

Preparation and Characterizations of Thermotropic Copolyesters of *p*-Hydroxybenzoic Acid, Sebacic Acid, and Hydroquinone

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SYNOPSIS

A series of copolyesters of *p*-hydroxybenzoic acid (HBA), sebacic acid and hydroquinone were prepared by melt polycondensation of *p*-acetoxybenzoic acid, sebacic acid and *p*-phenylene diacetate. The copolyesters were characterized by IR, NMR, DSC, polarized microscopy, and X-ray diffraction. It was found that the copolyesters exhibited liquid crystallinity when the HBA content was 25–67 mol %. The copolyesters with an HBA content of 25–43 mol % showed a nematic phase and a biphasic range, and the isotropization temperature increased as the HBA content increased. The copolyesters with an HBA content of 54–67 mol % showed a nematic phase up to above 400°C. The liquid crystalline order increased as the HBA content increased due to the increase of the average length of the rigid moieties.

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INTRODUCTION

The polyesters of 4'-hydroxyphenyl-4-hydroxybenzoate and an aliphatic diacid were found to exhibit interesting liquid crystalline behavior.^{1–3} The liquid crystalline behavior was dependent on the length of the spacer. In addition, the chemical structure (i.e., an ordered structure or a random structure, depending on the polymerization process) also influenced the transition temperatures. Strzelecki and Liebert¹ prepared this type of polyester by polymerization of 4'-acetoxyphenyl-4-acetoxybenzoate with an aliphatic diacid (i.e., a transesterification method). Some of the polyesters showed an obvious nematic phase over a broad temperature range (170–300°C) and a biphasic region spanned about an additional 50°C as observed in the polarized microscope. Krigbaum, et al.² also prepared this type of polyester by the same method and similar liquid crystalline behavior was observed. They also indicated that the endotherm of crystal–nematic tran-

sition was broad and the nematic–isotropic transition could not be monitored by differential scanning calorimetry (DSC).² By another method, Krigbaum et al.² also prepared a polyester by polymerization of 4'-hydroxyphenyl-4-hydroxybenzoate with azelaoyl chloride (i.e., a diacid chloride method). The polyester prepared by the diacid chloride method showed an ordered structure and exhibited two sharp DSC endotherms corresponding to the crystalline–nematic and nematic–isotropic transitions. This behavior is more typical of that seen in other semi-rigid polymers^{4–6} and is different from that of the polyesters prepared by the transesterification method. Krigbaum et al.² described the transesterification reaction as occasionally involving the internal ester linkage, in the rigid monomer unit, in the preparation of the polyesters by the transesterification method, and resulting in polyesters with a more random sequence rather than the ordered structure found in polyesters prepared by the diacid chloride method. Moore and Stupp³ prepared some polyesters by polycondensation (polymerization) of 4'-acetoxyphenyl-4-acetoxybenzoate with pimelic acid. The polyesters were characterized by ¹³NMR and were confirmed to show a random structure.

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The polyesters with a random structure exhibited a broader DSC endotherm corresponding to the crystalline–nematic transition, but the nematic–isotropic transition could not be monitored by DSC, and a biphasic region over a wide temperature range was observed in the polarized microscope.^{1–3}

Carter⁷ prepared the copolyesters of *p*-hydroxybenzoic acid (HBA), azelaic acid, and hydroquinone (HQ) with a molar composition of 1 : 1 : 1 by polycondensation of *p*-acetoxybenzoic acid, *p*-phenylene diacetate, and azelaic acid. The copolyesters showed a random structure and exhibited liquid crystalline properties similar to those of the polyesters with a random structure prepared from 4'-acetoxyphenyl-4-acetoxybenzoate and an aliphatic diacid. When the content of HBA in the copolyester of HBA, an aliphatic diacid, and HQ is changed, the average length of the rigid mesogenic units will be changed; consequently, the liquid crystalline behavior will be influenced. However, little was known about the effects of the composition and thus the length of mesogenic moieties on the liquid crystalline behavior. This effect may be similar to that on the thermotropic copolyesters described by Tsai, et al.^{8,9}

In this paper, the preparation and characterizations of a series of random copolyesters of HBA, sebacic acid (SA), and HQ with a full composition range are presented. The effect of the composition on their thermotropic behavior is discussed.

