Synthesis and Characterization of Wholly Aromatic Polyesters Derived from 6-Hydroxy-5-phenyl-2-naphthoic Acid or 4′-Hydroxy-3′-phenylbiphenyl-4-carboxylic Acid and 4-Hydroxybenzoic Acid

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ABSTRACT: Two series of new, wholly aromatic copolyesters were prepared from 6-hydroxy-5-phenyl-2-naphthoic acid (HPNA) or 4′-hydroxy-3′-phenyl-biphenyl-4-carboxylic acid (HPBA) and 4-hydroxybenzoic acid (HBA) in varying mole ratios. In addition to these copolyesters, the homopolyesters of 6-hydroxy-5-phenyl-2-naphthoic acid and 4′-hydroxy-3′-phenylbiphenyl-4-carboxylic acid were synthesized. These polyesters were characterized by differential scanning calorimetry, wide angle X-ray diffractometry, thermogravimetry, and polarized microscopy for the study of their thermal transitions, crystallinity, thermal stability, and mesophases. In general, the HPNA copolyesters revealed greater degrees of crystallinity and higher melting temperatures than the HPBA copolyesters. This difference is attributed to the planar naphthalene moiety in the HPNA structure. In contrast, the two phenylene rings of the HPBA unit along the backbone are conjectured not to be coplanar. All of the polyesters formed liquid crystalline mesophases above their melting temperatures.

Introduction

Thermotropic liquid crystalline polyesters have been of considerable interest scientifically and commercially because of their excellent mechanical properties, thermal stabilities, chemical resistance, and flame resistance. The representative thermotropic aromatic polyesters, poly(4-hydroxybenzoic acid) (PHBA) and poly(*p*-phenylene terephthalate), however, have such high melting temperatures that melt processing is not feasible before thermal degradation.[1,2]

There are several methods of structural modifications that can be adopted to decrease the melting temperatures of this class of polymers to a convenient level in order to prevent thermal degradation during melt processing. Among them, copolymerization and the use of unsymmetrically substituted monomers are the most widely investigated methods.[3−12] Especially, utilization of unsymmetrically substituted aromatic monomers is known to be very efficient in the preparation of aromatic polyesters with melting temperatures low enough for melt processing. Such a melting point depression is caused not only by an increase of interchain distance and hindrance of effective chain packing but also by their positional irregularity along the polymer chain. Such an example is the homopolymer of terephthalic acid and phenyl-substituted hydroquinone, which has a much lower melting temperature, T_m, of 340 °C[4,12] when compared to the unsubstituted homopolyester. One, however, has to be very careful in the selection of a proper substituent, because it may lower the thermal stability of the resulting polymers in addition to its undesirable influence on physical and mechanical properties. In connection with this work Bhowmik et al.[13,14] reported the crystalline and liquid crystalline properties of a series of aromatic polyesters derived from phenyl-substituted 4,4′-biphenols.

Recently, we reported[15,16] the synthesis and characterization of homopolyesters of 1-phenyl-2,6-naphthalenedicarboxylic acid (PNDA) and 3-phenyl-4,4′-biphenyldicarboxylic acid (PBDA) with various aromatic diols. In this paper, we describe the synthesis and characterization of two series of copolyesters based on 6-hydroxy-5-phenyl-2-naphthoic acid (HPNA) or 4′-hydroxy-3′-phenylbiphenyl-4-carboxylic acid (HPBA) with 4-hydroxybenzoic acid (HBA). The structures and designations of copolyesters I and II, which were prepared and characterized in this study, are shown in Chart 1. The main purpose of this research is to further clarify the effect of the phenyl substituent on the thermal and crystalline properties of the two series of aromatic copolyesters.

Experimental Section

Monomer Synthesis. 5-Bromo-6-hydroxy-2-naphthoic Acid (2). 6-Hydroxy-2-naphthoic acid (20.0 g; 10.6 × 10^{-2} mol) was dissolved in 300 mL of tetrahydrofuran. To this solution was added slowly, at room temperature, a solution of tetrahydrofuran (20 mL) containing 6.5 mL of bromine. After being stirred for 4 h at room temperature, the mixture was poured into distilled water. The precipitate was collected and washed with chloroform. The product was recrystallized from a mixture of ethanol and water (5/4 v/v). The yield was 23.2 g (81.1%), mp 275 °C. IR (KBr, cm^{-1}): 3450 (O−H stretch), 3400−2400 (acid O−H stretch), 1689 (C=O stretch), 1289 and 1192 (ether C−O stretch). ^{1}H-NMR (acetone-d_6, δ, ppm): 7.4−8.62 (m, 5H, aromatic), 9.55 (broad, 1H, OH). Anal. Calcd for $C_{11}H_7BrO_3$: C, 49.09; H, 2.63. Found: C, 49.24; H, 2.48.

Methyl 5-Bromo-6-hydroxy-2-naphthoate (3). Compound **2** (9.21 g; 7.14 × 10^{-2} mol) was dissolved in a mixture of 200 mL of dry methanol and 100 mL of dry THF, to which was added dropwise 9.5 mL of purified thionyl chloride. The mixture was stirred for 6 h at room temperature. The reaction mixture was poured into ice-cold distilled water. The mixture was neutralized to pH 7.0 with 5% $NaHCO_3$. The precipitate formed was collected on a filter and thoroughly washed with distilled water. The dry crude product was recrystallized from hexane. The yield was 19.0 g (93.8%), mp 170 °C. IR (KBr, cm^{-1}): 3336 (O−H stretch), 1692 (C=O stretch), 1282−1180 (ether C−O stretch). ^{1}H-NMR (acetone-d_6, δ, ppm): 3.95 (s, 3H, CH_3), 7.40−8.63 (m, 5H, aromatic), 9.55 (s, 1H, OH). Anal. Calcd for $C_{12}H_9BrO_3$: C, 51.27; H, 3.22. Found: C, 50.94; H, 3.11.

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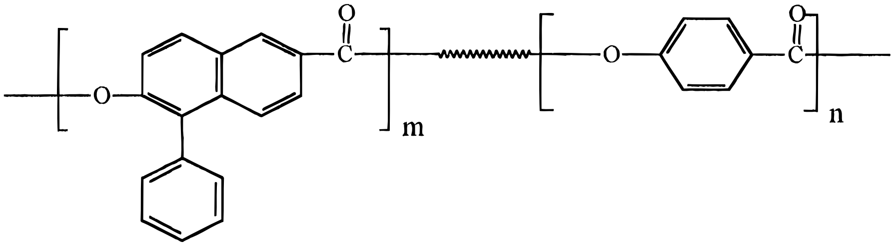
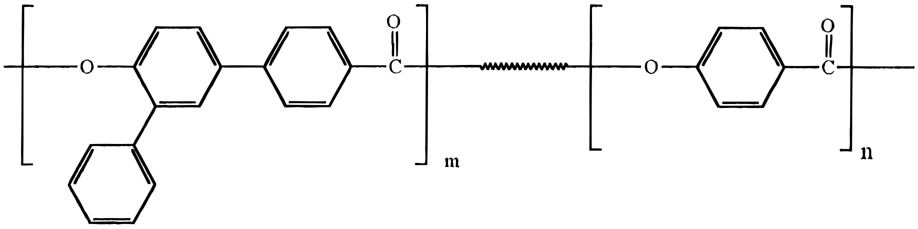
Chart 1



