Further Characterization of the Structure and the Thermal Transitions of Poly(p-Oxybenzoate-co-p-Phenylene Isophthalate) Polymers

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Synopsis

A series of poly(p-oxybenzoate-co-p-phenylene isophthalate)s were prepared by melt polycondensation of p-acetoxybenzoic acid, p-phenylene diacetate, and isophthalic acid followed by solid-state polymerization. The solid-state polymerization not only increased the molecular weight, but also annealed the copolyesters. The thermal stability, liquid crystallinity, thermal properties, and solid-state crystallinity of these copolyesters were investigated by TGA, polarized microscope, DSC, and wide-angle X-ray diffraction, respectively. It was found that copolyesters with HBA content of 50, 60, and 70 mol % showed explicit melt birefringence at 370°C and thus exhibited liquid crystalline state. The effect of annealing during solid-state polymerization on the thermal properties was discussed. The effect of copolymerization on their crystallinity was interpreted with X-ray diffraction qualitatively.

INTRODUCTION

The homopolymer of p-hydroxybenzoic acid (HBA), poly(p-oxybenzoate), decomposes before melt; the behavior at melt state cannot be observed. If the melting point can be depressed by chemical modification, liquid crystalline state may be formed for suitable composition. Copolymerization is a powerful method to lower the melting point of polymer. Various thermotropic liquid crystalline copolyesters based on HBA have been studied. Typical examples are copolyesters of HBA and poly(ethylene terephthalate) (X7G),[1] copolyesters of HBA and 2-hydroxy-6-naphthoic acid (Vectra),[2,3] copolyesters of HBA, 4,4'-biphenol, and terephthalic acid (Xydar),[4] copolyesters of HBA, 2,6-dihydroxynaphthalene and terephthalic acid,[5] and copolyesters of HBA, isophthalic acid (IPA), and hydroquinone (HQ).[6-10]

The chemical structure of copolyesters of HBA, IPA, and HQ–poly(p-oxybenzoate-co-p-phenylene isophthalate)s is shown below:

$$-(-CO-\langle \bigcirc \rangle -O-)_x-(-CO-\langle \bigcirc \rangle -CO-O-\langle \bigcirc \rangle -O-)_{1-x}-$$

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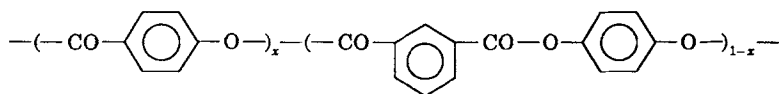
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where x is the molar fraction of HBA unit. The synthesis[6] and rheological studies[7] were carried out by some researchers. It was also described that copolyesters with HBA content from 33 to 43 mol % exhibited narrow temperature range of nematic phase, and those with HBA content from 50 to 75 mol % exhibited sufficiently broad nematogenic temperature regions.[6] And the solid-state structure of these copolyesters were investigated by X-ray diffraction.[6,9]

In this study, a series of copolyesters of HBA, IPA, and HQ were prepared by melt polycondensation of p-acetoxybenzoic acid, p-phenylene diacetate, and isophthalic acid. The products were then solid-state polymerized at 260–280°C under vacuum (0.5 mmHg) for 4 h. The thermal properties of as-made products and second-run thermal properties were determined by DSC to investigate the effect of solid-state polymerization on the thermal transitions. The effect of polymer composition on the X-ray diffraction patterns was also investigated.

EXPERIMENTAL

p-Acetoxybenzoic acid was prepared by reacting p-hydroxybenzoic acid (San Fu Chemical Co., Ltd., Taiwan) with acetic anhydride at 100°C, the product was recrystallized twice from acetone solution. T_m of the final product measured by DSC was 192°C. p-Phenylene diacetate was obtained by a similar method from hydroquinone (Merck reagent grade) and acetic anhydride (T_m of the product was 125–126°C).

All the copolyesters were prepared by melt polycondensation and followed by solid-state polymerization. A typical example follows.