EXPERIMENTAL

Sebacic acid was Merck reagent grade. *p*-Acetoxybenzoic acid and *p*-phenylene diacetate were prepared by reacting *p*-hydroxybenzoic acid and hydroquinone, respectively, with acetic anhydride as described previously.⁸ The copolyesters were prepared by melt polycondensation of *p*-acetoxybenzoic acid, sebacic acid, and *p*-phenylene diacetate similar to the method described in the previous paper.⁸ A typical procedure is described as follows: Under nitrogen gas, 45.0 g (0.25 mol) of *p*-acetoxybenzoic acid, 50.5 g (0.25 mol) of sebacic acid, and 48.5 g (0.25 mol) of *p*-phenylene diacetate were reacted in a one-liter reactor at 250°C. After most of the acetic acid was distilled out, the reaction temperature was raised to 290°C and vacuum was applied slowly to 0.5 torr and held for 2 h.

The intrinsic viscosity of the copolyesters in phenol/*syn*-tetrachloroethane (60/40 wt/wt) at 30°C was determined by an Ubbelohde Viscometer. The IR spectrum of the copolyesters was measured by a Bomen DA 3.002 FT-IR and their ¹H- and ¹³C-NMR

spectra were determined by a Bruker AM 400 MHz NMR. The thermal properties were determined by a Du Pont DSC 910 under nitrogen at a heating rate of 20°C/min. The liquid crystalline texture was investigated by a Leitz Polarizing Microscope equipped with a heating stage. The X-ray diffraction patterns of the copolyesters were determined by a Scintag PAD V Diffraction system using CuK α radiation.

RESULTS AND DISCUSSION

The charged composition and the intrinsic viscosity of the copolyesters are summarized in Table I. The copolyesters exhibited similar IR spectra. Figure 1 shows a typical IR spectrum of S6. The characteristic absorbance peaks were observed at 3112 cm⁻¹ (aromatic C—H stretching), 2929 and 2856 cm⁻¹ (aliphatic C—H stretching), 1742 cm⁻¹ (C=O stretching), 1601 and 1503 cm⁻¹ (aromatic absorptions) and 1263 cm⁻¹ (C—O stretching of ester groups). A typical ¹H-NMR spectrum of S6 is shown in Figure 2. The ¹H-NMR spectra could be used to identify the composition of the copolyesters. There were three groups of resonance peaks in the ¹H-NMR spectra. The peaks at $\delta = 8.1$ –8.5 ppm (H5) were due to the resonance of the aromatic protons ortho to the carbonyl group in the HBA unit. The peaks at $\delta = 7.0$ –7.5 ppm (H4) were due to the resonance of the aromatic protons ortho to oxygen of ester groups in both HBA and HQ units. The aliphatic protons of SA unit (H1–3) showed resonance peaks at $\delta = 1.4$ –2.9 ppm. The composition of the

Table I The Charged Composition and Intrinsic Viscosity of the Copolyesters

Sample No.	Charged Composition (Molar Ratio of HBA : SA : HQ)	Intrinsic Viscosity (dL/g)
S0	0.0 : 1.0 : 1.0	0.45
S1	0.1 : 0.9 : 0.9	0.20
S2	0.2 : 0.8 : 0.8	0.34
S3	0.3 : 0.7 : 0.7	0.58
S4	0.4 : 0.6 : 0.6	0.70
S5	0.5 : 0.5 : 0.5	0.57
S6	0.6 : 0.4 : 0.4	0.55
S7	0.7 : 0.3 : 0.3	0.44
S8	0.8 : 0.2 : 0.2	—
S9	0.9 : 0.1 : 0.1	—
S10	1.0 : 0.0 : 0.0	—

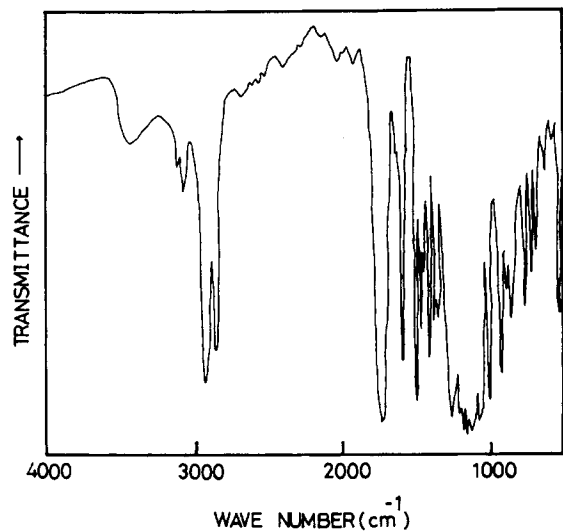


Figure 1 The IR spectrum of S6.

copolyesters was calculated from the integrated intensities of the three groups of peaks except S8, S9, and S10, which were insoluble in the solvent. The measured ratios of HBA : SA : HQ of the copolyesters agreed well with the charged composition (Table I).

