

Fine structures of copolyesters containing naphthalene and 9,10-dihydrophenanthrene rings

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Copolyesters composed of poly(ethylene 2,6-naphthalate) and poly(ethylene 9,10-dihydrophenanthrate) (PEN/PEHP copolymers) with different copolymer compositions were synthesized and their thermal properties and fine structures were investigated using thermal analysis and X-ray diffraction methods. T_g s of the copolymers increased with increasing molar fraction of the PEHP component; on the other hand, their T_m s decreased slightly and their crystallinity also decreased. The crystallites in the copolymers were assigned to the α - or β -polymorphic forms of PEN. In particular, 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, the crystallites formed in the copolymers are composed of PEN sequences, while PEHP sequences remain in the amorphous regions. PEHP sequences interfere with the crystallization of PEN/PEHP copolymers and have a strong influence on the chain packing mode of the unit cell in the copolymers. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Poly(ethylene 2,6-naphthalate) (PEN) exhibits excellent mechanical and thermal properties, and has been used for engineering plastic films and fibres¹. PEN molecules are stiffer than those of poly(ethylene terephthalate) (PET) because of replacement of flat and rigid naphthalene rings¹. The fine structures of PEN have been studied by various authors^{2–10}. PEN exhibits a polymorphism of two different crystal modifications which correspond to triclinic α -form and β -form. The lattice constants of the α - and β -forms are $a = 0.651$ nm, $b = 0.575$ nm, $c = 1.320$ nm, $\alpha = 81.33^\circ$, $\beta = 1.44^\circ$, $\gamma = 100^\circ$ ², and $a = 0.926$ nm, $b = 1.559$ nm, $c = 1.273$ nm, $\alpha = 121.6^\circ$, $\beta = 95.57^\circ$, $\gamma = 122.52^\circ$ ⁵, respectively. The formation of these forms is dependent on the annealing conditions⁵.

Recently, copolymers composed of PEN and *p*-hydroxy benzoic acid (PHB) or PET have been prepared and characterized^{3,11–15}. PEN/PHB copolymer formed a lattice of the crystallite which was assigned to one of the two crystal modifications of PEN³. Only 20 mol% PHB was required to make the copolyester liquid-crystalline¹¹, and those containing more than 50% PHB were completely liquid-crystalline¹³. In the case of PEN/PET copolymer, it was found that PET sequences crystallized in the samples containing more than 70% PET; in contrast, PEN sequences crystallized in the α -polymorphic form of PEN. Other samples containing 50 and 60% PEN exhibited completely amorphous properties. Furthermore, the structures of random copolyesters of PEN and PET were investigated in detail by use of X-ray diffraction¹⁶. The copolyesters

showed different crystal structures in two different composition ranges and the lattice parameters of each of these structures changed with the composition¹⁶.

In this study, copolyesters composed of poly(ethylene 2,6-naphthalate) and poly(ethylene 9,10-dihydrophenanthrate) (PEHP) with different copolymer compositions were synthesized and the thermal properties and fine structures of the PEN/PEHP copolymers were investigated using thermal analysis and X-ray diffraction methods. The PEHP chain contains comparatively flat and rigid dihydrophenanthrene rings in the backbone, so that it is possible that the PEHP sequences have some effects on the morphology and thermal and mechanical properties of the copolymers; in particular, they will enhance their moduli and glass transition temperatures. This paper focuses on the influence of the dihydrophenanthrene rings on the thermal properties and crystallization behaviour of the copolymers.

EXPERIMENTAL

Materials and sample preparation

PEN/PEHP copolymers with different copolymer compositions were synthesized in our laboratory¹⁷. The structural formula is shown in *Figure 1*. The copolymer compositions and their molecular weights are listed in *Table 1*. These samples are coded as NHP5, NHP10, NHP20, where the numbers denote the volume fraction of PEHP. PEN homopolymer was supplied by Teijin Co Ltd.

The samples were melt-pressed at 290°C, followed by quenching in ice-water. These quenched samples were annealed at various temperatures for 2 h in an N₂ purge, and then cooled at 10°C min⁻¹ to room temperature.

