PII: S0032-3861(97)10213-0

Polymer Vol. 39 No. 22, pp. 5523–5528, 1998

Fine structures of copolyesters containing naphthalene and phenanthrene rings

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(Received 28 March 1997; revised 29 July 1997; accepted 13 October 1997)

Copolyesters composed of poly(ethylene-2,6-naphthalate) and poly(ethylene-2,7-phenanthrate) (PEN/PEP copolymers) with different copolymer compositions were synthesized. The thermal properties and fine structures of the isotropic and oriented samples were investigated using thermal analysis and X-ray diffraction methods. The glass transition temperatures (T_g) of the copolymers increased with increasing molar fraction of the PEP component. The undrawn annealed samples containing 5% PEP (NP5) exhibited X-ray diffraction patterns showing the coexistence of the α and β-polymorphic forms of PEN. In samples containing 10 and 20% PEP (NP10 and NP20), the crystallites were of the β-form of PEN. On the other hand, drawn NP5 and NP10 exhibited the α-form. The WAXD pattern of the drawn NP20 was different from those of the above two samples, and could not be assigned to either the α or the β-form. PEP sequences interfere with the crystallization and have a strong influence on the chain packing mode of the unit cell in the copolymers. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: phenanthrene; poly(ethylene-2,6-naphthalate); poly(ethylene-2,7-phenanthrate))

INTRODUCTION

Poly(ethylene-2,6-naphthalate) (PEN) exhibits excellent mechanical and thermal properties, and has been used as an engineering plastic for films and fibres[1]. The fine structures of PEN have been studied by various authors[2–12]. Recently copolymers composed of PEN and *p*-hydroxybenzoic acid (PHB) or poly(ethylene terephthalate) (PET) have been prepared and characterized[3,13–18]. Copolymerization is an effective method of modifying the properties of polymers.

We have been interested in these copolymers because of their unique thermal properties and fine structures. We synthesized a series of copolyesters composed of PEN and poly(ethylene-9,10-dihydrophenanthrate) (PEHP) with different copolymer compositions, and have investigated their thermal properties and fine structures[19]. As the PEHP chain contains comparatively flat and rigid dihydrophenanthrene rings in the backbone, the PEHP sequences influenced their morphology and thermal properties. With increasing molar fraction of the PEHP component, the T_g of the PEN/PEHP copolymer increased, the T_m slightly decreased and the crystallinity also decreased. The crystal structures of the copolymers were assigned to the α or β-polymorphic forms of PEN. In particular, the annealed samples containing 5% and 10% PEHP exhibited X-ray diffraction patterns showing the coexistence of the α and β-forms. In the case of samples containing 20% PEHP the crystallites were of the β-form. Thus, PEHP sequences interfere with the crystallization of the copolymers and have a strong influence on the chain packing mode of the unit cell in the copolymers.

In our continuing research programme on the relationships between fine structures and copolymer composition for copolyesters, we now report the fine structures of copolyesters composed of PEN and poly(ethylene-2,7-phenanthrate) (PEP) with different copolymer compositions. The PEP chain contains phenanthrene rings in the backbone, which are flatter than the dihydrophenanthrene ring. Thus, it is expected that the PEP sequences will have unique effects on the morphology and thermal properties of the copolymers.

EXPERIMENTAL

Materials and sample preparation

PEN/PEP copolymers with different copolymer compositions were synthesized in our laboratory[20]. The structural formulae of the PEN/PEHP and PEN/PEP copolymers are shown in *Figure 1*. The copolymer compositions and their molecular weights are listed in *Table 1*. These samples are coded as NP5, NP10 and NP20, where the numbers denote the molar fractions of PEP.

The samples were melt-pressed at 290°C, followed by quenching into iced water. These quenched samples were annealed at various temperatures for 2 h in a N_2 purge, and then cooled at 10°C min^{-1} to room temperature. The quenched samples were drawn in an air oven at 150°C to approximately 6 times. After drawing, both ends of the drawn film were fixed with a brass holder, and then it was annealed at 210°C for 1 h.