Series I

I-1, m : n = 100 : 0
I-2, m : n = 70 : 30
I-3, m : n = 50 : 50
I-4, m : n = 25 : 75
I-5, m : n = 10 : 90
I-6, m : n = 5 : 95



Series II

II-1, m : n = 100 : 0
II-2, m : n = 75 : 25
II-3, m : n = 50 : 50
II -4, m : n = 30 : 70
II-5, m : n = 10 : 90

Methyl 5-Bromo-6-methoxy-2-naphthoate (4). Compound **3** (18.9 g; 6.68 × 10^{-2} mol) was dissolved in a mixture of 350 mL of acetone and 13.8 g (9.98 × 10^{-2} mol) of K_2CO_3, to which was added dropwise 0.6 mL of dimethyl sulfate. The mixture was stirred for 6 h at room temperature. The reaction mixture was poured into distilled water. The precipitate formed was collected on a filter and thoroughly washed with distilled water. The product was recrystallized from a mixture of acetone and water (1/1 v/v). The yield was 19.0 g (95.7%), mp 164 °C. IR (KBr, cm^{-1}): 1707 (C=O stretch), 1280−1180 (ether C—O stretch). ^{1}H-NMR (acetone-d_6, δ, ppm): 3.95 (s, 3H, $COOCH_3$), 4.12 (s, 3H, OCH_3), 7.40−8.63 (m, 5H, aromatic). Anal. Calcd for $C_{13}H_{11}BrO_3$: C, 52.90; H, 3.75. Found: C, 52.72; H, 3.70.

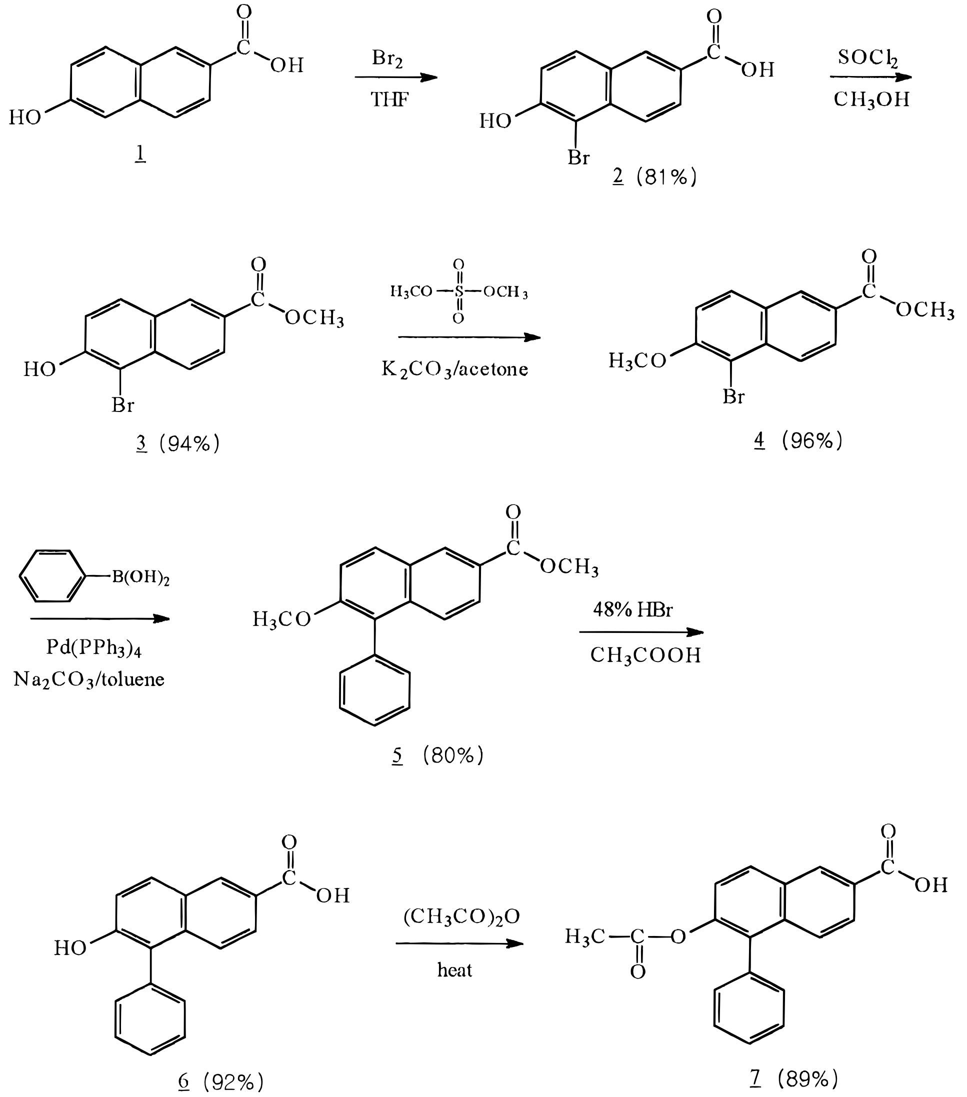
Methyl 6-Methoxy-5-phenyl-2-naphthoate (5). Compound **4** (18.88 g; 0.635 mol) was dissolved in 400 mL of toluene, to which solution was added 2.2 g (0.19 × 10^{-2} mol) of $Pd(PPh_3)_4$, 95 mL of a 2 M Na_2CO_3 solution, and 11.6 g (9.51 × 10^{-2} mol) of phenylboronic acid dissolved in 5 mL of ethanol.[17] The mixture was refluxed for 24 h with vigorous stirring under a nitrogen atmosphere. After cooling, solvents were removed from the mixture using a rotary evaporator. The residue was thoroughly washed with 1 M Na_2CO_3 and then with distilled water. The precipitate was extracted with diethyl ether. The ether phase was dried over anhydrous Na_2SO_4. The solvent was removed, and the crude product was recrystallized from a mixture of ethanol and water (1/1 v/v). The yield was 14.9 g (79.8%), mp 141 °C. IR (KBr, cm^{-1}): 1710 (C=O stretch), 1280−1180 (ether C—O stretch). ^{1}H-NMR (acetone-d_6, δ, ppm): 3.89 (s, 3H, $COOCH_3$), 3.94 (s, 3H, OCH_3), 7.32−8.64 (m, 10H, aromatic). Anal. Calcd for $C_{19}H_{16}O_3$: C, 77.54; H, 5.51. Found: C, 77.81; H, 5.47.

6-Hydroxy-5-phenyl-2-naphthoic Acid (6). Compound **5** (13.5 g; 4.059 × 10^{-2} mol) was dissolved in 500 mL of acetic acid, to which was added dropwise 80.0 mL of 48% HBr.[18] After being refluxed for 14 h, the mixture was poured into distilled water. The precipitate formed was collected on a filter and thoroughly washed with distilled water. The dry crude product was recrystallized from a mixture of ethanol and water (1/2 v/v). The yield was 11.2 g (92.0%), mp 197−198 °C. IR (KBr, cm^{-1}): 3530 (O—H stretch), 3200−2400 (acid O—H stretch), 1681 (C=O stretch), 1230−1170 (C—O stretch). ^{1}H-NMR (acetone-d_6, δ, ppm): 7.39−8.63 (m, 10H, aromatic). Anal. Calcd for $C_{17}H_{12}O_3$: C, 77.30; H, 4.48. Found: C, 77.01; H, 4.50.