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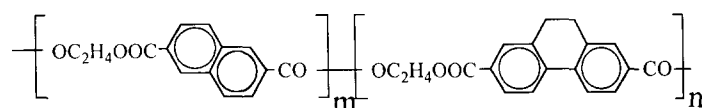


Figure 1 Structural formula of PEN/PEHP copolymer

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

Code name	PEN (mol%)	PEHP (mol%)	Viscosity ^a η_{sp}/C	\bar{M}_w^a	\bar{M}_w/\bar{M}_n^a
NHP5	95	5	0.847	3.85×10^4	2.68
NHP10	90	10	0.824	3.84×10^4	2.69
NHP20	80	20	0.827	2.95×10^4	2.62

^a Solvent: hexafluoro isopropanol: chloroform = 2:1; $\eta - sp$ is specific viscosity and C is concentration of solutions

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 a mixed solution of hexafluoro isopropanol and chloroform (weight ratio = 2:1) with polystyrene calibration, using a JASCO HPLC equipped with a Shodex KD-80M column at 40°C.

Thermal properties

Thermal analyses of the copolymer samples were performed on a Seiko SSC/5200 (TG/DTA 220) thermal analyzer at a heating rate of 10°C min⁻¹ for thermogravimetric analysis.

The thermal properties of the samples were investigated using a differential scanning calorimeter (DSC 200; Seiko Instruments & Electronics Ltd) under an N₂ 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 CuK α 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 1 \times 1° receiving slit. The diffractometry was performed in transmission. The WAXD traces were obtained by a step-scanning method: the step width and fixed time were programmed for steps of 0.05° every 4s. The WAXD photographs were taken by a flat Laue camera with a 0.5 mm diameter pin-hole collimator.

RESULTS

Thermal properties of quenched PEN/PEHP copolymers

The copolymers exhibited comparatively high thermal stability, as shown in Figure 2. Their thermal degradation temperatures were approximately 415°C, close to that of PEN homopolymer.

Figure 3 shows d.s.c. thermograms of the samples quenched in ice-water from the melt. Base line shifts corresponding to glass transition (T_g), exothermic and endothermic peaks were observed on the d.s.c. traces of NHP5 and NHP10 samples. Their d.s.c. profiles were similar to that of PEN. On the other hand, there was no

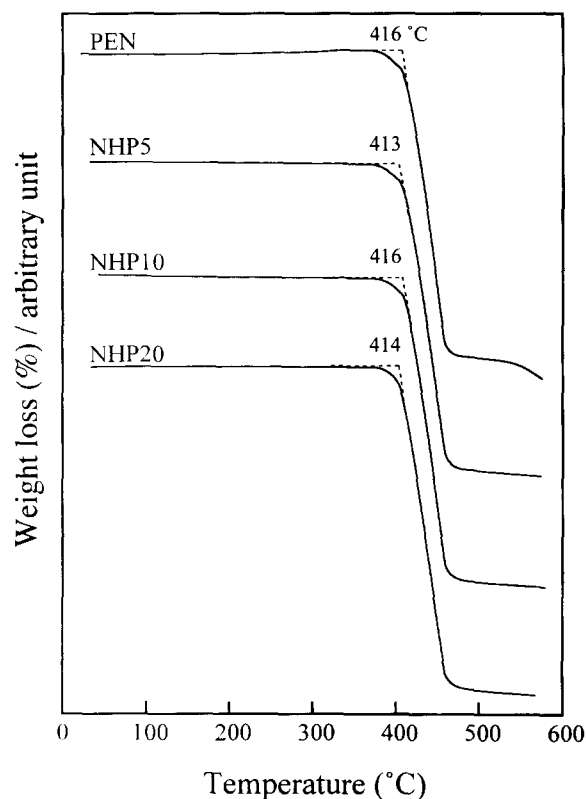


Figure 2 T.g.a. curves of NHP5, NHP10, NHP20 and PEN

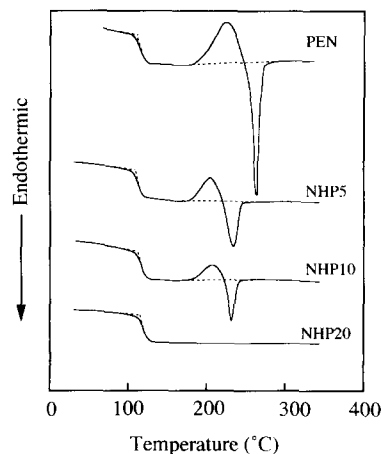


Figure 3 D.s.c. traces of the PEN/PEHP copolymers quenched into ice-water from 290°C