Viscosity and molecular weight measurements

Viscosity measurements were carried out using a Cannon–Fenske viscometer at 30°C. Molecular weights were determined by size exclusion chromatography in mixed solvents of hexafluoroisopropanol and chloroform (weight ratio = 2:1) with polystyrene calibration using a JASCO HPLC equipped with a Shodex KD-80M column at 40°C.

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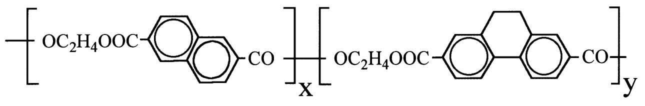
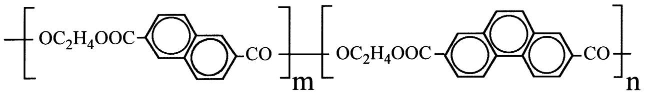
Table 1 Molar fractions, reduced viscosities and molecular weights of copolymers

Code name	PEN (mol %)	PEP (mol %)	Viscosity* η_{sp}/°C	$\bar{M}_w$*	$\bar{M}_w/\bar{M}_n$*
NP5	95	5	0.745	2.55×10^4	2.60
NP10	90	10	0.720	2.37×10^4	2.73
NP20	80	20	0.696	2.17×10^4	2.70

*Solvent; hexafluoroisopropanol:chloroform = 2:1.



PEN/PEHP copolymer



PEN/PEP copolymer

Figure 1 Structural formulae of PEN/PEHP and PEN/PEP copolymers

Thermal properties

Thermogravimetric analyses of the copolymer samples were performed on a Seiko SSC/5200 (TG/DTA 220) thermal analyser at a heating rate of 10°C min^{-1}. Thermal properties of the samples were investigated using a differential scanning calorimeter (DSC 200, Seiko Instruments and Electronics Ltd) under a N_2 purge; the heating and cooling rates were 20°C min^{-1} and 10°C min^{-1}, respectively.

X-ray diffraction measurements

X-ray diffraction experiments were carried out on a RAD-rA diffractometer (Rigaku Denki Co. Ltd) equipped with a heating device. Nickel-filtered CuKα radiation was employed. Wide-angle X-ray diffraction (WAXD) traces were recorded by a scintillation counter system with a 1.0 mm diameter pin-hole collimator and a 1 × 1° receiving slit. The WAXD traces were obtained by a step-scanning method: the step width and counting time were programmed for steps of 0.05° every 4 s. The WAXD photographs were taken by a flat Laue camera with a 0.5 mm diameter pin-hole collimator and by a cylindrical camera with 50 mm camera radius and a 1 mm diameter pin-hole collimator.

RESULTS AND DISCUSSION

Thermal properties of PEN/PEP copolymers

The copolymers exhibited fairly high thermal stability; their thermal degradation temperatures were approximately 415°C, close to that of PEN and PEN/PEHP copolymers[19]. The samples quenched from the melt exhibited a dark field under a polarizing optical microscope with crossed polarizers and their X-ray scattering patterns showed only an amorphous scattering ring for all copolymer compositions. *Figure 2* shows d.s.c. thermograms of the quenched samples. The baseline shift corresponding to the T_g, exothermic and endothermic peaks were observed on the d.s.c. trace of NP5. The exothermic peak on heating is attributed to cold crystallization. The d.s.c. profile was similar to that of PEN. The enthalpy changes of both peaks are much smaller than those of PEN. There was no peak in the d.s.c. traces of NP10 and NP20, where only a large baseline shift was observed. Cold crystallization hardly occurred in these samples. The presence of PEP sequences decreased the crystallinity, because the copolymers are random copolymers prepared by transesterification. The tendency is similar to that of PEN/PEHP copolymers[19].