6-Acetoxy-5-phenyl-2-naphthoic Acid (7). Compound **6** (9.1 g; 3.43 × 10^{-2} mol) was dissolved in excess acetic anhydride. The mixture was refluxed for 6 h. After cooling, the mixture was poured into distilled water. The precipitate formed was collected on a filter and thoroughly washed with distilled water. The crude product was recrystallized from a mixture of ethanol and water (1/1 v/v). The yield was 9.3 g (89.4%), mp 236−237 °C, IR (KBr, cm^{-1}): 3400−2400 (acid O—H stretch), 1763 and 1683 (C=O stretch), 1195 (C=O stretch). ^{1}H-NMR ($CDCl_3$, δ, ppm): 2.12 (s, 3H, CH_3), 7.32−8.75 (m, 10H, aromatic). Anal. Calcd for $C_{19}H_{14}O_4$: C, 74.50; H, 4.60. Found: C, 74.76; H, 4.69.

Methyl 3′-Bromo-4′-hydroxybiphenyl-4-carboxylate (9). 4′-Hydroxybiphenyl-4′-carboxylic acid (20.0 g; 9.34 × 10^{-2} mol) was dissolved in 400 mL of 1,4-dioxane. To this solution was added dropwise at 0−5 °C a solution of dioxane (15 mL) containing 5.3 mL (0.10 mol) of bromine. After standing overnight, the reaction mixture was poured into distilled water. The precipitate formed was collected on a filter and washed thoroughly with distilled water. The crude product **8** (25.8 g; 8.80 × 10^{-2} mol) containing 3′,5′-dibromo-4′-hydroxybiphenyl-4-carboxylic acid was esterified by the same procedures as described above in the synthesis of compound **3**. The dry crude product was found by column chromatography to consist of 3′-bromo-4′-hydroxybiphenyl-4-carboxylic acid (major product) and 3′,5′-dibromo-4′-hydroxybiphenyl-4-carboxylic acid (minor product) in the ratio of 3:1. The major product was separated by silica gel column chromatography using a mixture of ethyl acetate and hexane (1/5 v/v) as an eluent. The yield was 16.7 g (82.7%), mp 141 °C. IR (KBr, cm^{-1}): 3351 (O—H stretch), 1689 (C=O stretch), 1250−1160 (C—O stretch). ^{1}H-NMR (acetone-d_6, δ, ppm): 3.95 (s, 3H, CH_3), 7.22−8.12 (m, 7H, aromatic), 9.23 (s, 1H, OH). Anal. Calcd for $C_{14}H_{11}BrO_3$: C, 54.75; H, 3.60. Found: C, 55.22; H, 3.61.

Scheme 1. Synthetic Route to Monomer 7



3′-Bromo-4′-hydroxybiphenyl-4-carboxylic Acid (8). Hydrolysis of compound **9** was carried out in the same way as described above for the synthesis of compound **6**. The crude product was recrystallized from ethanol. The yield was 93%, mp 244–245 °C. IR (KBr, cm^{-1}): 3525 (O—H stretch), 3400–2400 (acid O—H stretch), 1687 (C═O stretch), 1291 and 1180 (C—O stretch). ^{1}H-NMR (acetone-d_6, δ, ppm): 7.12–8.15 (m, 7H, aromatic), 9.10 (broad, 1H, OH). Anal. Calcd for $C_{13}H_9BrO_3$: C, 53.27; H, 3.09. Found: C, 53.29; H, 3.01.

The subsequent reactions to obtain compound **13**, consisting of methylation, the Suzuki reaction with phenylboronic acid, hydrolysis, and acetylation (Scheme 2), were carried out by the same procedures as described above in the synthesis of compound **7**. Therefore, only the yields, physical data, and elemental analyses of compounds **10**–**13** are given below.

Methyl 3′-Bromo-4′-methoxybiphenyl-4-carboxylate (10). The crude product was recrystallized from acetone. The yield was 84%, mp 146 °C. IR (KBr, cm^{-1}): 1713 (C═O stretch), 1280–1180 (ether C—O stretch). ^{1}H-NMR ($CDCl_3$, δ, ppm): 3.95–3.98 (d, 6H, 2CH_3), 6.98–8.10 (m, 7H, aromatic). Anal. Calcd for $C_{15}H_{13}BrO_3$: C, 56.09; H, 4.07. Found: C, 55.34; H, 3.90.

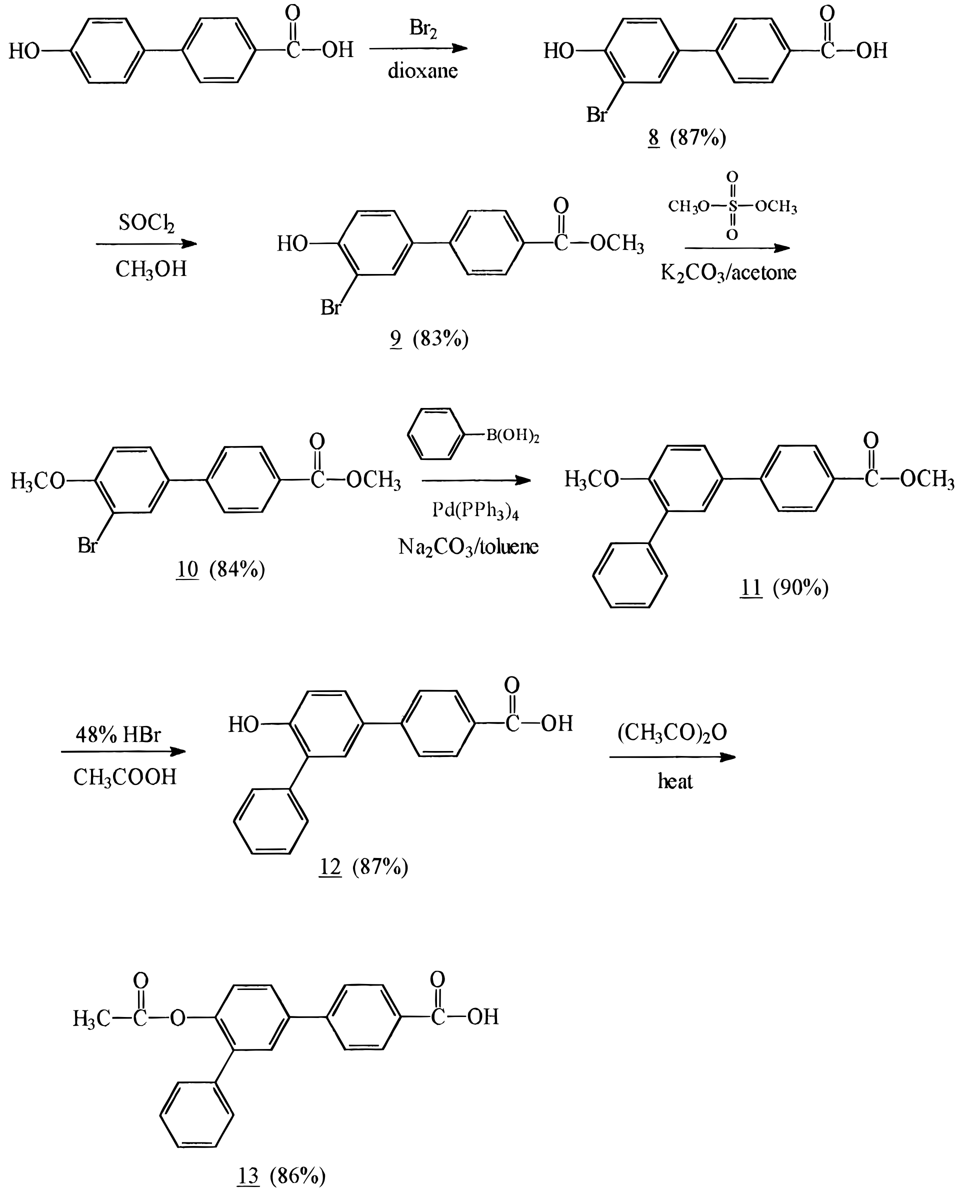
Methyl 4′-Methoxy-3′-phenylbiphenyl-4-carboxylate (11). The crude product was recrystallized from a mixture of ethanol and water (1/1 v/v). The yield was 90%, mp 131 °C. IR (KBr, cm^{-1}): 1716 (C═O stretch), 1280–1100 (C—O stretch). ^{1}H-NMR ($CDCl_3$, δ, ppm): 3.88–3.95 (d, 6H, 2CH_3), 7.12–8.20 (m, 12H, aromatic). Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.22; H, 5.69. Found: C, 79.32; H, 5.71.