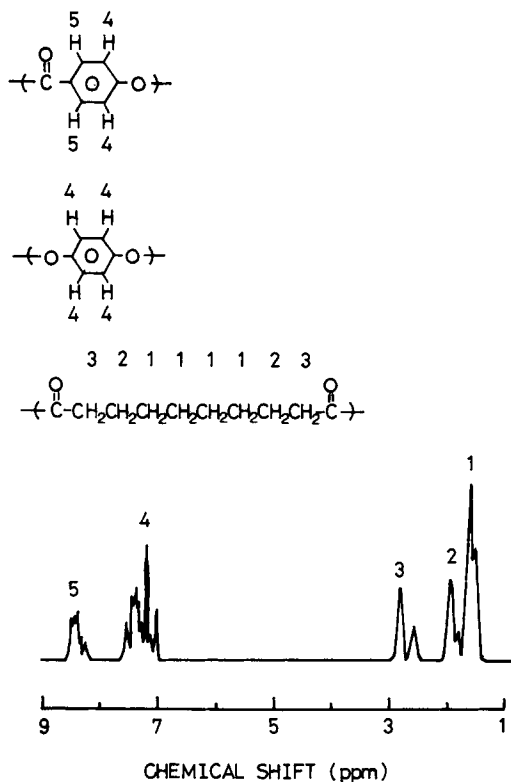


Figure 2 The ¹H-NMR spectrum of S6.

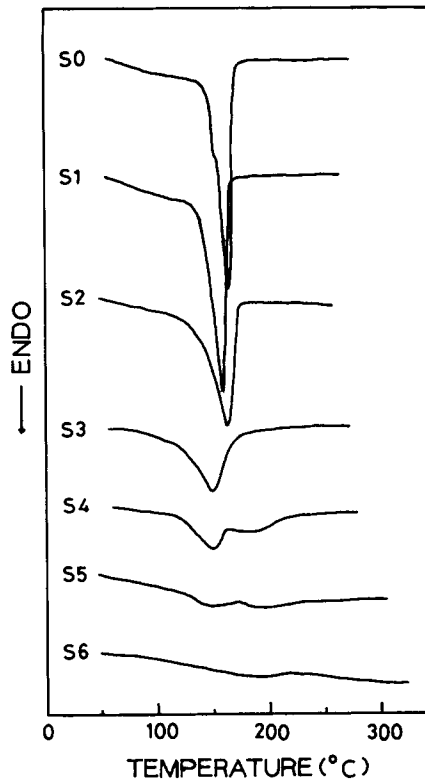


Figure 3 The second run DSC heating curves of copolyesters of S0 to S6.

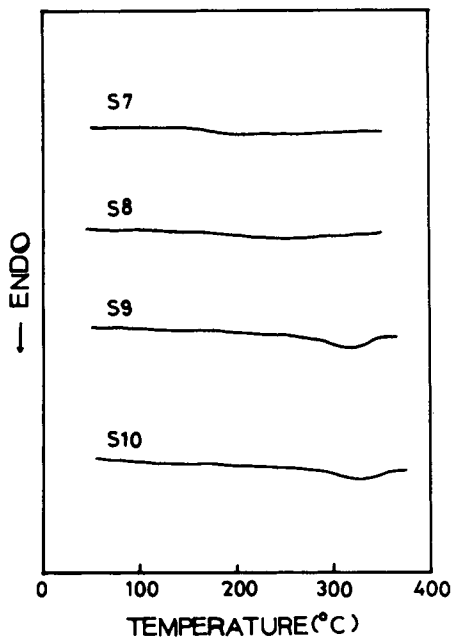


Figure 4 The second run DSC heating curves of copolyesters of S7 to S10.