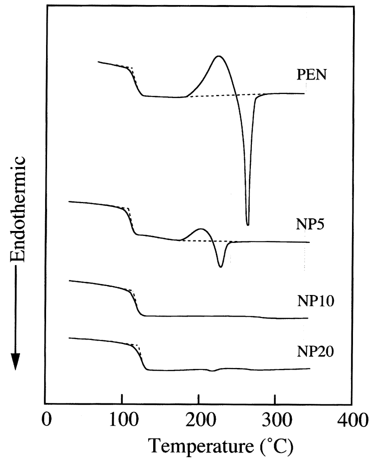


Figure 2 D.s.c. curves of the copolymers quenched into iced water from 290°C

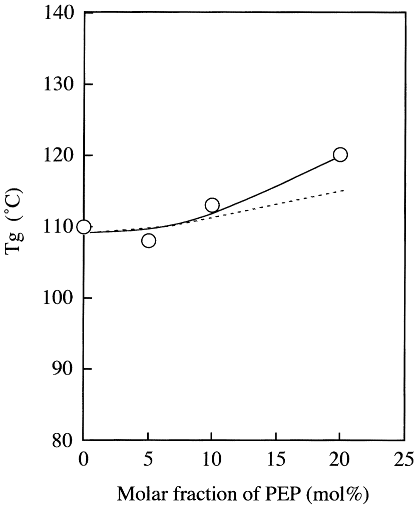


Figure 3 Change in T_g of the copolymer and PEN homopolymer samples quenched into iced water from the melt against molar fraction of PEP. Dotted line denotes the change in T_g of PEN/PEHP copolymers

Values of T_g increased monotonically with increasing molar fraction of the PEP component in the copolymers, as shown in *Figure 3*. The change in T_g of PEN/PEHP copolymers[19] is indicated by the dotted line. The increase in T_g of the PEN/PEP copolymer is larger than the PEN/PEHP copolymer at higher molar factions. Thus, flatter phenanthrene rings largely lower the mobility of their backbones.

Annealing effects of copolymers on the thermal properties

Figure 4 shows the d.s.c. thermograms of undrawn samples annealed at various temperatures above 150°C for 2 h. The d.s.c. profiles of the samples annealed below 150°C remained almost unchanged, i.e. they were similar to those of the quenched samples. An exothermic peak appeared in each sample annealed at 150°C. No exothermic peak was observed in any sample annealed above 180°C, because the annealing treatment increased their crystallinities. In these d.s.c. traces, small endothermic peaks were seen at the low

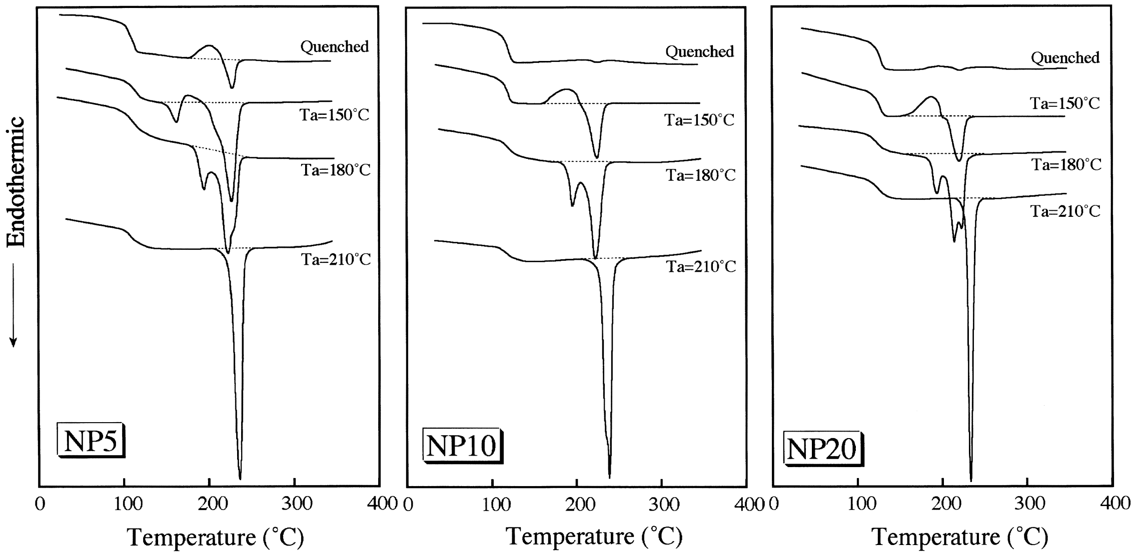


Figure 4 D.s.c. thermograms of the copolymer annealed at various temperatures for 2 h

