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Structures of wholly aromatic copolyesters composed of 4-hydroxybenzoic acid, biphenol and terephthalic acid: 1. Effects of copolymer composition on thermal properties

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The structures and phase transitions of thermotropic liquid-crystalline copolymers composed of 4-hydroxybenzoic acid (HBA), terephthalic acid (TPA) and biphenol (BP) (HBA/TPA/BP copolymer) with five different copolymer compositions were investigated using X-ray diffraction and thermal analyses. The HBA/TPA/BP copolymers exhibited nematic liquid-crystalline characteristics at elevated temperatures, and complicated fine structures formed in the solid state when cooled from the anisotropic nematic melt. The crystal to smectic E (S_E) type and S_E type to hexagonal phase transitions inevitably occurred at approximately 100°C and 300°C, respectively, in the samples of varied copolymer compositions. Particularly, the molecular chain of almost the same monomer fraction (HBA/TPA/BP = 35/32.5/32.5) showed sharp endothermic peaks on the differential scanning calorimetry curve; thereby, the crystallite size was considered to be comparatively uniform. The S_E-type structure was frozen in almost all the quenched samples. Highly ordered crystallites were formed in the samples when they were annealed above 300°C where the hexagonal interchain packing order was formed.

(Keywords: aromatic copolyester; liquid-crystalline polymer; phase transition)

INTRODUCTION

Wholly aromatic copolyesters composed of 4-hydroxybenzoic acid (HBA), terephthalic acid (TPA) and biphenol (BP) (HBA/TPA/BP copolymer) are currently receiving considerable attention for potential applications, because of their excellent mechanical properties, thermal stability and chemical resistance like other aromatic copolyesters[1,2]. Particularly, HBA/TPA/BP copolymer has an extremely high melting temperature among commercial aromatic copolyesters.

The copolymer exhibits thermotropic liquid-crystalline characteristics at elevated temperatures as the molecular chain is rigid and extended. It was reported by Blackwell *et al.*[3] that the copolymer chain sequence was assigned to be a random comonomer from the wide-angle X-ray diffraction (WAXD) pattern of the meridional reflections. Complicated fine structures were formed in the solid state when cooled from the anisotropic nematic melt. In the solid state, highly ordered coagulated structures were detected by an X-ray diffraction method[3,4]. The lattice parameters of the crystallite formed were determined by Kalika *et al.*[5], Shimamura *et al.*[6] and Yonetake[7]. The unit-cell parameters for the orthorhombic crystal of the copolymer containing 50 mol% of HBA were $a = 0.792$ nm, $b = 0.571$ nm and $c = 1.207$ nm (ref. 7).

Field *et al.*[4] investigated the phase transitions of HBA/TPA/BP copolymer (HBA/TPA/BP = 50/25/25), and they suggested that a phase transition occurred at 100°C, since the WAXD profiles changed above 100°C; some reflections, e.g. the 2 0 0 reflection, disappeared above 100°C. Kalika *et al.*[5] confirmed that the same phase transition occurred in the copolymer with another copolymer composition: HBA/TPA/BP = 68/16/16. By comparison with the phase transition of poly(4-hydroxybenzoic acid) (PHBA)[8], they proposed that the orthorhombic crystal to smectic E (S_E) type phase transition that was observed for PHBA occurred at 100°C and hexagonal interchain packing order was formed above 300°C[5].

In the case of PHBA, the orthorhombic to S_E type phase transition occurred at 340°C, and the S_E type structure transformed into the hexagonal interchain packing structure at 430°C. The lattice parameters of the orthorhombic crystal have been estimated by Hay[9],

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Lieser[10], Geiss *et al.*[11] and Yoon *et al.*[8]. The unit-cell parameters were $a = 0.747$ nm, $b = 0.567$ nm and $c = 1.255$ nm (ref. 8). The S_E type structure exhibited an ordered herringbone packing on the hexagonal net in the *ab* plane, showing the orthorhombic cell with $a = 0.924$ nm, $b = 0.528$ nm and $c = 1.250$ nm (ref. 8). Above 430°C the hexagonal interchain packing structure was kept but the herringbone packing order was lost[8]. Most of the phase transition temperatures of the HBA/TPA/BP copolymers decreased as compared with those of PHBA[8], because the chain conformation was randomized by copolymerization.

Little is known about the effects of copolymer composition on thermal properties. In this article, we investigate the structures and phase transitions of the HBA/TPA/BP copolymers with different copolymer compositions using X-ray diffraction methods and thermal analyses.