Into a 1-L three-neck glass reaction kettle equipped with a mechanical stirrer, nitrogen inlet tube, and a distillation head connected to a condenser were added: (1) 45.0 g (0.25 mol) of p-acetoxybenzoic acid, (2) 48.5 g (0.25 mol) of 4,4'-phenylene diacetate, and (3) 41.5 g (0.25 mol) isophthalic acid. The monomers were melted under nitrogen. The reactants were heated at 260°C for 1 h; acetic acid was distilled out at this stage. The reaction mixture was heated to 320–330°C; then vacuum was applied slowly to about 0.5 mmHg, and held for an hour. The polymer melt was poured as fast as possible into water. The polymer product (in this case denoted as HBA50) was dried and ground. The ground sample was then charged into a solid-state polymerization tube equipped with vacuum line. Vacuum (0.5 mmHg) was applied; then, the tube was heated to 260–280°C and held for 4 h.

The reduced viscosity of some copolyesters before and after solid-state polymerization was determined at 50°C in pentaflurophenol at a concentration of 0.5 g/dL by a Ubbelohde viscometer. The thermal stability was measured by Du Pont Instruments 951 thermogravimetric analyzer under nitrogen at heating rate of 20°C/min, and the melt birefringence was investigated by a Leitz polarizing microscope equipped with a hot stage (temperature limit: 370°C). The thermal properties of as-made samples from 60 to 400°C were determined by Perkin-Elmer DSC2 under nitrogen at heating rate of 20°C/min. The samples were cooled in DSC cell from 400 to 60°C at cooling rate of 20°C/min, and then second run was carried out. The heat of transition was determined by weighing the peak area compared to that of indium metal (heat of fusion: 6.8 cal/g). The X-ray diffraction patterns of powder samples (bound

with vaseline) were measured by an X-ray diffraction system of Scintag PAD V using Cu Kα radiation.

RESULTS AND DISCUSSION

The reduced viscosity of the copolyesters with HBA content from 0 to 70 mol % before solid-state polymerization is listed in Table I. Some copolyesters were insoluble in pentaflurophenol after solid-state polymerization. The reduced viscosity of the soluble copolyesters after solid-state polymerization was higher than that before solid-state polymerization as shown in Table I. Obviously, solid-state polymerization could increase the molecular weight of these copolyesters. After solid-state polymerization, HBA60 and HBA70 were insoluble in pentaflurophenol, but their melt viscosity (observed through shearing on the hot stage) at 370°C was found to be much higher than before solid-state polymerization. Thus, the molecular weight of HBA60 and HBA70 should also be increased after solid-state polymerization.

The thermogravimetric curve of as-made HBA50 (the term "as made" indicates the neat samples obtained after solid-state polymerization) is shown in Figure 1. Comparing with commercial liquid crystalline polymers, Xydar (obtained from Dartco) and Vectra A950 (supplied by Celanese), the thermal stability of HBA/IPA/HQ copolyesters was lower as shown in Figure 1. Xydar had the highest thermal stability and could persist to about 480°C. Vectra A950 also had higher thermal stability than HBA/IPA/HQ copolyesters; it could persist to about 450°C. All the HBA/IPA/HQ copolyesters could persist to about 400°C, but above 420°C, significant degradation was found. Although the thermal stability was lower for HBA/IPA/HQ copolyesters, the melting point or flow temperature was considerably lower for some compositions, well below 400°C, and this made melt processing possible.

TABLE I
Reduced Viscosity, Melt Birefringent Behavior at 370°C and T_g of HBA/IPA/HQ Copolyesters

Notation	Reduced viscosity (dL/g)		Melt birefringence at 370°C	T_g (°C)
	Before[a]	After[b]		
HBA0	0.10	0.34	Not melt	—
HBA10	0.10	0.34	No	—
HBA20	0.18	0.70	No	167
HBA30	0.12	0.53	No	150
HBA40	0.18	1.06	No	145
HBA50	0.46	3.20	Yes	135
HBA60	0.98	Insoluble	Yes	125
HBA70	0.51	Insoluble	Yes	120
HBA80	—	—	Not melt	—
HBA90	—	—	Not melt	—
HBA100	—	—	Not melt	—