Table II The Second Run DSC Endotherms (°C), Corresponding Transition Heats (J/g), and Calculated Average Sequence of Rigid Moieties of the Copolyesters

Sample No.	T_1 (ΔH_1)	T_2 (ΔH_2)	Calculated Average Sequence Length of Rigid Moieties
S0	165 (63.2)		1.00
S1	160 (58.3)		1.11
S2	163 (53.1)		1.25
S3	151 (42.0)		1.43
S4	149 (16.8)	188 (13.1)	1.67
S5	142 (3.9)	190 (4.2)	2.00
S6	182 (4.0)		2.50
S7	—		3.33
S8	—		5.00
S9	327 (2.2)		10.00
S10	330 (3.3)		—

Figures 3 and 4 show the typical second-run DSC heating curves of the copolyesters. The DSC endotherms and the corresponding transition heats are listed in Table II. S0, S1, S2, and S3 showed an endotherm. These four polymers became isotropic above the endotherm as observed in the polarized microscope. Thus, the endotherm corresponded to the melting of the crystalline phase. As the HBA content increased, the melting peak became broader, the melting transition heat decreased, and the melting temperature followed a decreasing trend due to copolymerization. S4 and S5 showed two broad endotherms. S6 showed a broad endotherm. For S7 and S8, no endothermic peak was observed up to 350°C. S4 to S8 showed melt birefringence in the polarized microscope and were thus liquid crystalline. The liquid crystalline properties of these five polymers will be discussed later. S9 and S10 showed a small endotherm at about 330°C. S9 and S10 did not melt up to 400°C in the polarized microscope. When the temperature was above 350–400°C, the

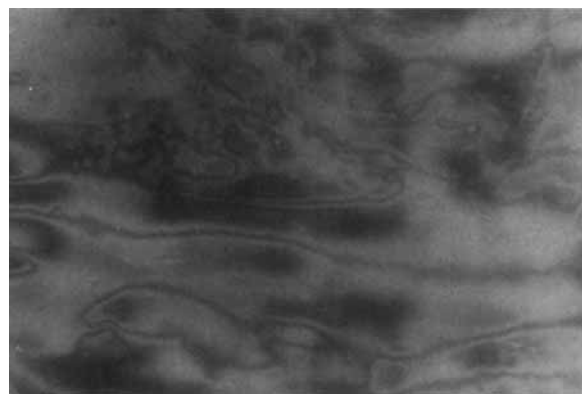
copolyesters showed significant degradation and their thermotropic behavior could not be observed. The endotherm of S9 and S10 at 330°C would be a crystalline–crystalline transition as described by Economy et al.¹⁰

The liquid crystalline behavior of S4–S8 observed by the polarized microscope is summarized in Table III. Within a temperature range, these five polymers exhibited a nematic phase. A typical nematic texture of S7 is shown in Figure 5(a). Upon heating, a melting range from about 140°C to 170°C was observed for S4. This could be related to the melting of different crystallites as indicated by the two broad endotherms detected by DSC. Above 170°C, S4 showed a nematic phase. When S4 was further heated to about 310°C, an isotropic area (dark area) appeared and became larger as the temperature was raised. This is a so-called “biphasic state” similar to that of the polyesters of 4'-hydroxyphenyl-4-hydroxybenzoate and an aliphatic diacid as described in the literature.^{1,2} Figure 5(b) shows the typical biphasic texture. Above 310°C, S4 became completely isotropic. After a melting range of 160–210°C, S5 showed a nematic phase upon heating. Then it exhibited a biphasic range from 310°C to 360°C and became isotropic at 360°C. S5 and S6 also showed a nematic phase and a biphasic temperature range (Table III) similar to S4. The biphasic range was above 400°C for S6. S7 and S8 exhibited a nematic phase after melt, and the nematic state maintained up to 400°C. The isotropization temperatures of S7 and S8 were above 400°C.