EXPERIMENTAL

Materials and sample preparation

Five HBA/TPA/BP copolyesters with different copolymer compositions were used. They were synthesized by Finestone's method[12] in our laboratory. The copolymer compositions are listed in *Table 1*. These samples are coded as HTB20, HTB35, HTB50, HTB65 and HTB80, where the numbers denote the volume fraction of HBA. The samples were melt pressed in the nematic state, followed by quenching into ice-water. They were annealed at various temperatures for 2 h in a N_2 purge, and then cooled at 0.2 or 10°C min^{-1} to room temperature.

Thermal properties

The thermal properties of the samples were investigated using a differential scanning calorimeter (DSC 200, Seiko Instruments and Electronics Ltd) under an N_2 purge; 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. Wide-angle X-ray diffraction (WAXD) traces were obtained by a step-scanning method: the step width and fixed time were programmed for steps of 0.05° every 4 s. Changes in WAXD patterns during stepwise heating and cooling processes were recorded by a scintillation counter system. The WAXD photographs were taken by a Laue camera with a 0.5 mm diameter pinhole collimator.

Table 1 Copolymer compositions of the samples used

Sample	HBA (mol%)	TPA (mol%)	BP (mol%)
HTB20	20	40	40
HTB35	35	32.5	32.5
HTB50	50	25	25
HTB65	65	17.5	17.5
HTB80	80	10	10

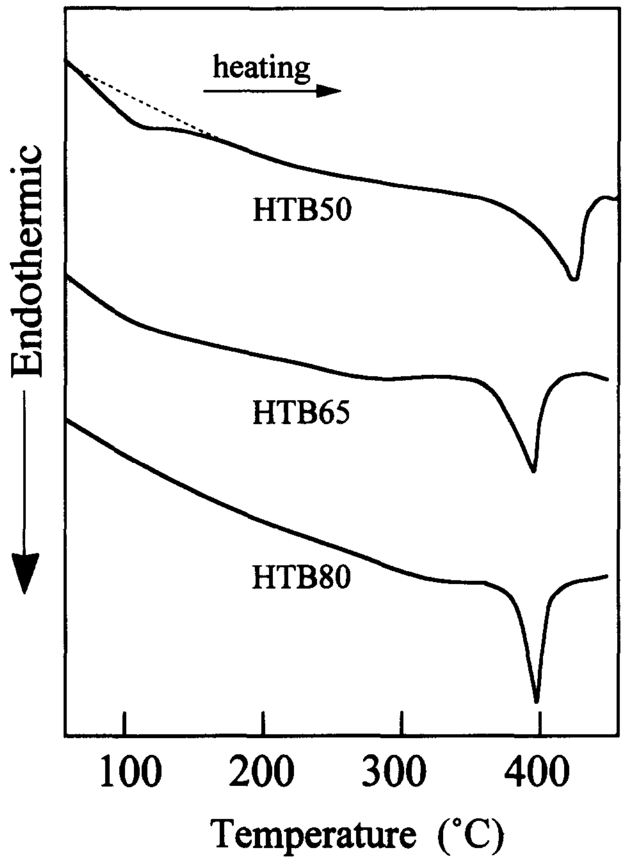

Figure 1 D.s.c. thermograms of the heating process for HTB50, HTB65, and HTB80. These samples were cooled at 10°C min^{-1} from the nematic melt

RESULTS AND DISCUSSION

Thermal properties of HBA/TPA/BP copolymers with different compolymer compositions

Figure 1 shows d.s.c. thermograms in the heating process for the samples of HTB50, HTB65 and HTB80, which were cooled at 10°C min^{-1} from the nematic melt. In HTB50, HTB65 and HTB80, endothermic peaks are observed at 425, 395 and 397°C, respectively. Above these temperatures, the samples showed nematic liquid-crystalline characteristics; broad X-ray scattering patterns and nematic optical textures were observed. In addition, a small and broad endothermic peak also appears at 110°C in the case of HTB50. This feature was identical with that reported by Field *et al.*[4]. On the other hand, in the samples of HTB20 and HTB35, two endothermic peaks appear clearly in low- and high-temperature regions as shown in *Figure 2*.

As shown in *Figure 3*, a small endothermic peak can be observed at about 100°C in the d.s.c. thermograms of HTB65 and HTB80, when they were cooled slowly at 0.2°C min^{-1} from the nematic melt. Field *et al.*[4] suggested that crystal–crystal phase transition occurred at about 100°C for the sample composed of HBA/TPA/BP = 50/25/25, since the WAXD profiles changed above 100°C. Similarly Kalika *et al.*[5] reported that there was orthorhombic crystal to S_E type phase transition at 100°C in the copolymer with HBA/TPA/BP = 68/16/16 (mol%). Such a phase transition was first observed at 340°C in the PHBA system, and the order after the transition was considered to be analogous to that in the S_E phase of small rod-like molecules[5].