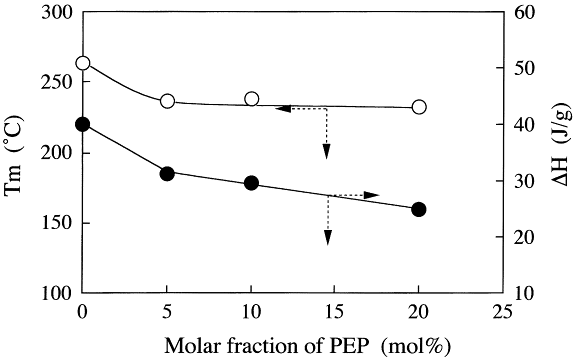


Figure 5 Changes in T_m and ΔH of the copolymers annealed at 21°C, 2 h

temperature side of the larger peak, which could be associated with thermodynamically unstable crystallites grown by the annealing treatment. The peak shifted to higher temperature with increasing T_g. Finally, only one large and sharp endothermic peak appeared in each sample annealed at 210°C. These thermal behaviours are analogous to those of the PEN/PEHP copolymer[19].

Figure 5 represents changes in T_m and ΔH of the samples annealed at 210°C against molar fraction of PEP. Both T_m and ΔH decreased with increasing PEP, i.e. increasing PEP lowered the crystallinity of the copolymers. Random copolymer sequences and bulky phenanthrene rings are considered to interfere with the rearrangement of the polymer chains during annealing.

Fine structures of PEN/PEP copolymers

The WAXD traces of the above annealed samples are shown in *Figures 6–8*. The WAXD profile of NP5 annealed at 150°C was similar to that of the α-form of PEN[5], which is assigned to a triclinic crystal form[2]. The lattice constants of the α-form PEN are $a = 0.651$ nm, $b = 0.575$ nm, $c = 1.320$ nm, $\alpha = 81.33°$, $\beta = 144°$, $\gamma = 100°$[2]. The $(010)_\alpha$, $(100)_\alpha$ and $(\bar{1}10)_\alpha$, which are typical reflections of the α-form, were observed at 15.7°, 23.3° and 27.0°, respectively, in *Figure 6*. The d-spacings of all reflections observed in NP5 were consistent with the theoretical values estimated from the above lattice constants of the α-form. Accordingly, the crystallites formed in this sample are composed of PEN sequences.

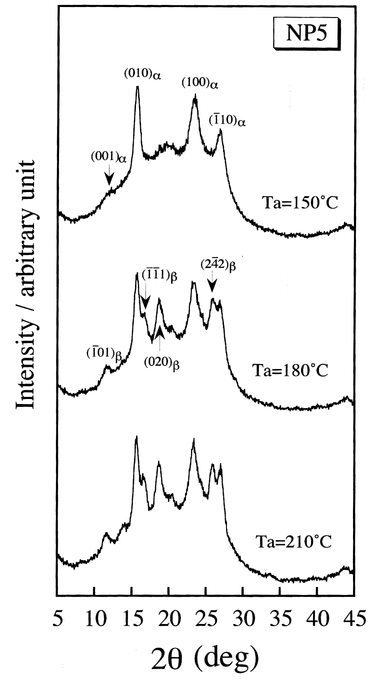


Figure 6 WAXD traces of NP5 annealed at various temperatures for 2 h

On the other hand, the WAXD profile of NP5 annealed at 180°C was different from that of NP5 annealed at 150°C. PEN exhibits another crystal modification, the triclinic β-form[5]. The lattice constants of the β-form are $a = 0.926$ nm, $b = 1.559$ nm, $c = 1.273$ nm, $\alpha = 121.6°$, $\beta = 95.57°$, $\gamma = 122.52°$[5]. The formation of these crystal forms is dependent on the annealing conditions[5]. In NP5 annealed at 180°C, there were some reflections inconsistent with those of the α-form. These reflections could be assigned to those of the β-form: the $(\bar{1}01)_\beta$, $(\bar{1}\bar{1}1)_\beta$, $(020)_\beta$ and $(2\bar{4}2)_\beta$, typical reflections for the β-form, which were observed at 11.6°, 16.5°, 18.6° and 25.6°, respectively. Thus, the α and β-form crystallites coexisted in the sample.