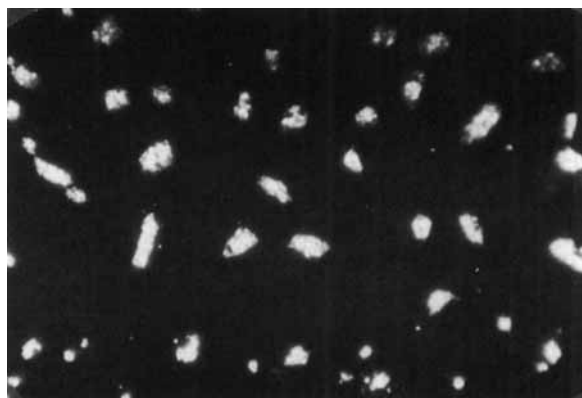
The above results show that the liquid crystalline behavior of the copolyesters depends greatly on their composition. When the HBA content ranged from 25 to 67 mol % (S4–S8), the copolyesters showed liquid crystallinity and the liquid crystalline order increased as the HBA content increased. This would be due to the effect of the average sequence length of the rigid moieties. Figure 6 shows a typical expanded ¹³C-NMR spectrum related to the carbonyl

Table III Transition Temperatures (°C) Observed by the Polarized Microscope

Solid	(Melting Range)	Nematic	(Biphasic Range)	Isotropic
S4	140–170		210–310	
S5	160–210		310–360	
S6	170–230		350–> 400	
S7	240–250		> 400	
S8	260–300		> 400	



(a)



(b)

Figure 5 The photographs of (a) S7 at 260°C ($\times 320$) and (b) S4 at 260°C ($\times 100$) by the polarized microscope.

resonances of S6. Four carbonyl resonance peaks were observed. The signal assignments are also shown in Figure 6. For a polyester of 4'-hydroxyphenyl-4-hydroxybenzoate and sebacic acid with an ordered structure as prepared by the diacid chloride method, no C4 is present and the ratio of C1 : C2 : C3 is 1 : 1 : 1. The presence of a C4 resonance signal indicates that our copolyesters did not exhibit an ordered structure. The ratio of the integrated intensity of C2 : C1 and that of C4 : C3 increased as the HBA content increased, indicating that our copolyesters would exhibit a random structure. For a random copolyester, the average sequence length of the rigid moieties (taken as the average number of *p*-phenylene units of the rigid moieties) is equal to $1/(1-x)$, statistically, where x is the molar fraction of *p*-oxybenzoate in units of *p*-oxybenzoate and *p*-

phenylene sebacate (see Table I). Table II lists the calculated average sequence length of the rigid moieties for the copolyesters. From Tables II and III, it can be seen that the average sequence length of the rigid moieties significantly affected the liquid crystalline behavior of the copolyesters. An average sequence length of the rigid moieties of 1.43 was not long enough for S3 to form a nematic phase. However, an average sequence length of the rigid moieties of 1.67 was long enough for S4 to exhibit nematic liquid crystallinity. Considering S4, S5, and S6, the isotropization temperature increased as the HBA content increased, indicating that when the HBA content increased, the average length of rigid mesogenic moieties increased, and liquid crystalline order also increased. The average sequence length of the rigid moieties was even longer for S7 and S8 and their isotropization temperature was higher than 400°C. When the HBA content was as high as S9 (82 mol % of HBA), the copolyesters showed high crystallinity and did not melt without decomposition. In this case, the copolymerization effect was not sufficient to lower the melting temperature of poly(*p*-oxybenzoate) to a significant extent to observe the liquid crystallinity.

Figure 7 shows the X-ray diffraction patterns of the copolyesters at room temperature. S0 showed two main diffraction peaks at $2\theta = 20.1^\circ$ and 21.8° , respectively. S1 showed two diffraction peaks at $2\theta = 20.7^\circ$ and 21.7° . The original peak of S0 at $2\theta = 20.1^\circ$ was shifted to $2\theta = 20.7^\circ$ for S1. Thus the crystalline structure was changed to some extent af-

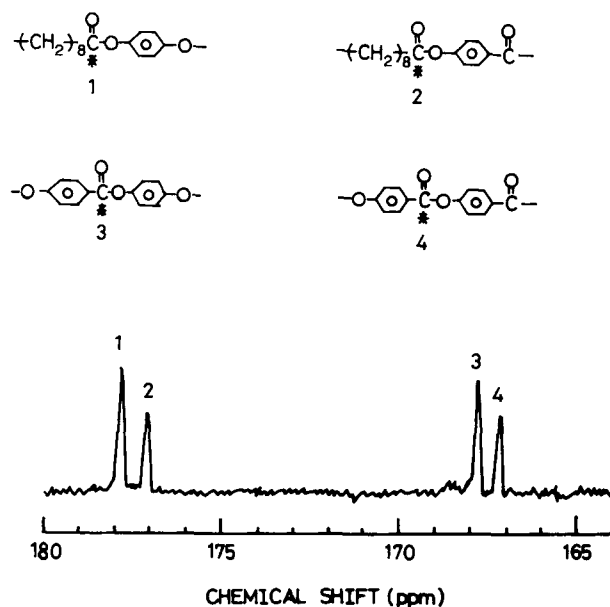


Figure 6 The expanded ^{13}C -NMR spectrum of S6.

