Crystalline and Liquid Crystalline Polyesters of Phenyl-Substituted 4,4′-Biphenols and 1,1′-Binaphthyl-4,4′-diol. 3. Copolymers with 6-Hydroxy-2-naphthoic Acid

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Received September 6, 1995; Revised Manuscript Received December 11, 1995[⊗]

ABSTRACT: Wholly aromatic, thermotropic copolyesters, derived from either 3-phenyl-4,4′-biphenol, 3,3′-diphenyl-4,4′-biphenol, or 1,1′-binaphthyl-4,4′-diol with either terephthalic acid or 2,6-naphthalenedicarboxylic acid and 30 mol % 6-hydroxy-2-naphthoic acid, were prepared by melt polycondensation reactions and characterized for their thermotropic liquid crystalline properties by a wide variety of experimental techniques. The three copolyesters containing phenyl-substituted 4,4′-biphenols had either lower fusion temperature, T_f, or lower crystal-to-nematic transitions, T_m, than those of an analogous series of copolyesters containing unsubstituted 4,4′-biphenol. Each of them formed a nematic phase above its T_f/T_m values, which was supported from the X-ray diffraction pattern obtained from each of the oriented fibers. Their nematic phases showed both a marbled texture and a Schlieren texture. In one case, a banded texture was also observed, without being subjected to shear. Although the polarized light microscopy study of the fourth copolymer containing 1,1′-binaphthyl-4,4′-diol suggested its nematic phase above its T_f value, X-ray diffraction pattern obtained from its oriented fiber indicated its localized sanidic or boardlike microstructure. No development of crystallinity occurred in each of these copolymers on annealing, which suggested that all of them had random microstructures in their polymer chains. Despite little to no crystallinity in these copolymers, they were not soluble in common organic solvents. As expected, each of them had a broad range of nematic liquid crystalline phase because of the copolymerization effect of the added monomer. They had higher glass transition temperatures, T_g, in the range of 128−180 °C than those of other liquid crystalline copolyesters. They exhibited high thermal stability, T_d, in the range of 417−494 °C suggesting their convenient melt processing in the nematic liquid crystalline phase at elevated temperatures.

Introduction

Both poly(4-oxybenzoate) and poly(6-oxy-2-naphthoate) have, in principle, the ideal structure for thermally stable, thermotropic homopolyesters. Yet, a regular array of dipole moments and van der Waals forces in these homopolymers provides an unusually high degree of crystallinity (>90%) and a very stable crystal lattice. Consequently, their crystal-to-nematic transitions, T_m, are sufficiently high that these homopolymers decompose before their melting transitions can be reached. Also, they are insoluble in the known solvents.

There are several types of structural modifications both to decrease the T_m values of this class of polymers to a convenient level in order to prevent thermal degradation during the nematic melt processing and to increase their solubility in common organic solvents in order to facilitate their solution characterizations. On the one hand, the common aggressive solvents in which they have very limited solubility are pentafluorophenol, 3,5-bis(trifluoromethyl)phenol, and a mixture of *p*-chlorophenol/1,1,2,2-tetrachloroethane. On the other hand, structurally modified thermotropic polyesters have also solubility in $CHCl_3$, CH_2Cl_2, tetrahydrofuran, and dioxane.[1−10] For such polymers, copolymerization is one of the most effective methods to disturb the regularity of their chemical structures and reduce the stability of their crystal lattices in order to decrease the T_m values and improve the solubility. Such an example is the copolymerization of the acetates of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA), which produces random copolyesters, which form a nematic melt with the decreased T_m values having a minimum temperature at 245 °C.[11,12] Another example of a processable wholly aromatic, thermotropic liquid crystalline polymer (LCP) is the copolyesters of 4,4′-biphenol (BP), terephthalic acid (TA), and HBA that form the basis of a Xydar family of LCPs, which have a minimum T_m value at about 400 °C, although this temperature is rather high for the nematic melt processing in conventional molding equipment.[13,14] Kricheldorf and co-workers also investigated a number of copolymers containing HBA as a comonomer for their thermotropic LC properties with either 3-chloro-4-hydroxybenzoic acid or 4-mercaptobenzoic acid.[15,16] We reported the results of a series of thermotropic copolyesters based on phenyl-substituted BPs, TA, or 2,6-naphthalenedicarboxylic acid (NDA) and 30 mol % HBA.[17] All of these copolyesters have been found to form a nematic LC phase at temperatures much lower than 400 °C. Their low T_m values arise because of two principal reasons: (a) the bulky phenyl group(s) appendaged to 4,4′-biphenylene moieties provide structural irregularities in the polyester chains and (b) the copolymerization effect of HBA units introduces additional irregularities in the copolyester chains. However, a large number of studies have been devoted to wholly aromatic, thermotropic copolyesters based on HBA,[11−22] but relatively few studies have been performed on this class of polymers based on HNA.[9,11,12,23]