The WAXD pattern of the sample annealed at 210°C also indicated coexistence of the α and β-form crystallites. The

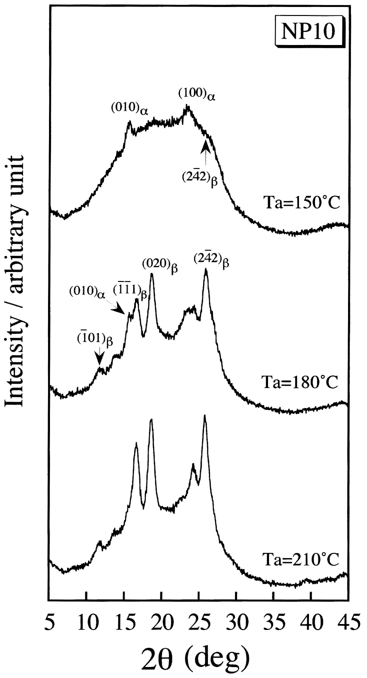


Figure 7 WAXD traces of NP10 annealed at various temperatures for 2 h

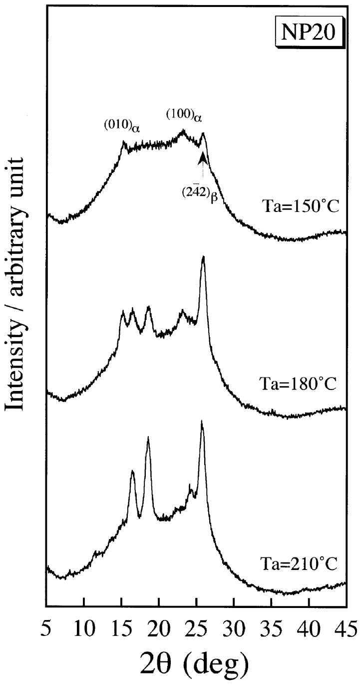


Figure 8 WAXD traces of NP20 annealed at various temperatures for 2 h

intensities of the β-form reflections increased, while those of the α-form reflections decreased; for instance, the intensity of $(010)_\alpha$ decreased and that of $(\bar{1}\bar{1}1)_\beta$ increased correspondingly. Thus, annealing at higher temperatures enhanced the formation of the β-form crystallites. In PEN homopolymer, the β-form crystallites grew on annealing at higher temperatures close to the T_m[5].

The WAXD patterns of annealed NP10 samples are shown in *Figure 7*. The intensities of crystalline reflections were lower than those of NP5 annealed at 150°C. Crystallites could not be grown by annealing at 150°C, unlike NP5. This also indicates that introduction of PEP sequences results in a lower crystallinity. The above results are consistent with the d.s.c. measurements mentioned in the previous section. Most of the reflections observed were assigned to those of the β-form. The intensities of the β-form reflections increased with annealing temperature. On the contrary, α and β-form crystallites coexisted in PEN/PEHP copolymer containing 10 mol% PEHP[19]. Thus, the PEP sequence enhanced the formation of β-form crystallites as compared with PEHP.

The change in WAXD patterns of NP20 shown in *Figure 8* was similar to that of NP10. The increase in the PEP component enhanced the formation of the β-form under these experimental conditions. Such a polymorphism induced by copolymerization also occurs in PEN/PEHP copolymer[19] and other copolymers[3,18].

As discussed, the PEP sequences in the molecular chains interfere with the crystallization and formation of the α-form crystallites. The rigidity of phenanthrene rings lowers the mobility of the backbones and the self-diffusion of the copolymer chains during crystallization. Since the X-ray reflections observed in all copolymer samples were assigned to the α-form or β-form of PEN, the crystallites were probably composed of PEN sequences. However, PEP sequences have a profound influence on the chain packing mode of the unit cell, compared with PEHP sequences. This is seemingly due to the flatter phenanthrene rings which resemble naphthalene rings. The effects of the phenanthrene rings on the fine structures were investigated using oriented copolymer samples in the next section.