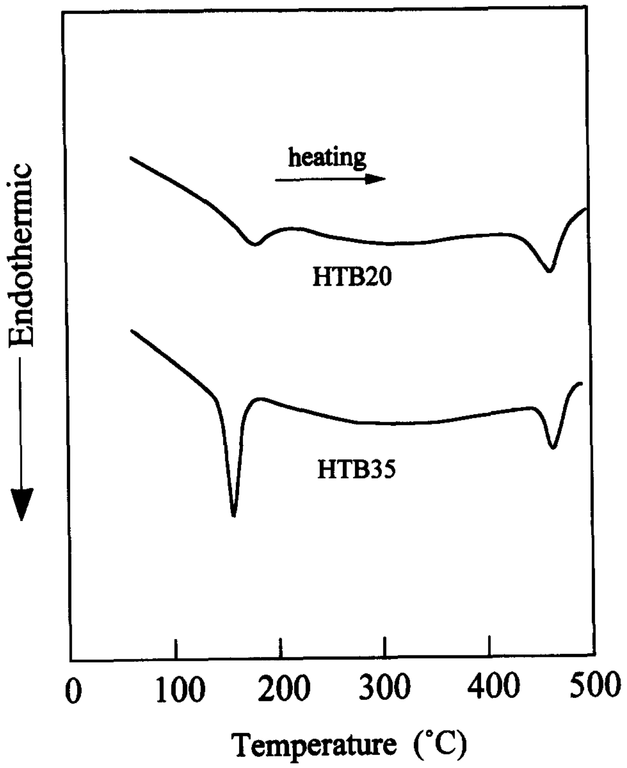

Figure 2 D.s.c. thermograms of the heating process for HTB20 and HTB35. These samples were cooled at 10°C min^{-1} from the nematic melt

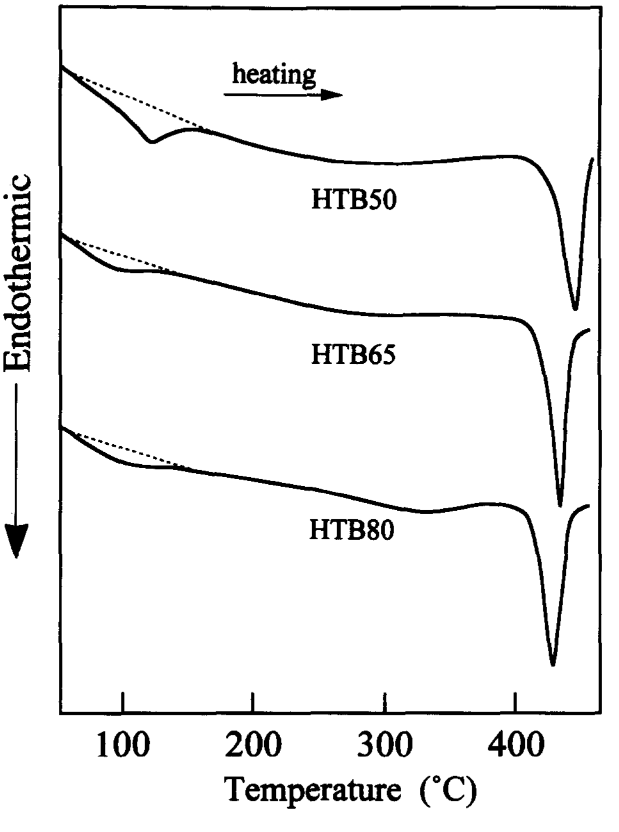

Figure 3 D.s.c. thermograms of the heating process for HTB50, HTB65, and HTB80. These samples were cooled slowly at 0.2°C min^{-1} from the nematic melt

Accordingly, the first lower endothermic peaks of the HBA/TPA/BP copolymers used in this study can be assigned to the crystal-S_E type phase transition. The phase transition will be described in detail in the next section.

Phase transition of HBA/TPA/BP copolymers

Changes in the WAXD traces of HTB20, HTB35, HTB50 and HTB80 during heating processes are shown in *Figure 4*. The WAXD traces of HTB65 are similar to those of HTB80. These samples were cooled at 0.2°C min^{-1} from the nematic melt. Three-dimensional ordered crystallites are formed in these samples, since many Bragg reflections are observed in their WAXD profiles obtained at room temperature. These WAXD patterns are almost the same whatever the copolymer composition. They are analogous to that obtained from the copolymer with HBA = 68 mol%, which was assigned to an orthorhombic form[5].

On heating, the intensity of the 1 1 0 reflection of $2\theta = 19°$ increases gradually in each sample. At the same time, the 2 0 0 reflection of $2\theta = 23°$ shifts to a lower 2θ angle. In HTB20 and HTB35, the 2 0 0 reflection disappears above 200 and 180°C, respectively. On the other hand, in HTB50, HTB65 and HTB80 such changes occur above 125, 100 and 75°C, respectively. These temperatures coincide with those of the lower endothermic peaks of their d.s.c. curves. Consequently, a phase transition from an ordered structure to a less ordered one occurred at each temperature.