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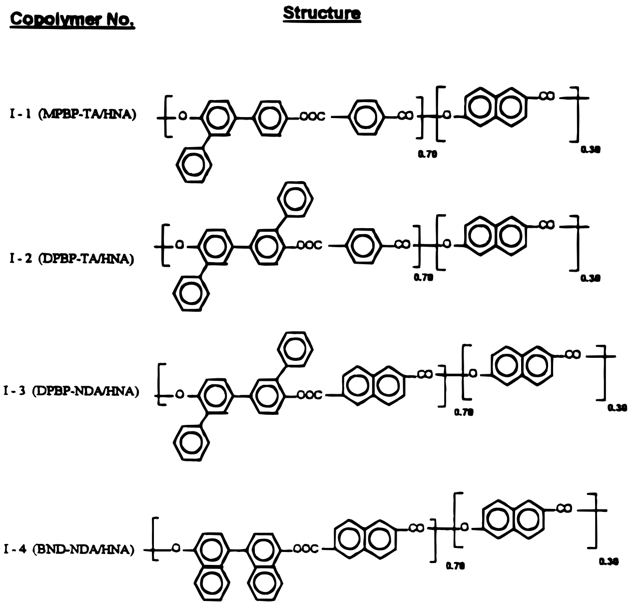
[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

0024-9297/96/2229-1910$12.00/0

In this article, we describe the preparation and characterization of a series of thermotropic copolyesters based on 3-phenyl-4,4′-biphenol (MPBP), 3,3′-diphenyl-4,4′-biphenol (DPBP), and 1,1′-binaphthyl-4,4′-diol (BND) with either TA or NDA and 30 mol % HNA. On copolymerization of these monomers with HNA, a random distribution of 6-oxy-2-naphthoate units should be obtained which would be expected to disturb the packing of the polymer chains resulting in a low-T_m polyester. Furthermore, in contrast to the linear 4-oxybenzoate unit, this unit would provide a linear offset structure in the copolyester chain imparting a disturbance in the crystal packing, which is essential in the preparation of low-T_m polyester. Copolymers with higher percentages of HNA were not included in the study because such copolyesters might contain blocklike sequences of HNA, which would impart a higher T_m.[18] The structures and designations of the copolyesters **I**, which were prepared and characterized in this study, are shown below. These wholly aromatic, thermotropic copolyesters were characterized by a variety of experimental techniques, including solution viscometry, Fourier transform infrared spectroscopy (FTIR), polarizing light microscopy (PLM), differential scanning calorimetry (DSC), thermomechanical analysis (TMA), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). Additionally, X-ray diffraction patterns of fibers drawn from their nematic LC phases were examined for the four copolyesters.



Experimental Section

Monomer Synthesis. The substituted BPs, MPBP and DPBP, and BND were received as diacetates from Schnectady Chemicals Inc., NY. The two aromatic dicarboxylic acids, TA and 2,6-NDA, were received from Amoco Chemicals and used without further purification. The preparation of HNA was performed according to a previously reported procedure.[24] Subsequently, it was acetylated[25] and recrystallized twice from ethyl acetate in very small needles.

Polyester Synthesis. All of the copolyesters with 30 mol % HNA were prepared from the copolymerization of 6-acetoxy-2-naphthoic acid and the requisite amounts of the other two comonomers by a melt polycondensation reaction without an added catalyst.[8] At the end of the polymerization reaction, the solidified polyester was dissolved in a mixture of p-chlorophenol and 1,1,2,2-tetrachloroethane, precipitated from solution with a 10-fold excess of ethanol, and washed several times with boiling ethanol. The copolyester was dried for 72 h under vacuum. The usual polymerization time was 24 h, and the yield of copolymerization was nearly quantitative.