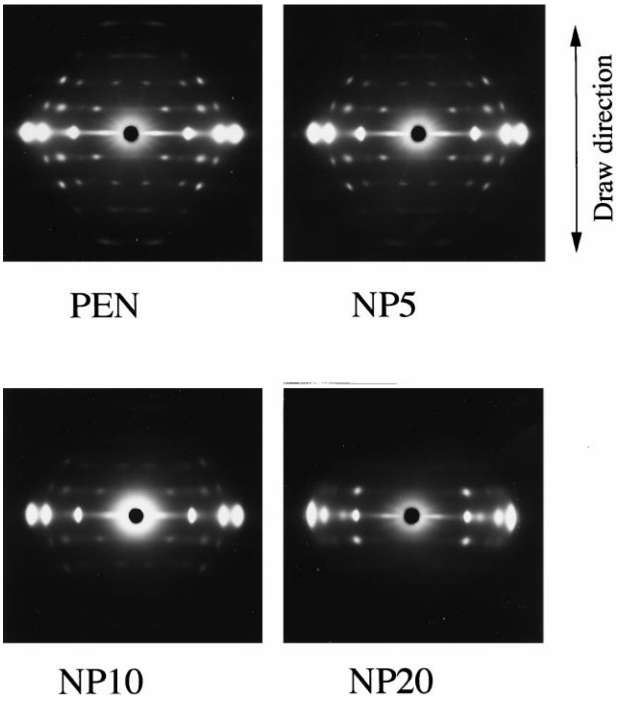


Figure 9 WAXD patterns of drawn PEN/PEP copolymer and PEN films. The films were drawn to approximately 6 times at 160°C and then annealed at 210°C for 1 h

Fine structures of oriented PEN/PEP copolymers

The quenched films were drawn at 150°C to approximately 6 times. They were annealed at 210°C for 1 h, because as-drawn samples exhibited diffuse fibre patterns due to low crystallinity. Their WAXD photographs are shown in *Figure 9*. The draw direction (fibre axis) is indicated by the arrow. A lot of reflections were observed in these photographs. The number of reflections decreased and the reflections became diffuse with increasing the PEP

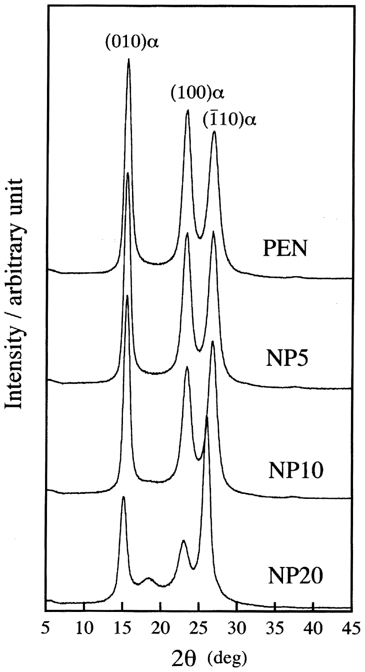


Figure 10 Equatorial intensity profiles of the WAXD patterns from the drawn PEN/PEP copolymer and PEN films. The films were drawn at 150°C and then annealed at 210°C

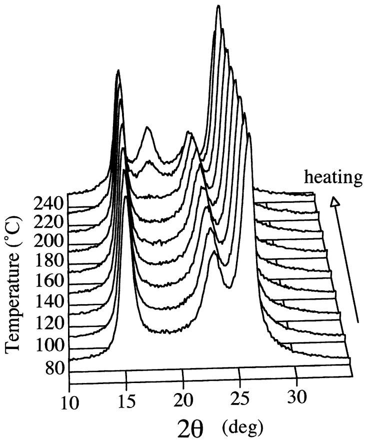


Figure 11 Change in equatorial intensity profiles of WAXD patterns from the drawn NP20 films during heating process

Table 2 d-spacings of the drawn PEN/PEP copolymer films. The films were drawn to approximately 6 times at 150°C and then annealed at 210°C for 1 h

