{ENE} in the PEN polymer and f_{HNH} in PHN polymer, given by the fraction of triads centred on naphthalene as listed in *Table 3*:

$$f_{\mathrm{ENE}} = \frac{A_5}{A_5 + A_{11} + A_{17} + A_{22}} \tag{9}$$

$$f_{\mathrm{HNH}} = \frac{A_{11}}{A_5 + A_{11} + A_{17} + A_{22}} \tag{10}$$

Equation (9) can be used when the crystalline units are only PEN polymer, whereas equation (10) is applied when the crystalline units are only PHN polymer. If A and B sequence units could crystallize independently at each crystal formation or cocrystallize together, P could be represented as $P = f_{\mathrm{ENE}} + f_{\mathrm{HNH}}$. Here, P is different with each f_{ENE} or f_{HNH}. However, from the results of the thermodynamic parameter, it is known that when only A sequence units are crystallized P depends on the molar fraction, f_{ENE}, of PEN. Hence, P can be expressed as $P = f_{\mathrm{ENE}}$. When only B sequence units are crystallized, P also can be represented by the molar fraction, f_{HNH}, of PHN.

Figure 7 shows the melting temperatures of the annealed PEN/PHN copolymers at various compositions (black circles and continuous solid line) and those predicted by Flory's theories (curves A and C derived from X_a, curves B and D from P). Melting point depression was observed up to about 60 mol% of HD in the PEN/PHN copolymers. From the T_m behaviour of the annealed PEN/PHN copolymers, the molar fraction exhibiting a minimum in the melting point, the so-called eutectic point, was predicted; that point was at HD content of about 60 mol%. After passing through the eutectic point corresponding to about 60 mol% of HD, an increasing amount of HD raised the melting point of the copolymer. The experimental data are also fitted very well by equation (8) whereas equation (7), which considers only the copolymer composition, gives a smaller melting temperature depression than that observed experimentally.

Considering the relatively good fit of the experimental values to the theoretical line of *Figure 7*, it can be seen that the melting point depression is a result of different sequence distributions and the minimum point in the melting temperature may correspond to the point having the shortest average sequence length in the copolymer composition, not that at which the cohesive energies for the two components (as estimated by the group contribution method) are identical.

X-ray measurements and crystallizable sequence length

WAXD diffractograms for the annealed homopolymers and PEN/PHN copolymers are shown in *Figure 8*. The PEN sample annealed at 210°C crystallizes mainly in the α-modification studied by Buchner *et al.*[11]. For the PEN homopolymer the peak at the diffraction angle of 15.5° is assigned to the 0 1 0 plane while those at diffraction angles of 23.4° and 26.8° correspond to 1 0 0 and $\bar{1}$ 1 0 planes. These peaks are also observed in the copolyesters (EH1, EH2, EH3); consequently the copolymers in the composition range of PEN to EH3 are made up of PEN crystal formations only. On the contrary, the copolymers in the composition range of

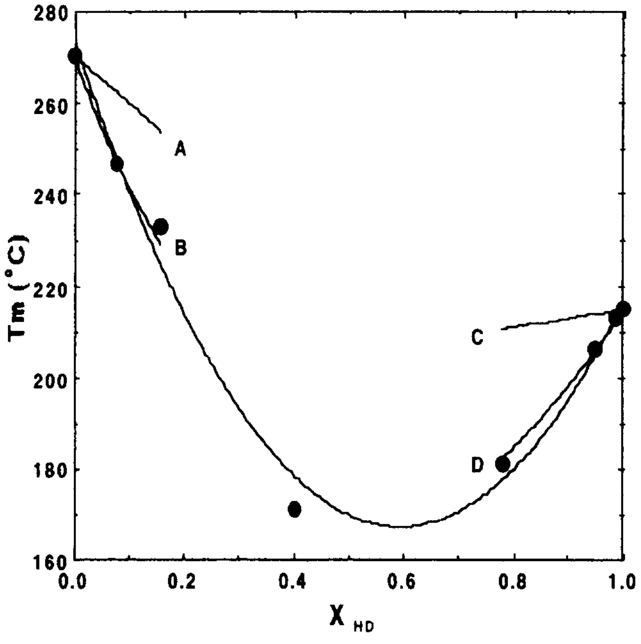

Figure 7 Melting temperatures (T_m) of PEN/PHN copolymers *versus* copolymer composition (X_{HD}): experimental data (●); curves A to D are theoretically predicted by Flory (A and C derived from molar fraction, B and D from sequence propagation probability P)