Polymer Characterization. Inherent viscosities, IV, of the copolyesters were measured in p-chlorophenol at 50 °C at a polymer concentration of 0.2 g/dL with a Cannon Ubbelohde-type viscometer. Infrared spectra were recorded with a Nicolet Fourier transform infrared analyzer using neat films of polyesters in KBr pellets. The phase transitions temperatures were measured with a Perkin-Elmer DSC-2 instrument, calibrated with indium and tin, under a nitrogen flow with the heating and cooling rates of 20 °C/min. Polymer samples weighing 5−10 mg were used for this analysis. The peak maximum of the phase transition temperatures was recorded from the first heating cycle only for polymers **I-2** and **I-3** because no melting endotherm was observed in the second heating cycle. The glass transition temperature, T_g, was taken as the onset of this transition during either the first or second heating cycle, whichever was more prominent. It was also measured on a DuPont 2100 TMA instrument with a heating rate of 20 °C/min under a load force of 100 mN. For each of the polymers **I-1** and **I-4**, there was no phase transition temperatures in either the first or second heating cycle, and in this case a fusion temperature, T_f, was recorded as the temperature of the onset of flow as observed for the sample on a hot-plate melting point apparatus and verified by use of a hot stage on a polarizing light microscope from the observation of a typical nematic texture on the edge of the sample, that is, at the thinnest part of the specimen. The LC texture of each of the copolyesters was observed on a polarizing light microscope (Leitz, Model Ortholux) equipped with a pair of crossed polarizers and a Mettler hot stage. TGA was obtained on a DuPont TGA 951 instrument with a thermal analyzer 2100 system at a heating rate of 20 °C/min under a nitrogen flow.

For wide-angle X-ray diffraction studies, samples were heated to above the T_m or T_f and allowed to cool to fixed temperatures in the LC phase. Oriented fibers were pulled from the LC phase and quenched in cold water. The sample was X-rayed using pinhole collimation using a Statton camera, evacuated to backing pressure (10^{-2} Torr). The radiation used was Cu Kα using a nickel filter, and the X-ray patterns were recorded on photographic films. Microstructures of fiber samples were characterized using a JEOL JSM-T330A scanning electron microscope with an accelerating voltage of 30 kV. They were then mounted on aluminum stubs and sputtered with gold using an Eiko Engineering IB-3 sputter-coater for enhanced conductivity. Fibers were also drawn typically for this analysis on heating the sample well above its T_m or T_f and pulling with tweezers.

Results and Discussion

Solution Properties. All of the copolyesters were prepared by the melt polycondensation reaction and were soluble in p-chlorophenol. As mentioned earlier, a wholly aromatic, thermotropic polyester, generally, has exceedingly low solubility in all known organic solvents. The low solubility of this class of polymers is related to their extended rigid structures and relatively high crystallinity. The present series of copolyesters had little or no crystallinity, as discussed later, but was not soluble in common organic solvents, such as $CHCl_3$, tetrahydrofuran, and dioxane. Their insolubility in these common solvents clearly demonstrates that their solubility is a complicated consequence of crystallinity and main-chain solvation and, therefore, difficult to predict. However, the data in Table 1 show that their IV values were in the range of 0.80−1.51 dL/g, indicating their moderate to high molecular weights. Therefore, their thermal properties, optical textures, and other properties can be compared neglecting the effect of molecular weight on these properties.

FTIR Spectra. Figure 1 shows a FTIR spectrum of polymer **I-1** taken at room temperature, which is typical for all of the copolyesters. Their IR spectra showed the

Table 1. Thermal Properties of Thermotropic Copolyesters of MPBP, DPBP, and BND

copolymer no.	monomer[a]	IV[b] (dL/g)	T_g[c] (°C)	T_m[d] (°C)	T_f[f] (°C)	T_i[g] (°C)	T_d[h] (°C)	texture by PLM
I-1	MPBP + TA + HNA	1.36	128 (127)		185	>450	494	nematic
I-2	DPBP + TA + HNA	1.06	140 (162)	332[e]		450	491	nematic
I-3	DPBP + NDA + HNA	1.51	151 (155)	334[e]		>450	427	nematic
I-4	BND + NDA + HNA	0.80	180 (199)		250	>450	417	nematic