α-crystal of PEN calc.		NP5 obs.			NP10 obs.		
d	hkl	*d*	int.	layer	*d*	int.	layer
7.76	001	7.73	s	1	7.74	s	1
6.14	$10\bar{2}$	6.17	m	2	6.18	m	2
5.66	010	5.67	vs	0	5.69	vs	0
4.57	$\bar{1}12$	4.56	s	2	4.60	s	2
4.54	$0\bar{1}1$	4.53	s	1	4.54	s	1
4.26	$10\bar{3}$	4.22	m	3	4.22	m	3
3.88	002	3.88	vs	2	3.88	vs	2
3.81	100	3.80	vs	0	3.81	vs	0
3.74	$\bar{1}\bar{1}1$	3.76	s	1	3.79	s	1
3.63	$\bar{1}13$	3.60	m	3	3.59	m	3
3.30	$\bar{1}10$	3.32	vs	0	3.33	vs	0
3.07	$\bar{2}04$	3.10	s	4	3.11	s	4
2.83	020	2.84	vw	0			
2.69	$\bar{1}21$	2.66	m	1	2.66	m	1
2.51	$\bar{1}23$	2.49	w	3	2.49	w	3
2.47	$1\bar{1}1$	2.42	m	1	2.42	m	1
2.38	$\bar{1}20$	2.39	vw	0	2.40	w	0
2.24	$21\bar{5}$	2.31	m	5	2.26	m	5
2.08	$\bar{2}16$	2.07	m	6	2.07	m	6
2.08	$\bar{1}15$	2.06	s	5	2.06	s	5
2.08	$\bar{2}\bar{1}1$	2.09	vw	1	2.10	vw	1
1.91	$\bar{2}\bar{1}6$	1.92	vw	6	1.92	vw	6
1.85	$\bar{2}10$	1.85	m	0	1.85	s	0
1.84	031	1.84	vw	1			
1.72	$\bar{1}\bar{3}1$	1.72	vw	1	1.72	vw	1
1.65	$\bar{2}20$	1.65	w	0	1.65	w	0

composition. This suggests that the crystallinity and crystalline order for the copolymers decreased with increasing PEP.

The WAXD intensity profiles on the equator are shown in *Figure 10*. The profiles of NP5 and NP10 were similar to that of PEN. On the other hand, the profile of NP20 is different from those of NP5 and NP10. The reflection observed at $2\theta \approx 27°$ corresponding to $(110)_\alpha$ shifted to a lower angle. Moreover, the reflection intensity was much higher than the others. The reflection at $2\theta \approx 23°$ corresponding to $(100)_\alpha$ also shifted to a lower angle.

The reflections observed in the WAXD photographs of the oriented samples were indexed using the lattice parameters of the α-form and the β-form of PEN. The results are summarized in *Table 2*. Most of the observed d-spacings for the drawn NP5 and NP10 samples were consistent with the calculated d-spacings of the α-form, within experimental error. This implies that the α-form crystallites existed in both oriented samples. Few reflections of the β-form were observed in both oriented samples. This result is different from that of undrawn samples described in the previous section. The finding is consistent with drawn PEN samples[10,11,21]. However, the β-form crystallites were formed in the PEN fibres spun by high-speed spinning methods[11]. The crystal form in the fibres depends on the spinning speeds[12].

On the other hand, X-ray reflections of the drawn NP20 could not be assigned to the α and β-forms. A different crystal form occurred in NP20 by the drawing procedure. *Figure 11* illustrates the change in WAXD intensity profiles on the equator for drawn NP20 during the heating process. The starting sample was an as-drawn film. The d-spacings of the reflections increased linearly with temperature by thermal expansion, and they decreased reversibly on cooling by thermal shrinkage. A new reflection appeared above 220°C at $2\theta \approx 18°$, which is close to the (020) of the β-form. The WAXD profile is similar to that of the fibre sample spun by high-speed spinning, which exhibited the coexistence of α and β-form crystallites[21]. The reflection remained on cooling. Finally, the WAXD profile of the cooled sample was consistent with that of the annealed NP20 shown in *Figure 10*. This implies that the polymorphism occurred on heating in NP20. Thus, it is hard to analyse the structure of drawn NP20. Further, the crystal structures in the drawn samples were different from the isotropic samples, although the PEP sequences had an influence on the packing mode of the crystal unit cell. The chain packing mode in the drawn sample is related to the conformation of the oriented PEN/PEP copolymer chains. NP20 has high crystallinity in spite of 20 mol% of PEP, and exhibits complicated polymorphism as described above. This suggests that the PEP sequences are taken in the crystallites of NP20. The effects of structural changes in oriented samples on the thermal and mechanical properties are currently under study.