peak in the d.s.c. trace of NHP20, where only a large base line shift was observed. The T_g temperatures increased monotonically with increasing molar fraction of PEHP component in the copolymers, as shown in Figure 4. Thus, bulky 9,10-dihydrophenanthrene rings lower the mobility of their backbones.

The enthalpy changes of exothermic and endothermic peaks (ΔH_c and ΔH_m) were almost the same in each sample. The exothermic peak on heating is attributed

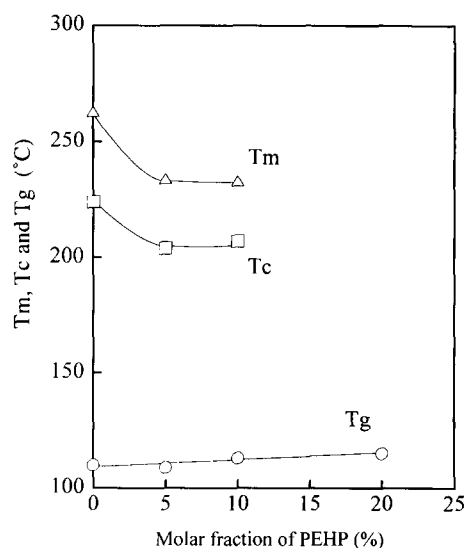


Figure 4 Changes in T_m , T_c and T_g of copolymers and PEN homopolymer samples quenched into ice-water from the melt versus molar fraction of PEHP

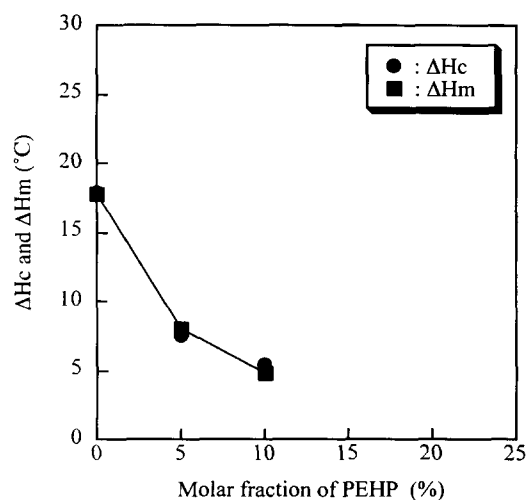


Figure 5 Changes in ΔH_c and ΔH_m of quenched copolymers and PEN versus molar fraction of PEHP: ●, ΔH_c ; ■, ΔH_m

to cold crystallization. This means that the quenched samples were amorphous. Additionally, the quenched samples exhibited a dark field under the polarizing optical microscope with crossed polarizers and their X-ray scattering patterns showed only an amorphous scattering pattern in spite of the different copolymer compositions.

The values of ΔH_c and ΔH_m were smaller than those of PEN homopolymer. Both of them became smaller with increasing molar fraction of PEHP, as shown in Figure 5. In particular, no peak appeared in the d.s.c. curve of NHP20; that is, cold crystallization hardly occurred in NHP20. Consequently, crystallinity of the copolymers was decreased by presence of PEHP sequences. This can be understood from the following reasoning. As transesterification is a statistical copolymerization which cannot control comonomeric sequence, the copolymers are considered to be random copolymers. The random sequences of the copolymer chains cannot make a regular chain conformation, so they interfere with the crystallization. Furthermore, as bulky 9,10-dihydrophenanthrene rings lower the mobility of the backbones as described above, they disturb the self-diffusion of the copolymer chains during crystallization.