4′-Hydroxy-3′-phenylbiphenyl-4-carboxylic Acid (12). The crude product was recrystallized from benzene. The yield was 87%, mp 210 °C. IR (KBr, cm^{-1}): 3525 (O—H stretch), 3400–2400 (acid O—H stretch), 1300–1100 (C—O stretch). ^{1}H-NMR (acetone-d_6, δ, ppm): 7.10–8.13 (m, 12H, aromatic), 8.75 (broad, 1H, OH). Anal. Calcd for $C_{19}H_{14}O_3$: C, 78.61; H, 4.86. Found: C, 78.19; H, 4.88.

4′-Acetoxy-3′-phenylbiphenyl-4-carboxylic Acid (13). The crude product was recrystallized from a mixture of acetone and water (1/1 v/v). The yield was 86%, mp 273–274 °C. IR (KBr, cm^{-1}): 3400–2400 (acid O—H stretch), 1758 and 1683 (C═O stretch), 1280–1180 (C—O stretch). ^{1}H-NMR (DMSO-d_6, δ, ppm): 2.12 (s, 3H, CH_3), 7.32–8.12 (m, 12H, aromatic). Anal. Calcd for $C_{21}H_{16}O_4$: C, 75.89; H, 4.85. Found: C, 75.47; H, 4.82.

Synthesis of Polymers. All of series I and II polyesters were prepared by melt polycondensation reaction of the respective acetylated monomers. Since all of them were synthesized in the same manner, only a representative procedure is described for the preparation of the I-3 copolyester. 6-Acetoxy-5-phenyl-2-naphthoic acid (2.09 g; 0.7×10^{-2} mol) and 4-acetoxybenzoic acid (1.26 g; 0.7×10^{-2} mol) were charged into a polymerization tube which was equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum distillation connection. The tube was immersed in a salt bath at 250 °C. The reaction mixture was stirred at 250 °C for 80 min, at 280 °C for 40 min, at 320 °C for 30 min, at 350 °C for 60 min, and then at 360 °C for 30 min under a nitrogen atmosphere. Finally, the pressure was reduced to and kept at 1 Torr at 360 °C for 30 min. The product obtained was powdered, subjected to Soxhlet extraction with ethanol for 3 days, and washed several times with boiling THF. Elemental analysis of the polymers was performed using a Carlo Erba 1108 (Carlo

Scheme 2. Synthetic Route to Monomer 13



Erba Co.) instrument by the Organic Chemistry Research Center, Sogang University, Seoul, Korea.

Identification and Characterization of Intermediates and Polyesters. Melting points were determined either with a Fisher-Johns melting point apparatus or on a differential scanning calorimeter (DSC). IR spectra were recorded on a Bomen MB-Series FT-IR instrument by means of KBr pellets. The inherent solution viscosities of series I polymers were measured at 60 °C for the solutions of 0.1 g/dL in pentafluorophenol. But the values for series II were measured at 30 °C for the solution of 0.1 g/dL in a 30/30/40 wt % mixture of pentafluorophenol/*p*-chlorophenol/chloroform using a Cannon-Ubbelhode type viscometer. The thermal properties were studied on a Perkin-Elmer DSC 7 at a heating rate of 80, 20, or 10 °C/min under a N_2 atmosphere. Indium was employed for calibration. Thermogravimetry was conducted on a DuPont 9900 instrument at a heating rate of 80 °C/min under a N_2 atmosphere.

Optical textures were examined with a Mettler FP82HT hot stage on a Leitz Metallux polarizing microscope. The wide angle X-ray diffractograms were obtained on a Rigaku Geiger Flex b-Max III_a instrument using Ni-filtered Cu Kα radiation. ^{1}H-NMR end group analyses were conducted after 20 mg of series I polymers was hydrolyzed in a mixture of 0.4 mL of 4 M NaOD in D_2O and 0.6 mL of CD_3OD in a 5 mm-o.d. NMR tube. The ^{1}H-NMR spectra were recorded on a Bruker AMS 500 spectrometer.

Results and Discussion

Synthesis of Monomers. 6-Acetoxy-5-phenyl-2-naphthoic acid (**7**), a new monomer, was prepared as shown in Scheme 1. 5-Bromo-6-hydroxy-2-naphthoic acid (**2**) was obtained by bromination of 6-hydroxy-2-naphthoic acid (**1**) in tetrahydrofuran (THF) solution. Compound **2** was esterified to give **4**, which was then condensed with phenylboronoic acid in the presence of the Pd(0) catalyst (Suzuki reaction)[17] to produce **5**, methyl 6-methoxy-5-phenyl-2-naphthoate. Compound **5** was hydrolyzed[18] and finally acetylated to produce 6-acetoxy-5-phenyl-2-naphthoic acid (**7**).

Another monomer, 3′-phenyl-4′-acetoxybiphenyl-4-carboxylic acid (**13**), was synthesized from 4′-hydroxybiphenyl-4-carboxylic acid through the steps shown in Scheme 2. The synthetic steps are the same as for the synthesis of monomer **7**, with the only difference being in the structures of the starting materials. 4-Acetoxybenzoic acid[19] was prepared by acetylation of 4-hydroxybenzoic acid with excess acetic anhydride. The structures of the intermediates and the final compounds were confirmed by elemental analyses and IR and NMR spectroscopy.

Table 1. Synthetic Results of the Series I Polyesters

polymer	feed HPNA:HBA[a]	yield, %	elemental anal., wt %			final polymer HPNA:HBA[b]
				C	H	
I-1	100:0	92	calcd	82.92	4.09	100:0
			found	82.44	3.86	
I-2	70:30	81	calcd	80.68	3.97	72:28
			found	79.81	3.88	
I-3	50:50	84	calcd	78.68	2.85	50:50
			found	78.81	3.82	
I-4	25:75	86	calcd	75.25	3.65	26:74
			found	74.91	3.62	
I-5	10:90	90	calcd	72.41	3.49	12:88
			found	72.85	3.48	
I-6	5:95	90	calcd	72.02	3.38	5:95
			found	72.02	3.38	

[a] Feed ratio of 6-hydroxy-5-phenyl-2-naphthoic acid and 4-hydroxybenzoic acid. [b] Molar ratio of comonomers as determined from ^{1}H NMR spectral analyses.