CONCLUSION

The T_g of the PEN/PEP copolymer increased with increasing molar fraction of PEP. Flatter phenanthrene ring largely lowers the mobility of their backbones. The enthalpy changes of exothermic and endothermic peaks decreased, because of their low crystallinity by introducing PEP. The α and β-form crystallites coexisted in the annealed isotropic samples containing 5% PEP, and annealing at higher temperatures enhanced the formation of the β-form crystallites. The crystallites in the unoriented samples containing 10 and 20% PEP were assigned to the β-form. PEP sequences interfered with the formation of α-form crystallites. In drawn NP5 and NP10 samples, on the other hand, α-form crystallites formed with no reflection of the β-form. The formation of crystallites in the oriented samples are different from the isotropic samples. The crystallites of oriented NP20 could not be assigned to the α and β-forms. The chain packing mode in the drawn sample is related to the conformation of the oriented PEN/PEP copolymer chains. PEP sequences interfere with the crystallization and have a strong influence on the chain packing mode of the unit cell in the copolymers. It is possible that the PEP sequences are taken in the crystallites.

REFERENCES

1. Ouchi, I. and Noda, H., *SEN-I GAKKAISHI*, 1973, **29**, P405.
2. Mencik, Z., *Chemicky Prumysl.*, 1967, **17**, 78.
3. Zachmann, H. G., Wiswe, D., Gehrke, R. and Riekel, C., *Makromol. Chem. Suppl.*, 1985, **12**, 175.
4. Cheng, S. Z. D. and Wunderlich, B., *Macromolecules*, 1988, **21**, 789.
5. Buchner, S., Wiswe, D. and Zachmann, H. G., *Polymer*, 1989, **30**, 480.
6. Ghanem, A. M. and Porter, P. S., *J. Polym. Sci. Polym. Phys. Ed.*, 1989, **27**, 2587.
7. Cakmak, M., Wang, Y. D. and Simhambhatla, M., *Polym. Eng. Sci.*, 1990, **30**, 721.
8. Ito, M., Honda, K. and Kanamoto, T., *J. Appl. Polym. Sci.*, 1992, **46**, 1013.
9. Nakamae, K., Nishino, T., Tada, K., Kanamoto, T. and Ito, M., *Polymer*, 1993, **34**, 3322.
10. Murakami, S., Nishikawa, Y., Tsuji, M., Kawaguchi, A., Kohjiya, S. and Cakmak, M., *Polymer*, 1995, **36**, 291.
11. Nagai, A., Murase, Y., Kuroda, T., Matsui, M., Mitsuishi, Y. and Miyamoto, T., *SEN-I GAKKAISHI*, 1995, **51**, 470.
12. Iizuka, N. and Yabuki, K., *SEN-I GAKKAISHI*, 1995, **51**, 463.
13. Jackson, W. J. Jr, *Macromolecules*, 1983, **16**, 1027.
14. Ezquerra, T. A., Balta-Calleja, F. J. and Zachmann, H. G., *Acta Polymer*, 1993, **44**, 18.
15. Chen, D. and Zachmann, H. G., *Polymer*, 1991, **32**, 1612.
16. Calleja, F. J. B., Cruz, C. S., Chen, D. and Zachmann, H. G., *Polymer*, 1991, **32**, 2252.
17. Cruz, C. S., Calleja, F. J. B. and Zachmann, H. G., *J. Mater. Sci.*, 1992, **27**, 2161.
18. Lu, X. and Windle, A. H., *Polymer*, 1995, **36**, 451.
19. Yonetake, K., Yashiro, H., Ueda, M. and Masuko, T., *Polymer*, 1997, **38**, 2461.
20. Jpn., Kokai Tokkyo Koho, 1994, JP 06 119, 526.
21. Nagai, A., Murase, Y., Kuroda, T., Matsui, M., Mitsuishi, Y. and Miyamoto, T., *Sen-i gakkaishi*, 1995, **51**, 478.