Annealing effects of copolymers on the thermal properties

Figure 6 represents the d.s.c. thermograms of copolymer 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, and were similar to those of the quenched samples. An exothermic peak appeared in each sample annealed at 150°C. It is evident that these samples had comparatively low crystallinity. On the other hand, there was no exothermic peak in any sample annealed at 180°C.

Small endothermic peaks were seen at the low temperature side of larger peak, corresponding to T_m , in the samples annealed at 150°C and 180°C. The small peaks occurred at 10–20°C higher than the annealing temperatures. Thus the peaks could be associated with the thermodynamically unstable crystallites grown by the annealing treatment. The peak shifted to higher temperature with increasing T_a . Finally, only one large

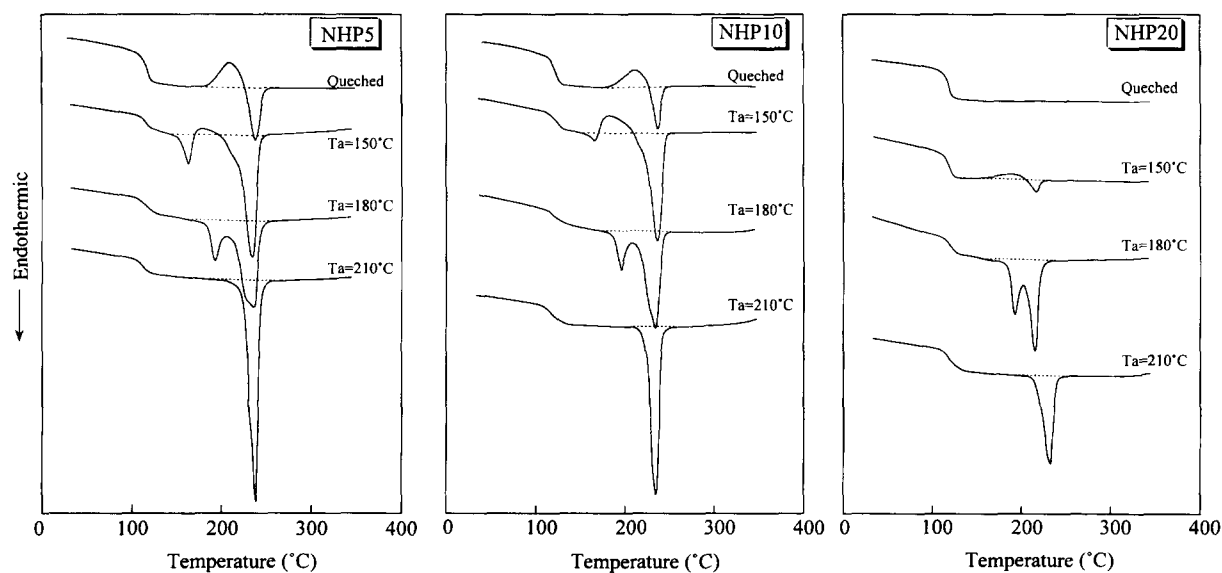


Figure 6 D.s.c. thermograms of copolymer annealed at various temperatures for 2 h

and sharp endothermic peak was obtained in each sample annealed at 210°C.

T_g of annealed NHP20 samples were the highest among those of the copolymers, but decreased with decreasing molar fraction of PEHP over the whole annealing temperature range. The T_g of each sample decreased with increasing annealing temperature, as shown in Figure 7. This implies that annealing treatment relaxed the molecular chains in the amorphous region. Such an annealing effect was observed in PEN homopolymer⁴. The decrease in T_g was extremely small in NHP20, because rigid PEHP sequences are rich in this sample.

Figure 8 shows changes in T_m and ΔH of the samples annealed at 210°C against molar fraction of PEHP. Both T_m and ΔH decreased with increasing PEHP; that is, increasing PEHP lowered the crystallinity of the copolymers.