On further heating, the 2 1 1 reflections of $2\theta = 27°$ for HTB35 and HTB80 disappear above 350°C and those for HTB50 and HTB65 disappear above 300°C. These features are nearly consistent with that of the copolymer with HBA = 68 mol% (ref. 5). The orthorhombic to S_E type phase transition occurs at approximately 100°C and the S_E type structure transforms into the hexagonal interchain packing structure at ca. 300°C in HTB35, HTB50, HTB65, and HTB80.

In the case of HTB20, however, the WAXD profile remains almost unchanged in the temperature range of 200–350°C, as shown in *Figure 4*. The WAXD profile probably changes at even higher temperature, since HTB20 is an HBA-rich sample. In the case of PHBA, the hexagonal structure was formed above 400°C[8]. As a result, the changes in the WAXD profiles described above imply that the same phase transitions occur in these samples in spite of varied copolymer compositions.

The *d* spacings of the reflection of $2\theta = 19°$ were measured at elevated temperatures during the heating process. The reflection was clearly observed at the equator of the fibre diagram for each polymer[7,13]. The changes in the *d* spacings are shown in *Figures 5a* and *5b*. The *d* spacings increase linearly with increasing temperature, and then they decrease drastically above 100°C, as shown in *Figure 5a*. After decreasing, the *d* spacing increased linearly again. In the case of HTB50, the temperature dependence of *d* spacing is similar to that reported by Field *et al.*[4]. The drastic change in *d* spacings is ascribed to the fact that the orthorhombic to S_E type phase transitions occurred in the temperature ranges. The onset temperatures of decrease in *d* spacings can be compared with those of the endothermic peaks of their d.s.c. curves in *Figures 1* and *2*.