[a] Before solid-state polymerization.
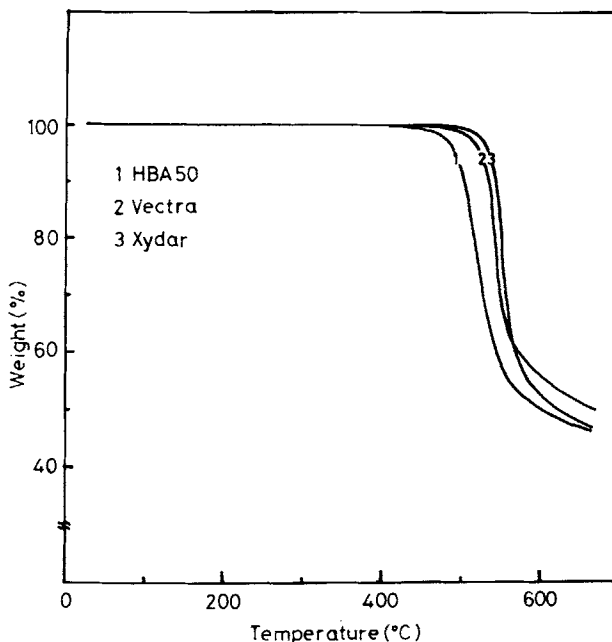[b] After solid-state polymerization.

Fig. 1. Thermogravimetric curves of Xydar, Vectra A950, HBA50.

The melt birefringence of the copolyesters was observed at 370°C on the polarized microscope. The results are shown in Table I. The copolyesters with HBA content from 50 to 70 mol % showed explicit melt birefringence and thus exhibited liquid crystalline state.

The DSC thermograms up to 400°C of as-made copolyesters with lower HBA content are shown in Figure 2, and those of as-made copolyesters with higher HBA content are shown in Figure 3. As-made HBA0 showed a main melting peak at 387°C and a small endotherm at 315°C. As-made HBA10 exhibited two large endotherms at 323 and 367°C, and as-made HBA20 showed two endotherms at 324 and 349°C. As-made HBA30, HBA40, HBA50, and HBA60 showed only one melting peak at 320, 323, 344, and 367°C, respectively. The melting endotherms and the corresponding heat of transitions are characterized in Table II. HBA70 showed no endotherm up to 400°C, and HBA80, HBA90, and HBA100 showed one endotherm at 340, 352, and 355°C, respectively. According to the data in the literature,[6] the higher temperature transition (T_2) of as-made copolyesters with lower HBA content shown in Table II corresponded to the normal melting point of these copolyesters. The additional transition T_1 of HBA0, HBA10, and HBA20 would be due to the annealing effect of solid-state polymerization. This point could be verified by investigation of the second-run thermal properties.

The samples were cooled from 400°C at a cooling rate of 20°C/min to 60°C, and DSC second run was carried out at a heating rate of 20°C/min. The second-run DSC thermograms of copolyesters with lower and higher HBA content are shown in Figures 4 and 5, respectively. The second-run DSC thermogram, where the annealing effect would be eliminated, of HBA0 showed a doublet (374 and 384°C) melting peak, and the original endotherm at 315°C disappeared. Ob-
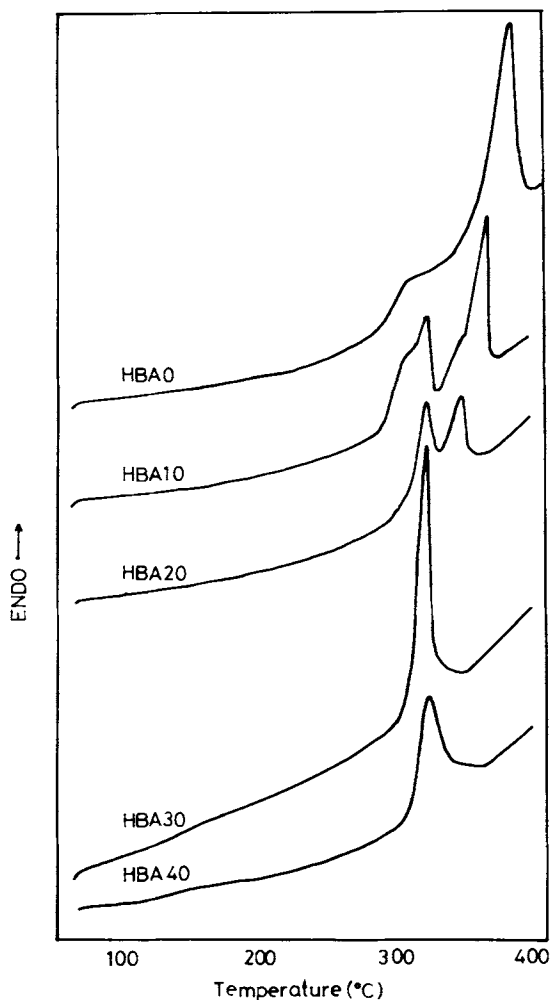
Fig. 2.   DSC thermograms of as-made copolyesters with lower HBA content.