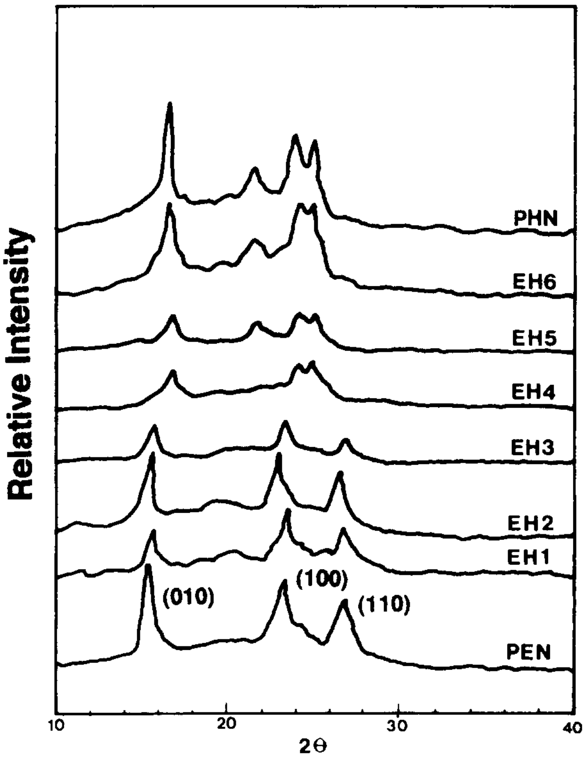

Figure 8 X-ray diffraction patterns of PEN/PHN copolyesters

EH4 to PHN are made up of PHN crystal formations only.

In PEN/PHN copolymers, the block length of ethylene units in EH3 exhibiting PEN crystal structure was $L_{nE} = 1.828$, whereas that of hexamethylene units was $L_{nH} = 1.294$. The block length of ethylene units in EH4 exhibiting the PHN crystal structure was $L_{nE} = 1.211$, whereas that of hexamethylene units was $L_{nH} = 2.151$. As mentioned earlier, sequences of a minimum length are essential for crystallization. Zhu and Wegner asserted that only the average sequence length, excluding shorter and longer sequence length is crystallized; in contrast, Briber and Thomas[7] insisted that all the sequence lengths participate in crystal formation.

Our study of PEN/PHN copolyesters has revealed that the minimum sequence length for PEN crystals may be close to 1.828, while that for PHN crystals is close to 2.151. It can be seen that the incorporation of PEN with PHN in the copolymers results in a weakening of the crystalline intensities of the copolymers. Increasing content of HD in the copolymers also results in a crystal lattice transition at about 40–78 mol% HD (i.e. at a composition between those of EH3 and EH4). It is well accepted that the crystal formation in PEN/PHN copolymers is related to the results of sequence propagation probability (*P*).

From *Figure 8*, the crystal lattice spacings of the PEN/PHN copolymers annealed for 2 h were calculated as a function of copolymer composition and the results are shown in *Figure 9*. With increasing HD content the trends of the *d*-spacings certainly fell into two classes, and also no variation of the unit cell was observed. It can be proved that when only A sequence units in the binary A/B random copolymer crystallize, B sequence units are exactly excluded from crystal formation. This agrees with the WAXD data shown earlier. However, the crystal lattice transitions occurred exactly in the interval between EH3 and EH4. Accordingly, this fact implies that as the content of HD increases, the lattice transition of the unit cell occurs at any composition point (that point may be considered as the eutectic point).

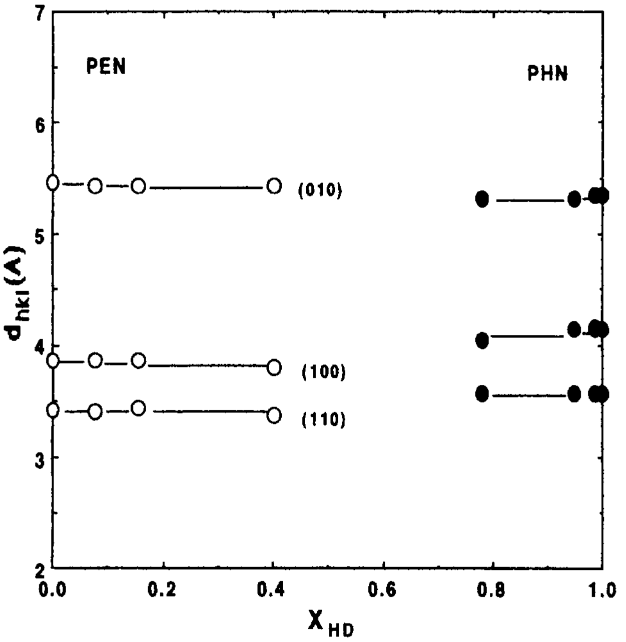

Figure 9 Changes in crystal lattice spacing (d_{hkl}) with copolymer composition (X_{HD})

CONCLUSIONS

The crystallization behaviour of poly(ethylene 2,6-naphthalate-*co*-hexamethylene 2,6-naphthalate) (PEN/PHN) random copolymers has been investigated.

From the T_m behaviour of the PEN/PHN copolymers, it was observed that the molar fraction exhibiting a minimum in the melting point was about 60 mol% HD content. The trends of melting temperatures were fitted very well by sequence propagation probability only. A crystal lattice transition occurred in the composition range between EH3 and EH4, and the copolymers rich in ethylene units formed the crystals with complete rejection of the hexamethylene units. From the results of the crystal lattice spacings it may be concluded that, when only sequences of ethylene units in the PEN/PHN random copolymer are crystallized, sequences of hexamethylene units are exactly excluded from the crystal formation.

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