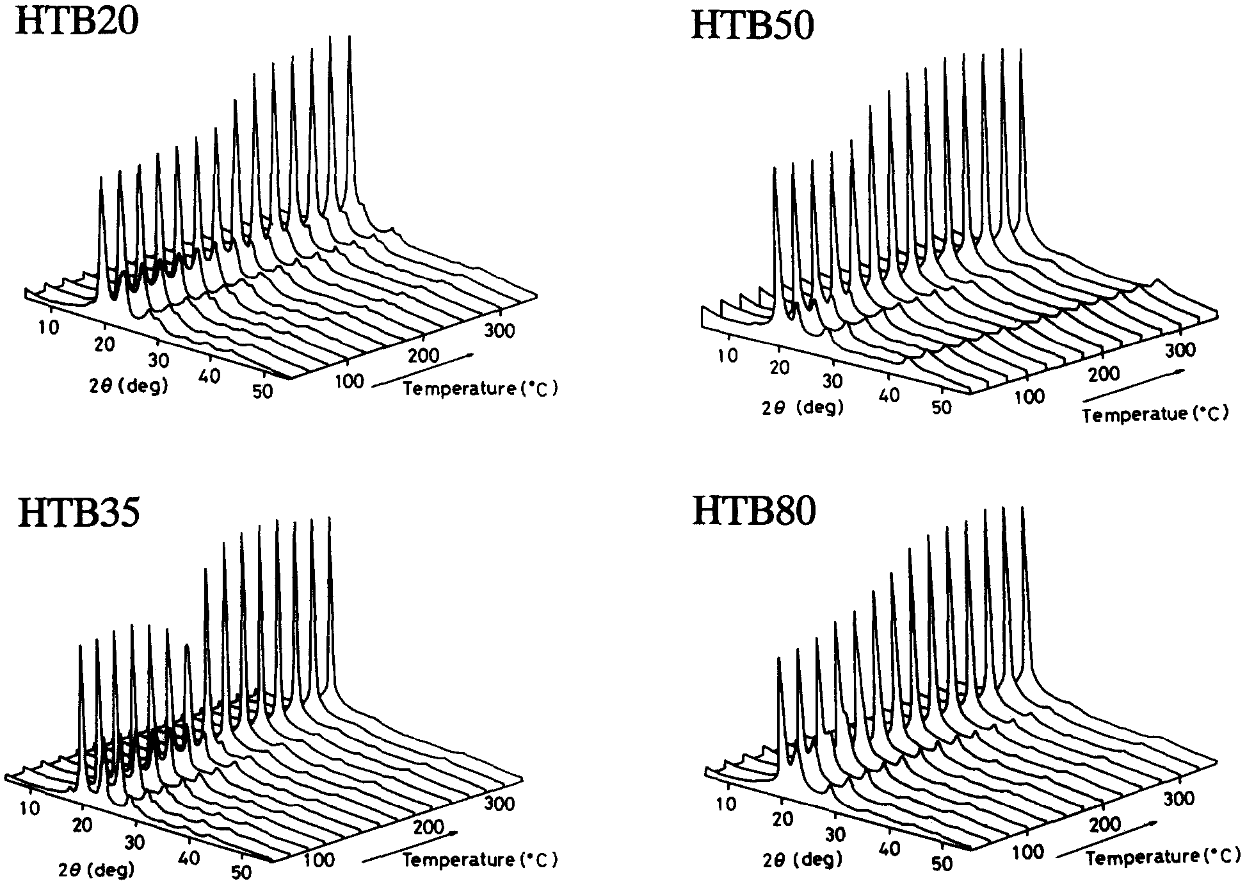

Figure 4 Changes in the WAXD traces of HTB20, HTB35, HTB50, and HTB80 during heating processes. These samples were cooled at 0.2°C min^{-1} from the nematic melt.

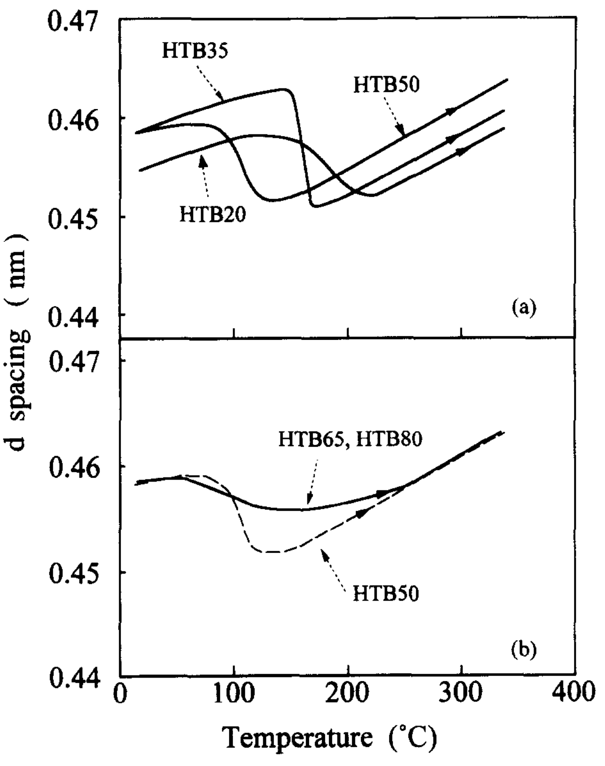

Figure 5 Changes in the d spacing of the reflection for $2\theta = 19°$ against temperature during the heating processes. (a) HTB20, HTB35, and HTB50; (b) HTB50, HTB65, and HTB80. The reflection of $2\theta = 19°$ was observed in the equator of the fibre diagram for each sample

Table 2 Linear expansion coefficients of samples, which were measured from changes in d spacing of the reflection for $2\theta = 19°C$

Sample	Temperature range (°C)	Linear expansion coefficient $\alpha \times 10^5$ K^{-1}
HTB20	25–100	8.79
	220–330	12.57
HTB35	26–150	6.96
	170–330	13.61
HTB50	25–70	4.70
	150–330	13.68
HTB65	150–250	4.41
	250–330	15.03
HTB80	150–250	6.64
	250–330	14.23

In HTB65 and HTB80, the d spacings decrease gradually above 100°C, as shown in *Figure 5b*. The changes in the d spacings are not so large compared with other samples. This is probably due to the thermodynamically stable crystallites, which were kept in the higher-temperature region in HTB65 and HTB80, because a number of the copolymer chains in both samples were composed of comparatively long successive HBA sequences. Thus, there may be broad distributions of crystallite sizes in HTB65 and HTB80 samples.

The linear expansion coefficients α can be measured from the straight lines of d spacings in *Figure 5*. The values of α are summarized in *Table 2*. The linear expansion corresponds to the thermal expansion mode normal to the chain direction, as the reflections of $2\theta = 19°$ were assigned to 1 1 0 reflections located at the equator of the fibre diagrams[7,13]. The values of α obtained in the lower-temperature ranges represent those of 10^{-5} order, which are generally associated with solid states. The values obtained in the higher-temperature ranges, on the other hand, represent those of 10^{-4} order, which are associated with mesomorphic states between solid and liquid. These results also suggest that the mesomorphic phase appeared above 100°C in each sample.