viously, the endotherm at 315°C would be due to the annealing effect of solid-state polymerization. The overall transition heat of second run (16.11 cal/g) was less than but close to T_2 transition heat of as made HBA0 (19.14 cal/g). As HBA0 was cooled slowly (cooling rate of 20°C/min) from 400°C, two types of crystallite (namely B and A) might be formed. Thus, there were two endotherms found at 374 and 384°C for the second run. At the stage of solid-state polymerization, the annealing effect caused the B-type crystallite to change to A type. But, at the same time, another type of crystallite (C) might be formed, and an additional endotherm at 315°C was found. The situation of HBA10 was similar to HBA0. The second run of as-made HBA10 showed a doublet at 348 and 365°C, which might be due to B- and A-type crystallites. The overall transition heat of this doublet (11.62 cal/g) was also close to that of higher temperature endotherm of as-made sample (11.25 cal/g). Similarly, C-type crystallite (peak at 323°C) might be also due to the annealing effect at solid-state
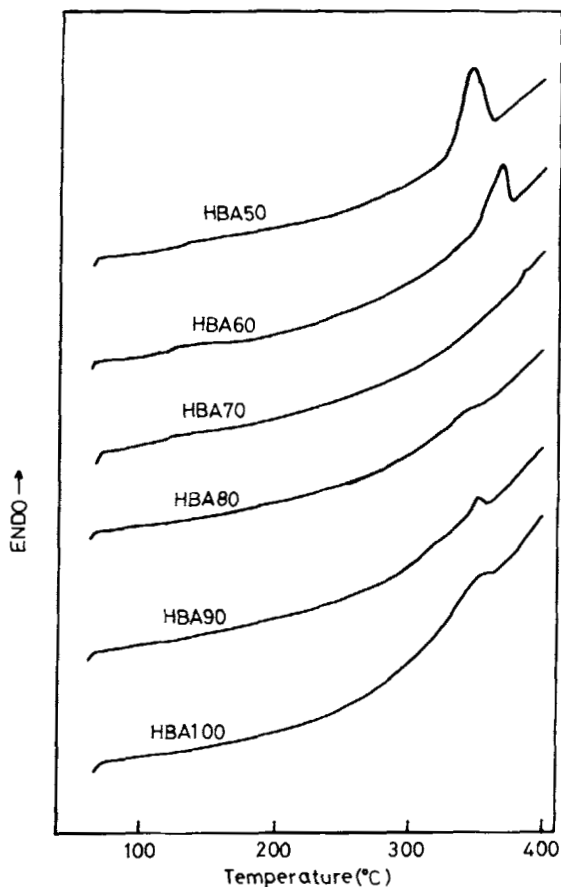
Fig. 3. DSC thermograms of as-made copolyesters with higher HBA content.