Fine structures of PEN/PEHP copolymers

The WAXD traces of above annealed samples are shown in Figures 9–11. PEN exhibits polymorphism: it has two different crystal modifications which are assigned to triclinic α -form² and β -form⁵, as described above. The WAXD profile of NHP5 annealed at 150°C was similar to that of the α -form of PEN⁵. (010) _{α} , (100) _{α} and ($\bar{1}10$) _{α} , which are typical reflections of the α -form, were observed at 15.7°, 23.3° and 27.0°, respectively, in Figure 9. The d -spacings of all reflections observed in

NHP5 were consistent with the theoretical values estimated from the lattice constants of the α -form. Accordingly, the crystallites formed in this sample are composed of PEN sequences while PEHP sequences remained in the amorphous regions.

On the other hand, the WAXD profile of NHP5 annealed at 180°C was not identical with that of the α -form, as shown in Figure 9. The reflections which were inconsistent with those of the α -form could be assigned to those of the β -form of PEN. They were ($\bar{1}01$) _{β} , ($\bar{1}\bar{1}1$) _{β} , (020) _{β} and (242) _{β} , typical reflections for the β -form, and were observed at 11.6°, 16.5°, 18.6° and 25.6°, respectively, in Figure 9. This finding suggests that the α - and β -form crystallites coexisted in this annealed sample.