Synthesis of Polyesters. All of the polyesters described here were prepared by melt polymerization of the monomers in varying molar ratios. No catalyst was utilized for polycondensations. All of the polyesters solidified as they formed because of their high melting temperatures. At the final stage of polymerization, vacuum (0.1 Torr) was applied to the polymerization tube at 360−390 °C for several hours depending on the composition prepared. All of the polyesters were subjected to Soxhlet extraction with ethanol for 3 days and were washed thoroughly with boiling THF before drying.

The synthetic results of series I polymers are summarized in Table 1. To determine the actual composition of the copolyesters prepared, they were hydrolyzed in $NaOD/D_2O/CD_3OD$ and the hydrolyzed mixtures were subjected to ^{1}H-NMR analysis.[20,21] The ^{1}H-NMR signals of hydrolyzed poly(5-phenyl-6-oxy-2-naphthoate) and poly(4-oxybenzoate) are well separated, and thus, the molar compositions could be calculated readily from these ^{1}H-NMR spectra. The results reveal that the molar compositions of the final polymers are very close to, or the same as, the feed ratios. The ^{1}H-NMR spectra of hydrolyzed polyesters also allow us to estimate number-average molecular weights of the polymers from the intensity of the acetate signal by assuming equivalent concentrations of two terminal groups, as previously described by others.[20,21] According to such analyses, all of the polymers were found to be of fairly high molecular weights, because we could not clearly detect the acetate signal due to its low concentration. Most probably, their MWs are higher than 25 000. The accuracy and reliability of this method, of course, depend on the chemistry of the condensation process, especially on potential side reactions modifying the end groups. This problem is common to all end group analyses.

Unfortunately, the series II polymers were resistant to hydrolysis, so their molar compositions and the number-average molecular weights could not be estimated by ^{1}H-NMR analyses. The relatively high inherent viscosity values (ca. 2.1−3.4 dL/g) of soluble polymers also strongly indicate high molecular weights for the present polymers.

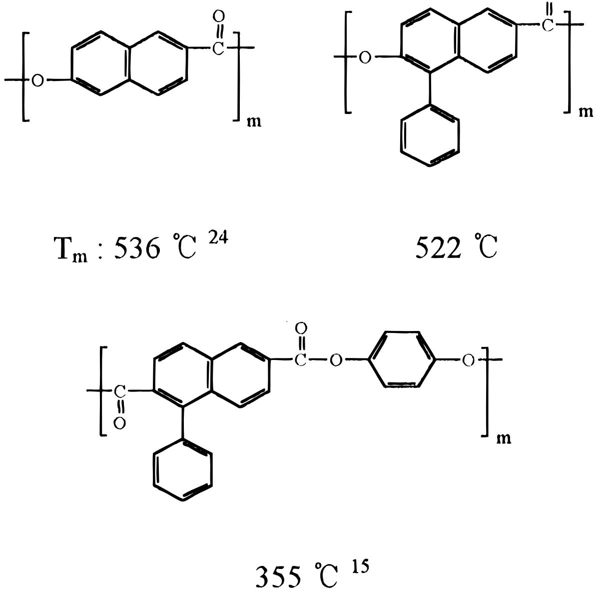
Table 2. General Properties of Series I (HPNA) Polymers

polymer	η_{inh}, dL/g	T_g, °C	$T_{k\text{-}k}$, °C	T_m, °C	$T_D{}^i$, °C[d]	$T_D{}^{max}$, °C[d]
I-1	ins	198	333	522	548	570
I-2	2.48[b]	195		418 (419)[c]	519	555
I-3	2.91[b]	190		393 (410)[c]	537	568
I-4	ins	180		356 (349)[c]	538	570
I-5	ins	170	305	522	538	562
I-6	ins	168	297	538	537	565
PHBA[a]			336	561		

[a] Quoted from ref 8. [b] Measured at 60 °C for 0.1 g/dL solution in pentafluorophenol. [c] Measured at the heating rate of 10 °C/min. Other data were obtained at the heating rate of 80 °C/min. [d] Initial and maximum rate decomposition temperatures, respectively.

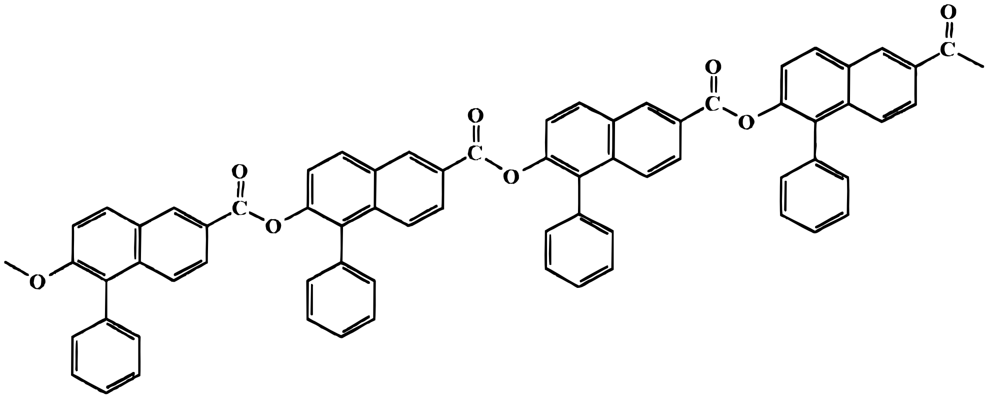
General Properties and Liquid Crystallinity. The data given in Table 2 show the general properties of series I polyesters. The glass transition temperatures (T_g) and melting temperatures (T_m) of series I polymers could be determined from the heating DSC curves; see Figure 1 and Table 2. The DSC thermograms of the polyesters were obtained at a heating rate of 80 °C/min under a nitrogen atmosphere. A rather fast heating rate was necessary to avoid thermal decomposition of polymers before reaching their melting temperatures. The T_g value of I-1, 198 °C, is the highest. It decreases steadily with increasing content of the HBA units. For example, the copolyester containing 95 mol % of the HBA unit shows a T_g value of 168 °C, which is the lowest among the T_g values of the copolyesters.

The T_m value of 522 °C for I-1 is only slightly lower than that (536 °C)[22] of unsubstituted poly(6-oxy-2-naphthoate), which suggests that the presence of the phenyl substituent does not affect molecular packing much. It was reported recently by us[15] that poly(*p*-phenylene 1-phenyl-2,6-naphthalenedicarboxylate) has a rather low melting temperature (355 °C). This comparison emphasizes how strongly regular or irregular placement of substituents can influence the melting temperature of polymers.[6] In polymer I-1, all of the phenyl substituents are placed in a fixed orientation. But the situation is completely different for poly(*p*-phenylene-1-phenyl-2,6-naphthalenedicarboxylate), as demonstrated in Chart 2. The irregular orientation of the phenyl substituents along the chain is expected to impair the chain's ability to pack efficiently in three dimensions and would, in turn, reduce the interchain interactions, resulting in the reduction in the T_m value.