TABLE II
Transition Temperatures and the Corresponding Heat of Transition
of HBA/IPA/HQ Copolyesters[a]

	As made		Second run	
Notation	T_1 (°C)	T_2 (°C)	T_1 (°C)	T_2 (°C)
HBA0	315 (3.80)	387 (19.14)	374	384 (total 16.11)
HBA10	323 (10.16)	367 (11.25)	348 (4.24)	365 (7.38)
HBA20	324 (6.83)	349 (7.46)	325 (1.92)	348 (6.03)
HBA30	—	320 (13.48)	303 (1.86)	325 (3.18)
HBA40	—	323 (10.31)	310	323 (total 4.42)
HBA50	—	344 (5.82)	—	317 (2.32)
HBA60	—	367 (3.23)	—	340 (1.08)
HBA70	—	—	—	—
HBA80	340 (0.69)	—	—	—
HBA90	352 (1.18)	—	—	—
HBA100	355 (1.90)	—	330 (0.80)	—

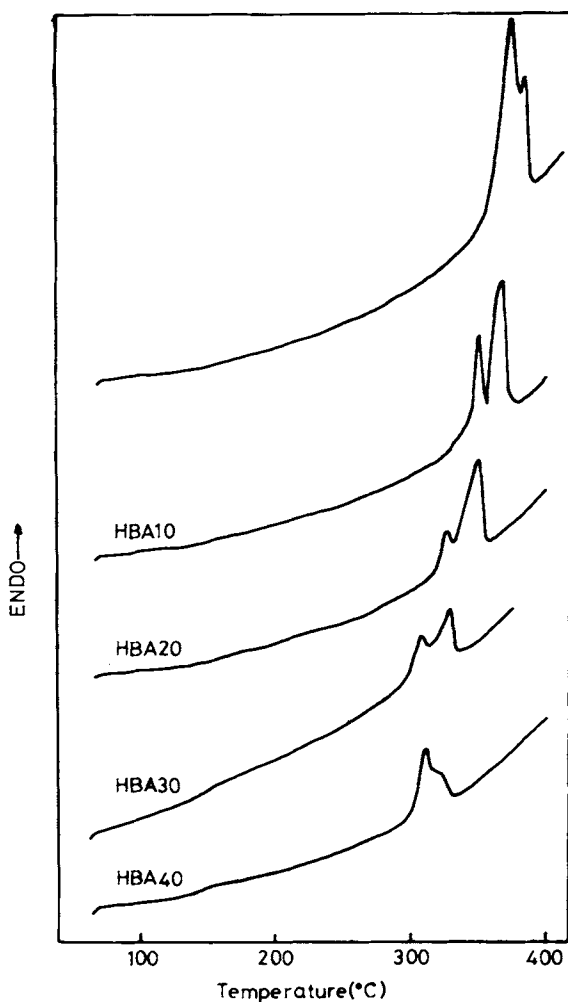[a] The number shown in the parenthesis is the corresponding heat of transition in cal/g.

Fig. 4.   Second-run DSC thermograms of copolyesters with lower HBA content.

polymerization step. For HBA20, the second run also exhibited a doublet at 325 and 348°C, and the overall transition heat of second run (7.95 cal/g) was also close to that of higher temperature endotherm of as-made endotherm (7.46 cal/g). The annealing effect of solid-state polymerization enlarged the peak at 324°C. Note that the endotherm of C-type crystallite located at about 320°C might be due to the condition of solid-state polymerization (260–280°C for 4 h). As-made HBA30, HBA40, HBA50, and HBA60 (with decreasing HQ/IPA component, respectively) showed no endotherm of C-type crystallite, and this indicated that C-type crystallite might be due to the HQ/IPA component.