As shown in *Figure 2*, the lower endothermic peak of HTB35 is very sharp compared with those of other samples. The enthalpy changes of the endothermic peak was $11.7\,\mathrm{J\,g^{-1}}$, which was three times as large as that of HTB50 ($3.9\,\mathrm{J\,g^{-1}}$). It accompanies as well a drastic *d* spacing change shown in *Figure 5a*. These results come presumably from the uniform size of crystallites. The HTB/TPA/BP copolymer is considered to be random. However, the comonomeric sequence of THB35 is probably homogeneous, because THB35 is composed of almost the same molar fractions of three monomers; thus the molecular chains cannot be distinguished from each other. In HTB35, the chain packing modes are similar to those in the crystallites; thereby, the size of most crystallites is comparatively uniform. Hence, the crystallites exhibit similar thermodynamic stability. In contrast, there are complicated fine structures in the samples containing higher or lower molar fraction of HBA, because their chain sequences are heterogeneous and their chain conformations are disordered.

Fine structures of HBA/TPA/BP copolymers annealed at various temperatures

The original samples were melt pressed in the nematic state, followed by quenching into ice–water. They were annealed at programmed temperatures (T_a) for 2 h in an N_2 purge, and then they were cooled at $10°\mathrm{C\,min^{-1}}$ to room temperature.

Figure 6 shows the d.s.c. thermograms of the heating process for HTB50 samples annealed at various T_a. The shapes of d.s.c. traces for the samples annealed below 300°C remain unchanged. Above $T_a = 300°\mathrm{C}$, however, the endothermic peaks become sharp, and the peak positions shift to higher temperatures with increasing T_a. Moreover, the endothermic peaks are observed at approximately 100°C. The enthalpy changes (ΔH) of the higher endothermic peaks are plotted against T_a in *Figure 7*. The values of ΔH increase above 300°C. These effects are ascribed to the increase in their crystallinity by an annealing effect.

As described in the previous section, the hexagonal phase in HTB50 formed above 300°C. It is acceptable that rearrangement of the rigid molecular chains can take place, since chain mobility is much larger in the hexagonal phase. Thus, fine-structural change is induced by annealing in this phase. Cheng *et al.*[14] investigated the thermal behaviour of HBA/TPA/BP (60/20/20) copolymer; the endothermic peak, which corresponds to nematic phase transition, becomes remarkably sharp and shifted to higher temperature with increasing annealing time at $T_a = 327°\mathrm{C}$. In our case, the heats of fusion also increased with annealing time at this annealing temperature, compared with the samples annealed at lower temperatures.

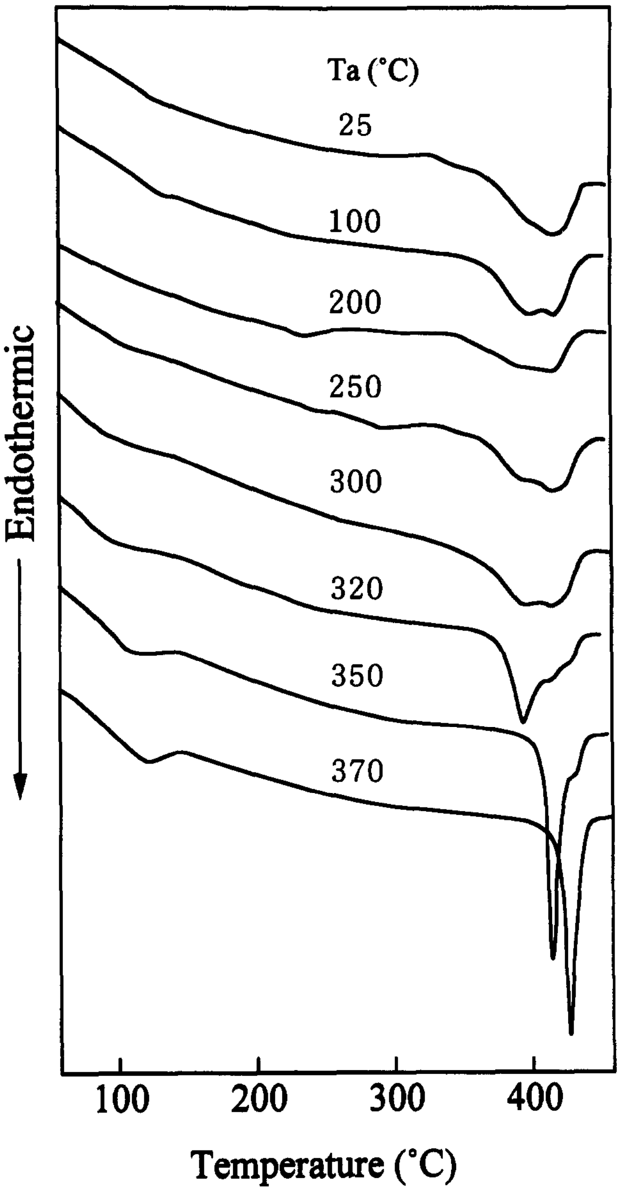

Figure 6 D.s.c. thermograms of the heating process for HTB50 samples annealed at various temperatures