The T_m values of the copolyesters exhibit an expected, usual depression for the compositions containing significant levels of the comonomer unit; the T_m value of homopolyester I-1 is 522 °C, whereas the value of the copolymer prepared at a mole ratio of HPNA:HBA = 1:1 (I-3) is 393 °C. The most surprising phenomenon observed for the T_m values of series I copolyesters is the

Chart 2



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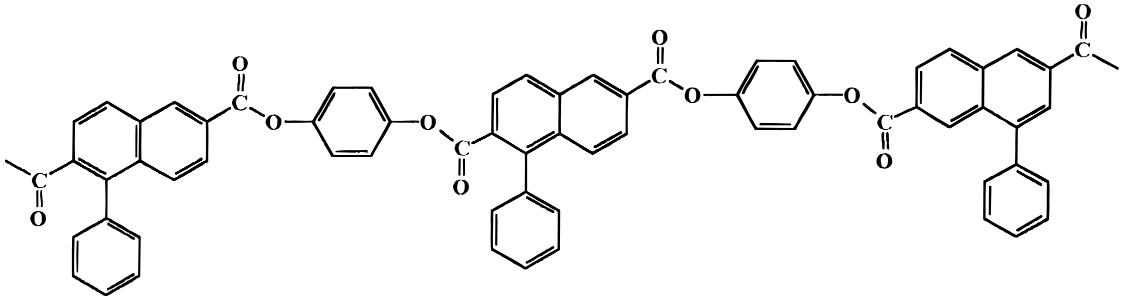

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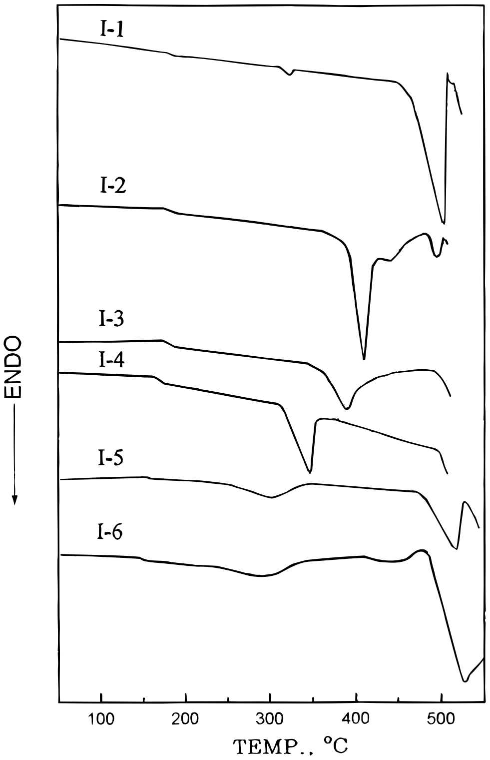


Figure 1. DSC thermograms of series I polyesters (heating rate: 80 °C/min).

fact that they are consistently higher than those prepared from the unsubstituted 6-acetoxy-2-naphthoic acid and 4-acetoxybenzoic acid.[22-24] It is our conjecture that the presence of the phenyl substituent tends to increase the lattice force in the crystalline region probably due to the enhanced polarizability of the repeating unit, which, in turn, is expected to cause higher T_m values. Some of the polyesters such as I-1, I-5, and I-6, exhibit low-temperature endothermic peaks at 333, 305, and 297 °C, respectively. These endothermic transitions are ascribed to crystal-to-crystal transitions. This point will be discussed further in detail later when X-ray analysis of I-6 is dealt with. And I-6 shows an additional broad endotherm around 450 °C, which is believed to correspond to the crystal-to-solidlike liquid crystal phase transitions, as reported by others[25-27] for poly(4-oxybenzoate). The exact nature of the transitions, however, requires further study. There has been some controversy on the nature of similar transitions occurring before the melting of poly(4-oxybenzoate).[25-27]

Table 2 also contains the data of initial decomposition temperatures of series I polyesters obtained by TGA under a nitrogen atmosphere at a heating rate of 80 °C/min. All of the initial decomposition temperature values are higher than 500 °C. The phenyl substituent certainly does not diminish the good thermal stability of the polyesters much, in comparison with other substituents such as chlorine, bromine, alkyl, and alkoxy groups which are known to decrease thermal stability.[28,29]

The optical textures of the polymer melts quenched above their T_m values were examined on a polarizing microscope. The optical textures of I-2, I-3, and I-4 imply that they form nematic melts. Figure 2 shows a Schlieren nematic texture for I-3 copolyester quenched at 440 °C. Therefore, it is believed that all of the compositions in series I polymers are thermotropic, although liquid crystallinity of I-1, I-5, and I-6 could not

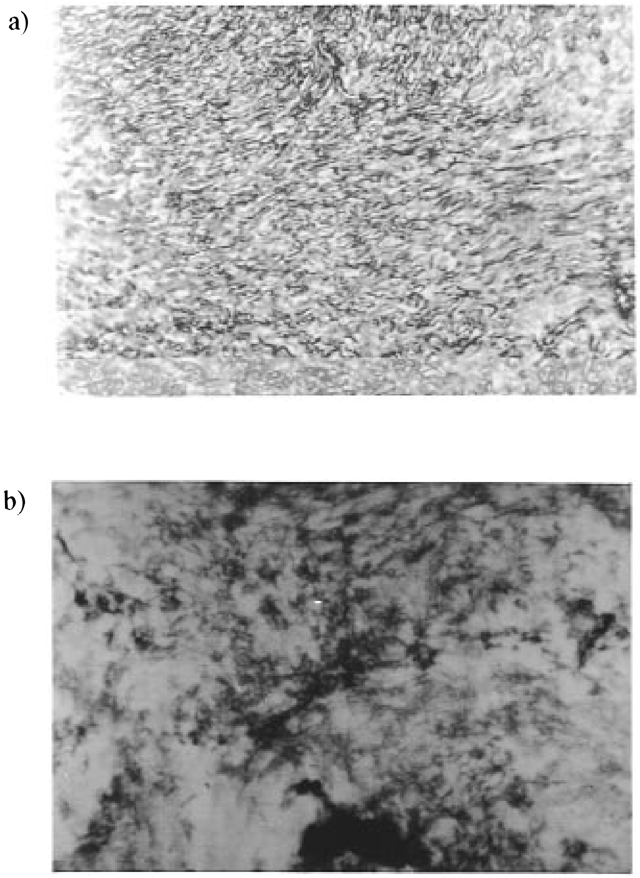


Figure 2. Photomicrographs of polyester (a) I-4 and (b) II-3 quenched at 440 °C (magnification 400X) (reduced to 65% of original size for publication).

Table 3. General Properties of Series II (HPBA) Polymers

polymer	η_{inh}, dL/g	T_g, °C	T_{k-k}, °C	T_m, °C	T_D^i, °C[d]	T_d^{max}, °C[d]
II-1	ins.	152	333	435 (424)[c]	519	550
II-2	ins.	156		395 (379)[c]	500	539
II-3	3.45[b]	161		339 (328)[c]	537	535
II-4	2.11[b]	153		amorphous	500	520
II-5	ins		337	505	510	550
PHBA[a]			336	561		

[a] Quoted from ref 8. [b] Measured at 30 °C for 0.1 g/dL solution in a mixed solvent of pentafluorophenol/*p*-chlorophenol/chloroform = 3/3/4 by volume. [c] Measured at the heating rate of 20 °C/min. Other data were obtained at the heating rate of 80 °C/min. [d] Initial and maximum rate decomposition temperatures, respectively.

be clearly examined due to their high melting temperatures. We, however, believe that the nature of the mesophase for I-5 and I-6 should be the same, i.e., nematic, as reported for poly(4-oxybenzoate) in light of the fact that they contain low levels of the HPNA unit. Although there are reports[26,30] on the formation of smectic phases by poly(4-oxybenzoate) right after initial melting, we did not study in detail the thermal and LC behavior of I-5 and I-6 because of their high melting temperatures.