The transition heat of lower temperature endotherm (C-type crystallite) of as-made copolyesters was interesting. HBA0 had lower value (3.80 cal/g), HBA10 had higher value (10.16 cal/g), and HBA20 had medium value (6.83 cal/g). As already described, C-type crystallite might be due to HQ/IPA component. In the absence of annealing effect, the crystallinity of HBA0 would be
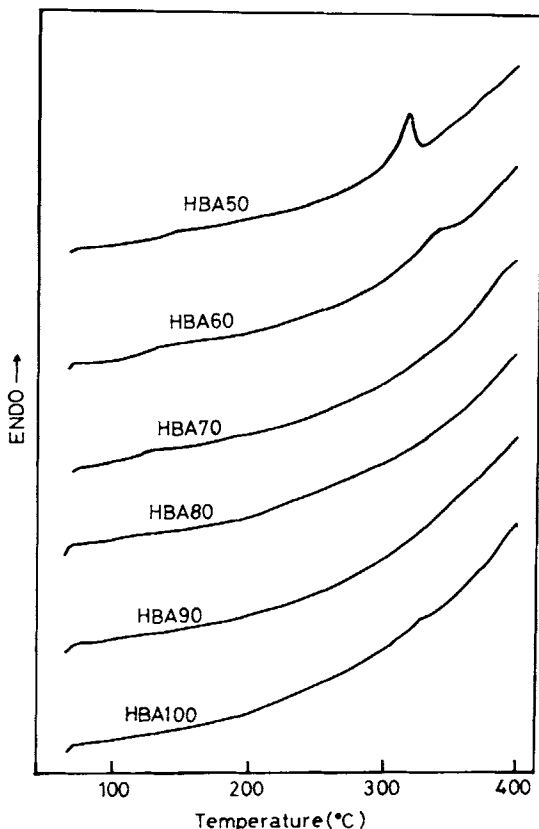
Fig. 5.   Second-run DSC thermograms of copolyesters with higher HBA content.

high as indicated by the high value of overall transition heat of second run (16.11 cal/g). Thus, there were fewer parts that could form C-type crystallite due to annealing. Thus the heat of lower temperature endotherm of as-made HBA0 was low. In the absence of annealing, the crystallinity of HBA10 (overall second-run transition heat: 11.62 cal/g) was lower than that of HBA0. This might be due to kinetic effect of the rupture of comonomer unit. After annealing, more parts could form C-type crystallite, and higher transition heat of lower temperature endotherm of as-made HBA10 (10.16 cal/g) was found. But, as comonomer content increased to some extent, the copolymerization effect greatly reduced the crystallinity and melting point, and also decreased the possible content of C-type crystallite. Thus as-made HBA20 showed smaller transition heat of lower temperature endotherm (6.83 cal/g). HBA30 and HBA40 showed normal melting temperatures close to about 320°C, and as-made samples showed no endotherm of C-type crystallite. Although as-made HBA50 and HBA60 had higher normal melting temperature than 320°C, they also showed no corresponded endotherm of C-type crystallite. Thus, C-type crystallite could be considered as due to the HQ/IPA component.

The DSC endotherm of copolyesters with higher HBA content was also interesting. As-made HBA100 showed a small endotherm (transition heat: 1.90 cal/g) at 355°C. Although the normal melting temperature was much higher

than this endotherm, this situation might be similar to the annealing effect on thermal transitions of HBA0 and HBA10. It was found by Economy and co-workers[11] that their HBA100 samples showed a DTA endotherm in the range of 325–360°C and was described to be a reversible crystalline transition in HBA100 polymer in which some of the crystal order was lost. The second-run DSC thermogram of HBA100 showed an even smaller endotherm (transition heat: 0.80 cal/g) at 330°C. This indicated that the annealing effect of solid-state polymerization would influence this transition. As-made HBA90 and HBA80 showed one DSC endotherm at 352 and 340°C, respectively, but the second run showed no endotherm. Thus, the endotherm of these two as-made samples should be also due to the annealing effect of solid-state polymerization.

For the copolyesters with medium HBA content, the annealing effect at solid-state polymerization stage had also significant influence on their crystallinity and normal melting temperature. As was expected, as-made HBA50 and HBA60 had higher melting temperature and higher transition heat and thus higher crystallinity as compared to the second run (Table II).