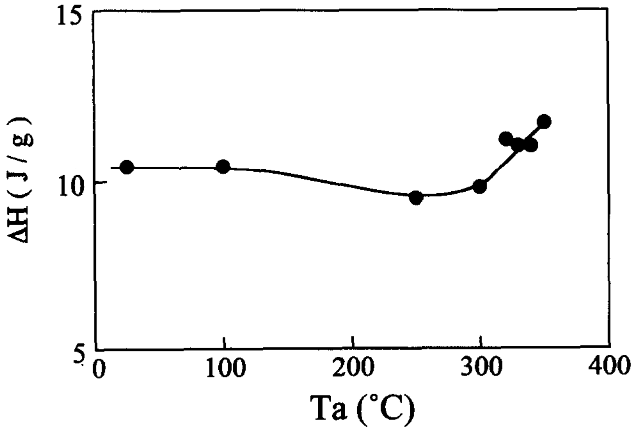

Figure 7 Changes in the enthalpy (ΔH) of the higher endothermic peaks for HTB50 against annealing temperature

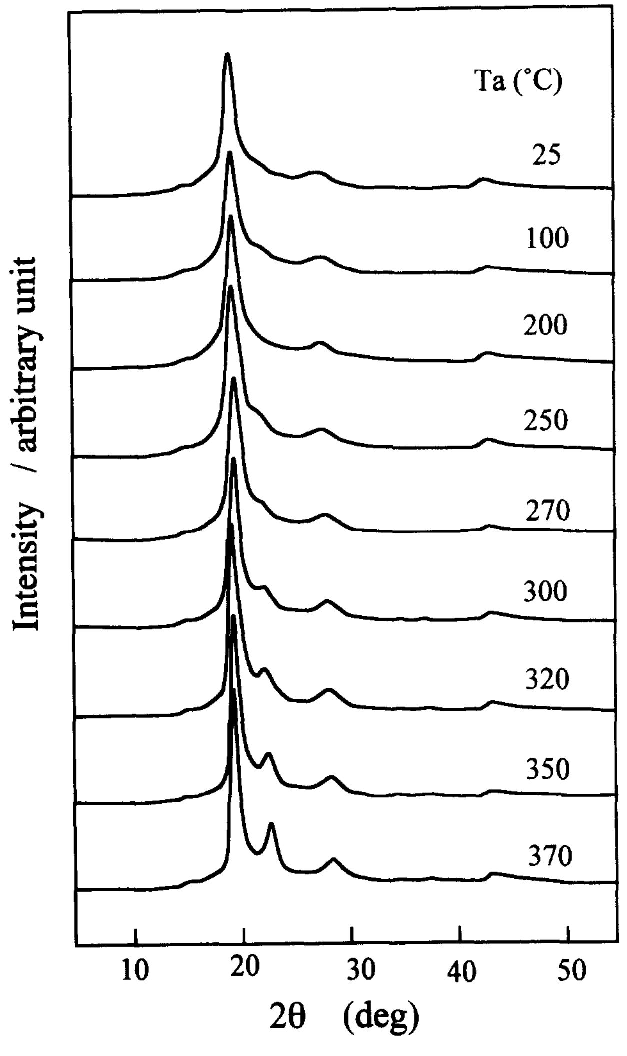

Figure 8 WAXD traces of HTB50 annealed at various temperatures. The quenched samples were annealed for 2 h and then cooled at 10°C min^{-1} to room temperature. These patterns were taken at room temperature.

The WAXD patterns of HTB50 annealed at various temperatures are shown in *Figure 8*. The WAXD pattern shows that the S_E type state was frozen in the quenched sample. The reflection of $2\theta = 23°$ assigned to 200 reflection is observed in the WAXD patterns for the samples annealed above 300°C. The WAXD patterns show that the orthorhombic crystallite[5,8] is formed in the sample.

In the cases of quenched HTB65 and HTB80 samples, frozen S_E type structures were also confirmed from the WAXD results. These findings were similar to that of HTB50. On the other hand, the 200 reflection is observed at $2\theta = 23°$ in the WAXD patterns of quenched HTB20 and HTB35 samples, though the reflection intensities are very low. Therefore, the crystal and the S_E type states coexist in both samples. The intensity of the reflection increases remarkably with increasing T_a above 300°C.

Changes in d spacings of the 1 0 0 reflection are plotted against T_a in *Figure 9*. The values of the d spacing increase drastically above $T_a = 300$°C. In the case of HTB35, the increase in the d spacing was very small, since comparatively high ordered crystallites are already formed in the quenched sample. As a result, the orthorhombic crystallites can be formed by annealing above 300°C, since the rearrangement of the rigid molecular chains is induced by annealing in the hexagonal phase.