Table 3 summarizes the general properties of series II polyesters. The glass transition temperatures (T_g) and melting temperatures (T_m) of series II polymers could be clearly determined from the heating DSC curves; see Figure 3 and Table 3. First of all, homopolymer II-1 shows a much lower melting temperature (435 °C) when compared with homopolymer I-1 (522 °C). The same is true for the T_m values of all the series II copolyesters; their T_m values are significantly lower than those of series I copolyesters (see Figure 4).

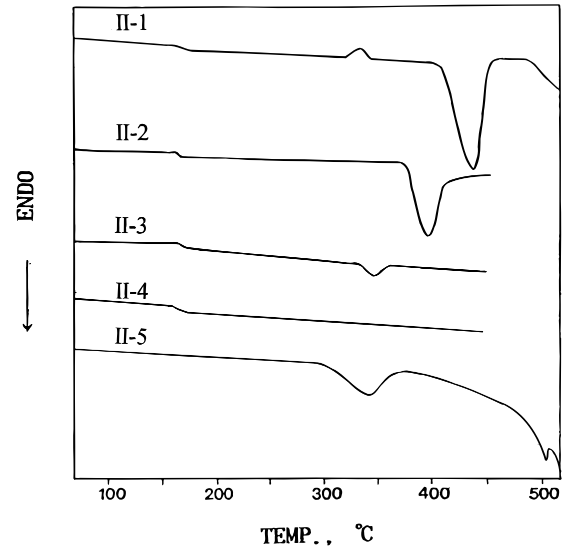


Figure 3. DSC thermograms of series II polyesters (heating rate: 80 °C/min).

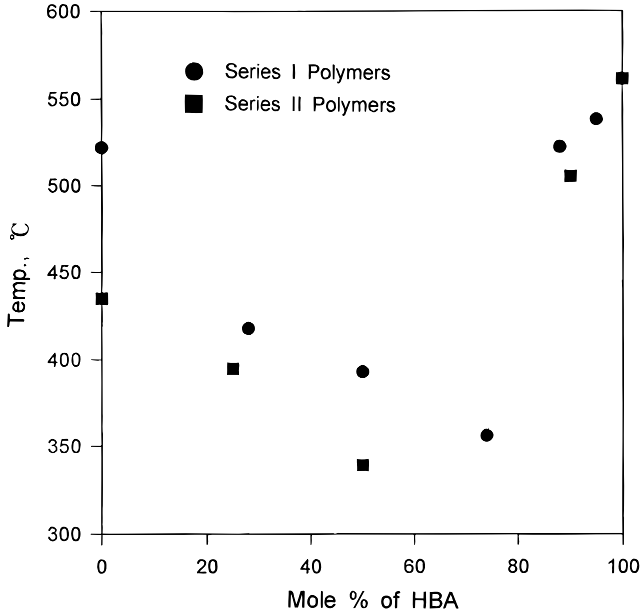
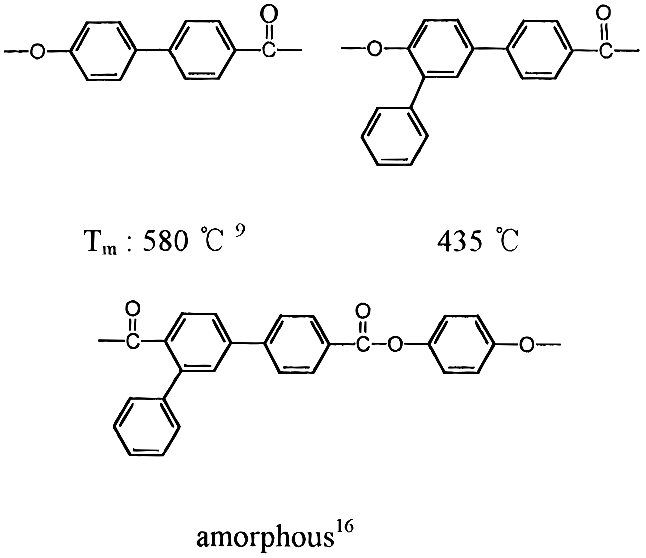


Figure 4. Comparison of melting points of series I and II polyesters.



It also should be noted that attachment of the phenyl substituent to poly(4′-oxy-1,1′-biphenyldiyl-4-carbonyl) greatly lowers the T_m value from 580 to 435 °C (II-1). As mentioned above, the same phenyl group did not lower the T_m value of polymer I-1 as much. Again it is emphasized that unsymmetrically substituted comonomer is far more efficient in decreasing the melting point, as shown above, for poly(*p*-phenylene 2-phenyl-4,4′-biphenyldicarboxylate), which is not even crystalline. The greater melting point depression by the phenyl substituent in series II than in series I is a great contrast to the reported fact[10,22,31] that the T_m values of the copolyesters prepared from 6-hydroxy-2-naphthoic acid and 4-hydroxybenzoic acid are much lower than the T_m's of the copolyesters derived from 4′-hydroxybiphenyl-4-carboxylic acid and 4-hydroxybenzoic acid. Another interesting, contrasting behavior lies in the fact that HPNA forms higher melting copolymers with HBA (series I) than unsubstituted 6-hydroxy-2-naphthoic acid, whereas HPBA produces lower melting copolyesters (series II) than unsubstituted 4′-hydroxybiphenyl-4-carboxylic acid.

As far as the T_g values are concerned, the values for series II polymers are significantly lower than those of the previous series. For example, the T_g value of homopolyester I-1 is 198 °C, whereas the value of homopolymer II-1 is lower (152 °C) by about 45 deg, which can be ascribed to the flat fused rings of the naphthalene unit that is expected to generate less free volume when compared with the twisted biphenyl unit.

Liquid crystallinity of homopolymer II-1 could not be clearly confirmed due to its high T_m value. And copolyesters II-2 and II-3 revealed a strong birefringence in the melt. The II-4 copolyester containing 70 mol % of the HBA unit is also definitely thermotropic. Figure 2 shows a Schlieren nematic texture observed through a polarizing microscope for II-3 copolyester quenched at 400 °C. Isotropization was not detectable up to 550 °C, where thermal degradation prevents further observation.

The DSC thermogram of II-5 exhibits a small endotherm at 337 °C before melting, which indicates the same change in crystal modifications already known for PHBA.[25-27] This copolyester contains 90 mol % of the HBA unit and is expected to exhibit thermal behavior very similar to that of the HBA homopolymer. According to the TGA thermograms, series II polyesters reveal an initial weight loss and the maximum rate of decomposition at slightly lower temperatures than series I polyesters. This observation can probably be explained by the presence of the single bond between the two phenylene rings in the backbone of the biphenyl units. In contrast, the naphthalene unit does not possess any single bond character.

X-ray Analysis of Solid Polymers. As mentioned above, all of the as-polymerized samples showed melting transitions on DSC thermograms, indicating that they are crystalline. Their crystalline nature can be further supported by the wide angle X-ray diffractograms of the series I polymer at room temperature (see Figure 5).