The second-run DSC thermograms of copolyesters with HBA content up to 40 mol % showed two endotherms as shown in Figure 4. This phenomenon was also found in a similar copolyester with lower HBA content as described in the literature.[8] The DSC data (Table II) of as-made copolyesters showed that annealing could shift the lower temperature endotherm to higher temperature endotherm. Thus, the lower temperature endotherm of second run would be a crystalline transition. A more detailed study of this transition behavior and the effect of annealing conditions on the crystalline behavior is being carried out.

The X-ray diffraction patterns of as-made copolyesters with higher HBA content are shown in Figure 6. The broad peak at about $2\theta = 12°$ was due to the scattering of Vaseline, which was used as a binder for powder samples. There were three main and some small diffraction peaks found for HBA100. The assignments of diffraction peaks of HBA100 were described in the literatures.[12,13] Here only the effect of copolymerization on the main diffraction peaks is concerned. HBA90 also exhibited three (similar) main diffraction peaks, but the peaks became broader. The diffraction peak at $2\theta = 23.4°$ disappeared for HBA80, and other peaks were also broader. For the copolyesters with HBA content $\geq$ 80 mol %, the diffraction peak at $2\theta = 19.9°$ was very sharp and became broader for higher HQ/IPA content. Thus, the crystallinity would be high. Due to high T_m of HBA component and high crystallinity of the as-made samples, copolyesters with HBA content $\geq$ 80 mol % showed no explicit melt birefringence at 370°C (did not melt). HBA70 and HBA60 exhibited one very broad diffraction peak. The crystallinity would be low for these two samples. Thus, as HBA content was less than 80 mol %, copolymerization greatly destroyed the crystallinity of HBA component.

The X-ray diffraction patterns of as-made copolyesters with lower HBA content are shown in Figure 7. The homopolyester HBA0 showed two main diffraction peaks at $2\theta = 18.4°$ and 25.6°, respectively and some other small peaks. The diffraction peaks of HBA10 were similar to that of HBA0. But for copolyesters with HBA content from 20 to 40 mol %, three additional main diffraction peaks at $2\theta = 16.8°$, 22.5°, and 27.4° appeared, and the original two diffraction peaks at $2\theta = 18.4°$ and 25.6° became broader and broader as HBA
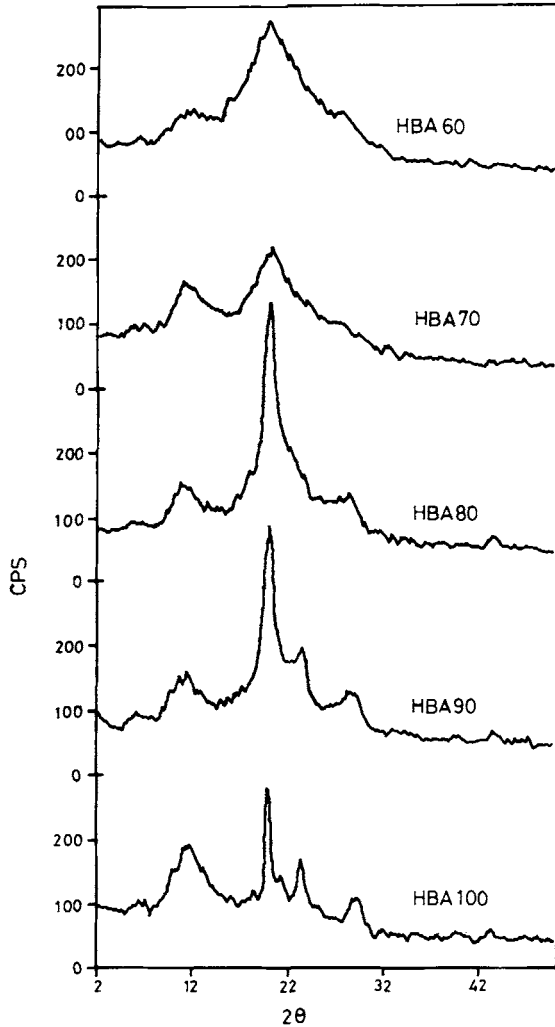
Fig. 6. X-ray diffraction patterns of as-made copolyesters with higher HBA content (CPS = counts per second).

content increased. These three additional diffraction peaks should be contributed to copolymerization. As HBA content was as high as 50 mol %, very broad diffraction pattern was found. As indicated by the X-ray diffraction patterns, the crystallinity decreased as HBA content increased for the copolyesters with lower HBA content, and the trend is consistent with DSC transition heat data.