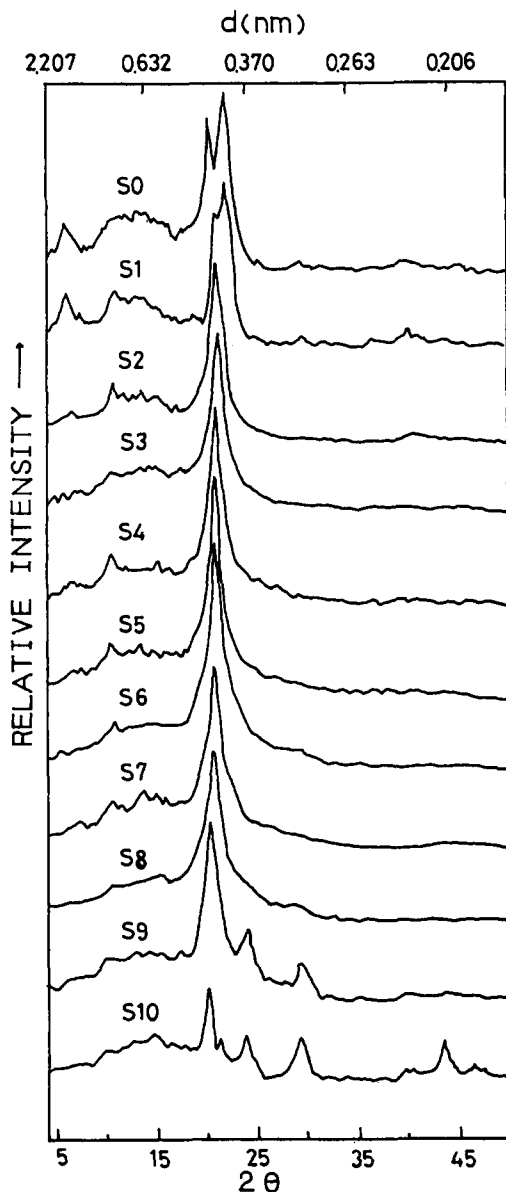


Figure 7 The X-ray diffraction patterns of the copolyesters.

ter copolymerization of a small amount of HBA. S2–S8 showed a main diffraction peak at about $2\theta = 20.6^\circ$. The crystalline structure of S0 was changed within this composition range. S10 showed diffraction peaks at $2\theta = 18.9^\circ, 21.1^\circ, 23.7^\circ, 29.2^\circ,$ and 43.3° , similar to the diffraction patterns of poly(*p*-oxybenzoate) described by Economy et al.¹⁰ S9 showed three diffraction peaks at $2\theta = 18.9^\circ, 23.8^\circ,$ and 29.2° , and some original peaks of S10 disappeared due to copolymerization. As the HBA content

was below about 70 mol % (such as S8), the crystalline structure of S10 was changed. Although no endotherm up to 350°C was detected by DSC for S7 and S8, their X-ray diffraction patterns showed that they might be crystalline at room temperature. These two polymers were solid at room temperature and could melt above certain temperatures to form a nematic phase.

CONCLUSIONS

The random copolyesters of *p*-hydroxybenzoic acid, sebacic acid, and hydroquinone can exhibit liquid crystallinity, depending on the composition. As the HBA content was 25–67 mol %, the copolyesters showed liquid crystallinity. The copolyesters with an HBA content of 25–43 mol % showed a nematic phase and a biphasic range, and the isotropization temperature increased as the HBA content increased. The copolyesters with a HBA content of 54–67 mol % showed a nematic phase up to above 400°C . The liquid crystalline order increased as the HBA content increased due to the increasing average length of the rigid mesogenic moieties.

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