It can be seen that the crystallinity decreases with increasing HBA content and the copolyester containing 50 mol % of HBA is almost amorphous. The X-ray diffraction patterns of copolyesters very rich in the 4-hydroxybenzoic acid (HBA) unit are nearly indentical with that of pure PHBA.[23] Recently, we[32] reported that homopolymer I-1, poly[oxy-2,6-(1-phenyl)naphthalenediyl carbonyl], prepared by constrained thin film polymerization, forms a lamellar crystal having an orthorhombic cell with $a = 29.60$ Å, $b = 5.08$ Å, and $c = 16.74$ Å. X-ray diffraction patterns of copolyester I-6 obtained at higher temperatures are compared with the pattern obtained at 30 °C in Figure 6. As can be seen from Figure 1, this polymer exhibits a broad endothermic change from about 250 °C. And Figure 6 clearly shows changes in diffraction pattern as the sample is heated from room temperature to 360 °C. The small scattering at $2\theta = 15.7°$ (5.6 Å) completely disappears. At the same time, the two peaks at $2\theta = 23.8°$ (3.7 Å) and 29.5° (3.0 Å) broaden and finally disappear as the polymer is heated further. A small new diffraction peak appears at $2\theta = 27.2°$ (3.3 Å). We do not presently understand exactly what crystalline modification causes these observations, although our conjecture is that a change in the orientation of the phenyl substituent may be one of the possible explanations.[33]

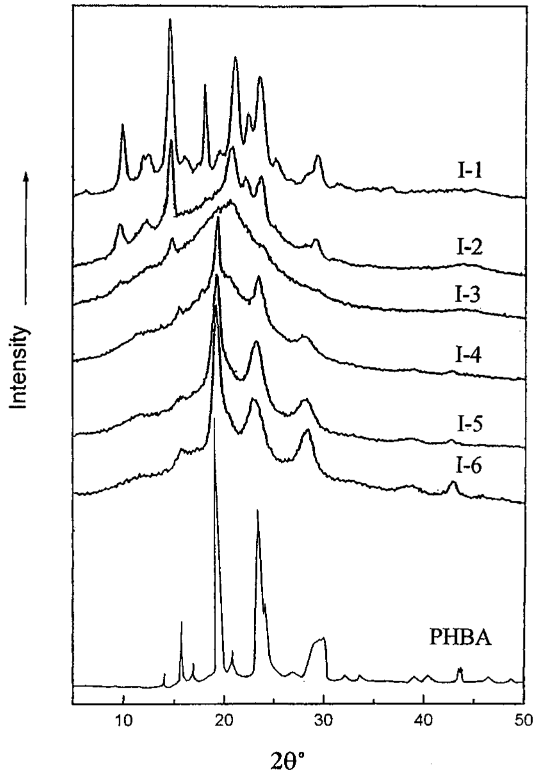


Figure 5. Wide angle X-ray diffractograms of series I polymers.

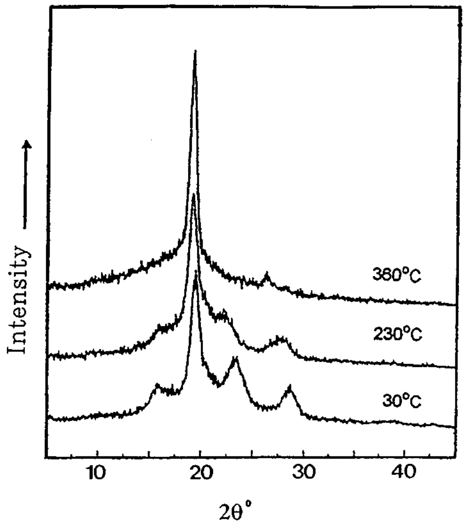


Figure 6. Temperature dependence of wide angle X-ray diffractograms of polyester I-6.

The X-ray diffractograms of series II polyesters show that copolymerization again strongly decreases crystallinity of the copolymers and polymers II-3 and II-4 are almost amorphous (Figure 7). The diffraction positions

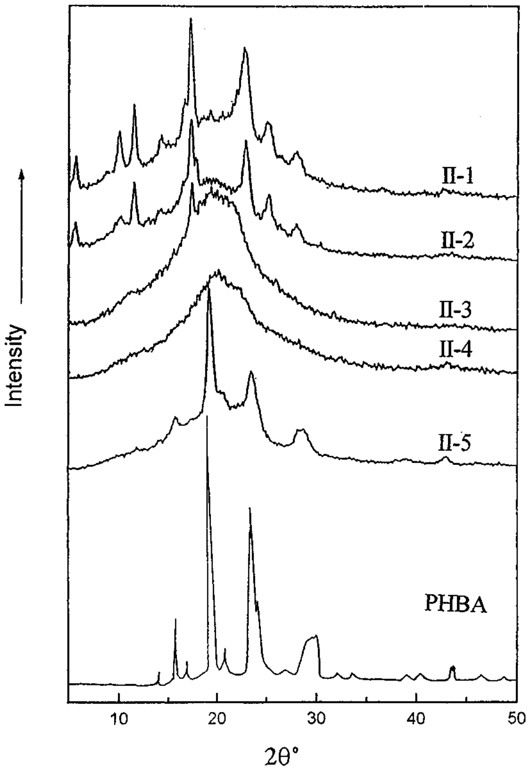


Figure 7. Wide angle X-ray diffractograms of series II polyesters.

of II-5 are almost the same as those for poly(4-oxybenzoate), although the peaks are much broader, indicating the presence of a higher degree of crystal defects. This behavior is expected, because only 10 mol % of the HPBA unit has been incorporated in the copolyester. All of the polymers were annealed for 6 h around 260 °C, but the thermal treatment produced little improvement in the level of crystallinity. It is pointed out that homopolymer II-1, poly[oxy-4,4′-(3′-phenyl)biphenyldiylcarbonyl] synthesized by the constrained thin film polymerization technique, produced single crystals of a monoclinic (pseudo-orthorhombic, $\alpha = 90°$) cell with $a = 15.24$ Å, $b = 3.94$ Å, and $c = 10.54$ Å.[32]

Conclusion

Attachment of a bulky substituent such as the phenyl group on the rings is very well-known to decrease the melting points of aromatic polyesters.[13,14] Moreover, according to the reports made earlier by others,[10,22,31] the melting temperatures of the copolyesters prepared from 4′-hydroxybiphenyl-4-carboxylic acid and 4-hydroxybenzoic acid are much higher than those of the corresponding copolyesters derived from 6-hydroxy-2-naphthoic acid and 4-hydroxybenzoic acid.

This investigation, however, provides us with rather unexpected, surprising results; not only is the phenyl group relatively inefficient in lowering the melting point of the naphthalene homopolyester II-1 (522 °C) when compared with that of the corresponding unsubstituted polyester (526 °C), but also the T_m values of series I copolyesters are consistently higher than those of copolyesters derived from the unsubstituted naphthalene monomer. In contrast, the same substituent is so efficient in lowering the T_m values of biphenyl homo- and copolyesters (series II) that the series II polymers exhibit lower melting points than the series I polymers, which is completely opposite of the melting behavior of the unsubstituted polyesters. The T_g values also are higher for series I than for series II. Although such a striking difference in the substituent effect by the phenyl group is rather perplexing and is not easy to explain unequivocally, one may be able to attribute it to the dissimilar packing behavior of the two series brought about by the substituent as described by us[32] recently for the two polyesters I-1 and II-1.

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