The presented X-ray data could not be used to describe the annealing effect of solid-state polymerization; however, the X-ray data had the insight to the crystallinity especially in the case of copolyesters with higher HBA content. HBA80, HBA90, and HBA100 showed no explicit melt birefringence (Table I) due to high crystallinity (could be verified by X-ray diffraction) with very high melting temperature.

The second-run DSC thermograms of copolyesters with HBA content from 20 to 70 mol % obviously showed glass transition as indicated by the stepwise
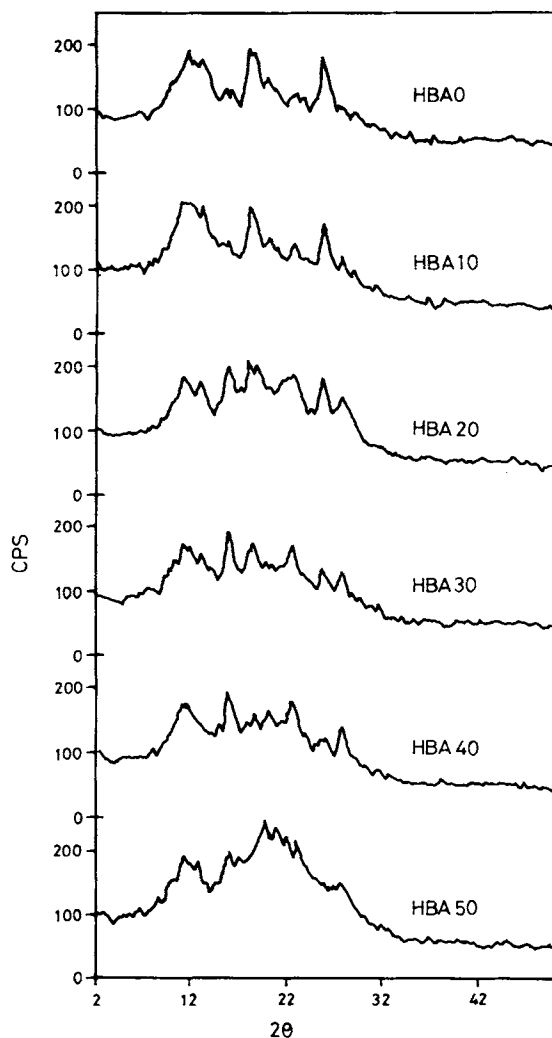
Fig. 7. X-ray diffraction patterns of as-made copolyesters with lower HBA content (CPS = counts per second).

increase of heat capacity. The glass transition temperature (T_g) was taken as the midpoint of the inflection and listed in Table I. T_g decreased as the HBA content increased within this range. It should be noted that T_g is always due to the large molecular chain motion in the amorphous region. Since the crystallinity of HBA0 and HBA10 (as indicated by the high transition heat determined by DSC), and HBA80, HBA90, and HBA100 (as indicated by the sharp X-ray diffraction patterns) was very high, their T_g could not be detected by DSC.

CONCLUSION

The copolyesters of p-hydroxybenzoic, isophthalic acid, and hydroquinone were prepared by melt polycondensation followed by solid-state polymerization.

After solid-state polymerization, the molecular weight was increased. The co-polyesters with HBA content from 50 to 70 mol % showed explicit melt bire-fringence, thus exhibiting liquid crystalline behavior. The DSC thermograms of as-made samples and those of their second run showed significantly different behavior. The differences were described as the annealing effect during solid-state polymerization. As-made samples showed either higher melting temper-ature and transition heat or an additional endotherm caused by annealing. The X-ray diffraction patterns showed that copolyesters with either very low or very high HBA content exhibited high crystallinity, and those with medium HBA content exhibited low crystallinity due to the copolymerization effect.

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