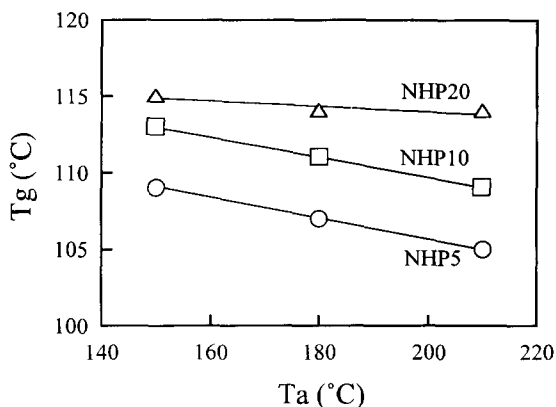


Figure 7 Changes in T_g of annealed copolymers versus annealing temperature

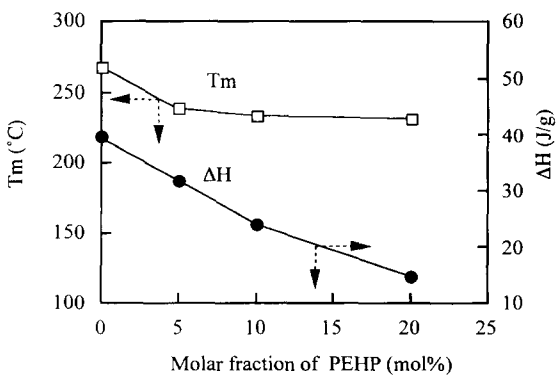


Figure 8 Changes in T_m and ΔH of copolymers annealed at 210°C for 2 h

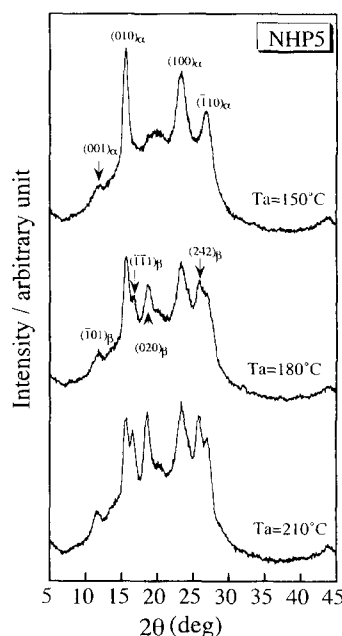


Figure 9 WAXD traces of NHP5 annealed at various temperatures for 2 h

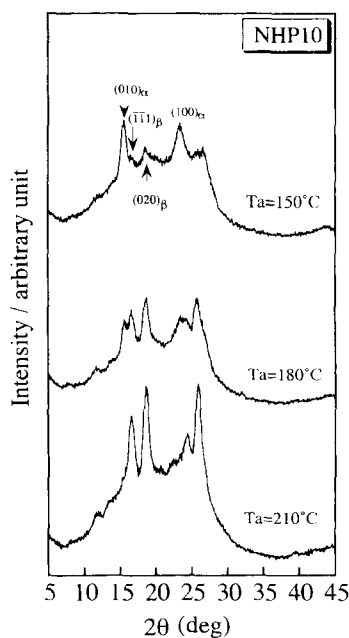


Figure 10 WAXD traces of NHP10 annealed at various temperatures for 2 h

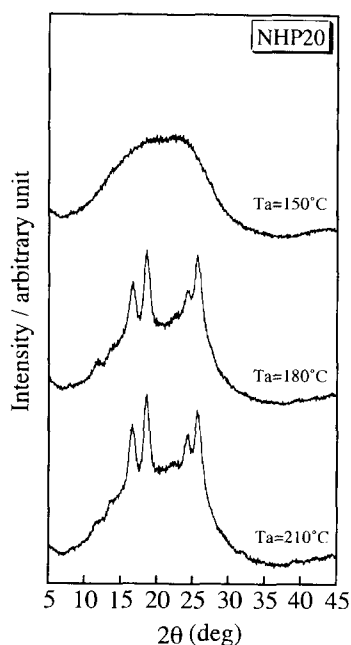


Figure 11 WAXD traces of NHP20 annealed at various temperatures for 2 h

In the sample annealed at 210°C, its WAXD pattern also indicated coexistence of the α - and β -form crystallites as shown in Figure 9. The 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 correlatively. Thus, annealing at higher temperatures enhanced the formation of β -form crystallites. It has been reported that the formation of the α -form and the β -form in PEN homopolymer is strongly dependent on annealing conditions; the β -form crystallites were formed by annealing at higher temperatures, close to T_m^5 .

The WAXD patterns of annealed NHP10 samples are shown in Figure 10. The intensities of reflections were lower than those of NHP5, as revealed by the WAXD pattern of the sample annealed at 150°C. The WAXD profile was similar to that of the α -form, but weak reflections associated with the β -form were already observed as shown in Figure 10. The intensities of the β -form reflections became higher in the sample annealed at 180°C. Most of the α -form reflections disappeared when the sample was annealed at 210°C.

Figure 11 shows the WAXD traces of NHP20. The sample annealed at 150°C exhibited amorphous patterns. But very weak reflections were observed in the WAXD photograph, so that it had extremely low crystallinity. In NHP20, the crystallites could not be grown by annealing at 150°C, unlike NHP5 and NHP10. This also indicates that introduction of PEHP sequences results in low crystallinity. The above results support those of the d.s.c. measurements mentioned in the previous section. Most of the reflections of NHP20 annealed at 180 and 210°C were assigned to those of the β -form. Hence, the PEN sequences in NHP20 crystallized in the β -form in these experimental conditions. Such a polymorphism induced by copolymerization also occurs in other copolymers^{3,16}.

As a result, the PEHP sequences in the molecular chains interfere with the crystallization and formation of

the α -form crystallites. The rigidity of 9,10-dihydropheanthrene 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 those of the α -form or β -form of PEN as described above, the crystallites were composed of PEN sequences without PEHP sequences. However, PEHP sequences have a profound influence on the chain packing mode of the unit cell. It is hard to explain the crystalline structures of PEN/PEHP copolymers in detail in terms of the above limited experimental data.

CONCLUSION

Quenched PEN/PEHP copolymer samples were almost amorphous in spite of different copolymer compositions. T_g s of the copolymers increased with increasing molar fraction of PEHP; on the other hand, enthalpy changes of exothermic and endothermic peaks decreased; thus, the crystallinity of the copolymers was lowered by introducing PEHP. When annealed above 150°C, the samples were capable of crystallizing. The crystallinity of the copolymers decreased with increasing molar fraction of PEHP. The crystallites of the NHP5 sample annealed at 150°C were assigned to the α -form of PEN; however, α -form and β -form crystallites coexisted in NHP5 annealed above 180°C. The WAXD pattern of annealed NHP10 indicated the coexistence of α - and β -form crystallites. Most of the X-ray reflections for NHP20 could be assigned to those of the β -form. Thus, the crystallites formed in the copolymers are composed of PEN sequences while PEHP sequences remain in the amorphous regions. In conclusion, PEHP sequences interfere with crystallization and have a strong influence on the chain packing mode of the unit cell in the copolymers.

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