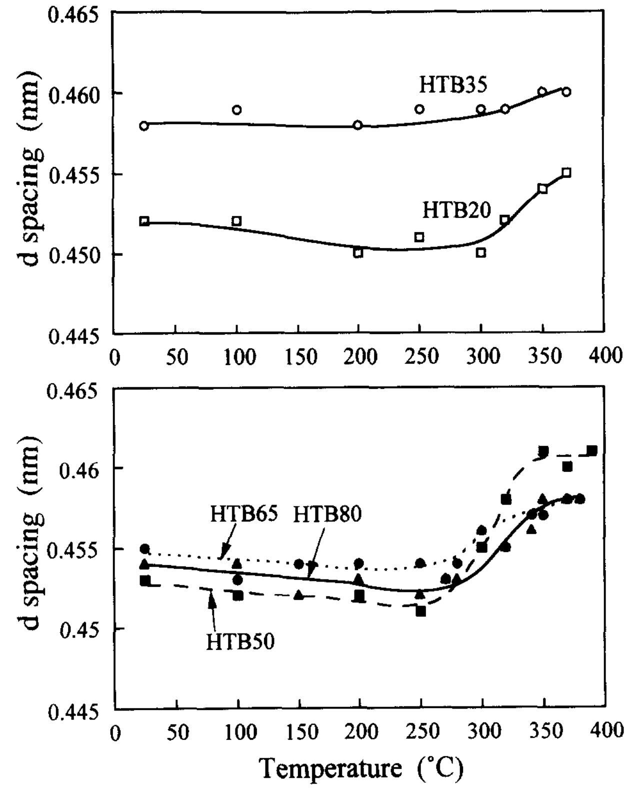

Figure 9 Changes in d spacings of the reflection for $2\theta = 19°$ against annealing temperature. The quenched samples were annealed at various temperatures for 2 h. □, HTB20; ○, HTB35; ■, HTB50; ●, HTB65; ▲, HTB80

CONCLUSIONS

The structures and phase transitions of HBA/TPA/BP copolymers with five different copolymer compositions were investigated and the following findings were obtained.

The orthorhombic to S_E type, hexagonal and nematic phase transitions inevitably occurred in the samples in varied copolymer compositions. These phase transitions were observed in the ranges of 100–200°C, 300–350°C and 400–470°C, respectively.

In the case of HTB35 composed of the same monomer fractions, the d.s.c. thermogram showed a very sharp endothermic peak at 180°C. This can be ascribed to the fact that the monomeric sequence of HTB35 is apparently homogeneous; thus, the crystalline size is comparatively uniform.

The S_E type state was frozen in quenched samples. Orthorhombic crystallites were formed when the quenched samples were annealed in the hexagonal phase, as a result of the rearrangement of the rigid molecular chains.

REFERENCES

1 Calundann, G. W. and Jaffe, M. *Proc. R. A. Welch Found. Conf. Chem. Res.* 1983, **26**, 246

2 Chung, T.-S. *Polym. Eng. Sci.* 1986, **26**, 901

3 Blackwell, J., Cheng, H. M. and Biswas, A. *Macromolecules* 1988, **21**, 39

4 Field, N. D., Baldwin, R., Layton, R., Frayer, P. and Scardiglia, F. *Macromolecules* 1988, **21**, 2155

5 Kalika, D., Yoon, D. Y., Iannelli, P. and Parrish, W. *Macromolecules* 1991, **24**, 3413

6 Shimamura, K., Ishitobi, M., Uchida, T., Inoue, T., Ohchou, M. and Yoshioka, T. *Polym. Prepr. Jpn.*1991, **40**, 4031

7 Yonetake, K., PPS-Tokyo'93, 1993, p. 102

8 Yoon, D. Y., Masciocchi, N., Depero, L.E., Viney, C. and Parrish, W. *Macromolecules* 1990, **23**, 1793

9 Hay, I., Abstracts of 39th Pittsburgh Diffraction Conference, Cleveland, Ohio, November, 1981

10 Lieser, G. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 1611

11 Geiss, R., Volksen, W., Tsay, J. and Economy, J. *J. Polym. Sci., Polym. Lett. Edn.* 1984, **22**, 433

12 Finestone, A. B., Belg. Patent BE 899785, 1984

13 Takehashi, A., Yonetake, K., Masuko, T., Murouchi, S. and Yoneta, H. *Polym. Prepr. Jpn.* 1993, **42**, 1221

14 Cheng, S. Z. D., Janimak, J. J., Zhang, A. and Zhou, Z. *Macromolecules* 1989, **22**, 4240