[a] Monomer designation: MPBP, 3-phenyl-4,4′-biphenol; TA, terephthalic acid; HNA, 6-hydroxy-2-naphthoic acid; DPBP, 3,3′-diphenyl-4,4′-biphenol; BND, 1,1′-binaphthyl-4,4′-diol. HNA (30 mol %) was included in each of the copolyesters. [b] Measured in *p*-chlorophenol at 50 °C. [c] Glass transition temperature, T_g, was recorded from the DSC thermogram, and the value in parentheses was determined with a thermomechanical analyzer. [d] Crystal-to-LC transition, T_m, was determined by DSC measurement. [e] From the first heating cycle. [f] Fusion temperature, T_f, was determined from the temperature of onset of flow as observed on a hot-plate melting point apparatus and verified by polarizing light microscope studies on observation of a typical nematic texture on the edge (the thinnest part of the sample). [g] Isotropization temperature, T_i, was determined on the hot stage of a PLM at which the disappearance of both the birefringence and the threaded texture occurred. [h] Thermal stability, T_d, was determined in nitrogen at a heating rate of 20 °C/min at a temperature at which a weight loss of 5% of the sample occurred.

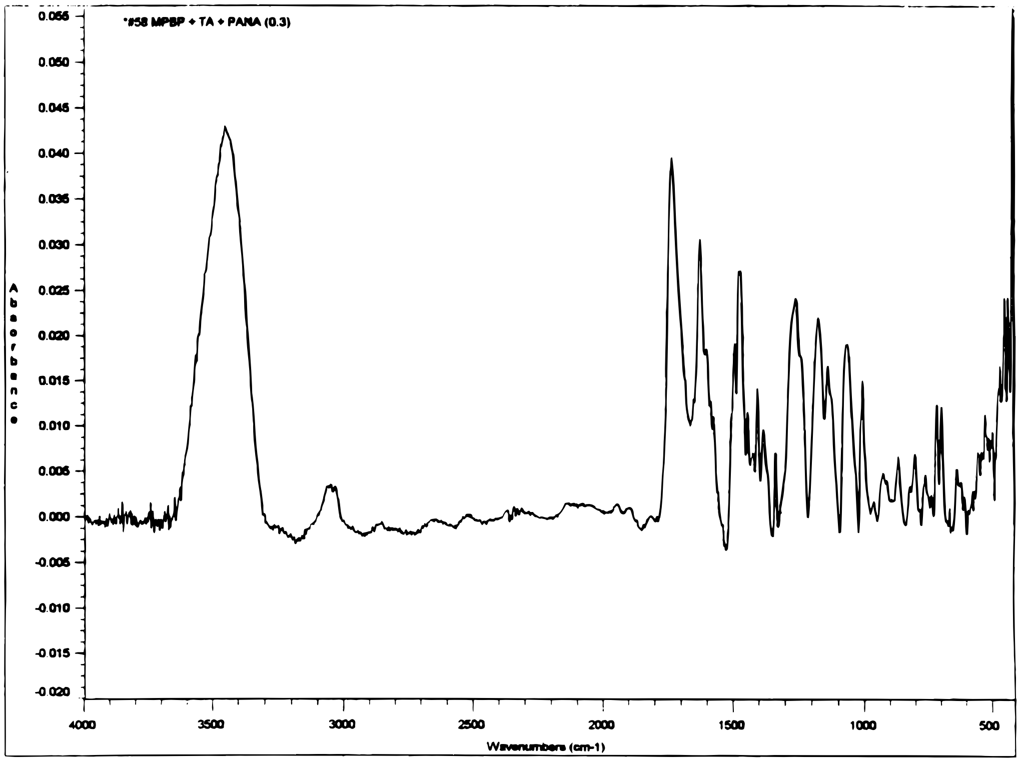


Figure 1. FTIR spectrum of copolymer **I-1** taken at room temperature.

following characteristic absorption bands: 3453−3460 (overtones of C=O), 3050−3150 (=C-H aromatic), 1740 (C=O), and 1270, 1179, and 1081 (C−O) cm^{-1}.

Thermal Properties. The DSC thermogram of copolyester **I-1**, prepared from MPBP, TA, and 30 mol % HNA, showed a T_g but neither a crystal-to-LC transition, T_m, nor an isotropization transition, T_i. However, it fused to form a LC phase at low temperature, T_f, shown in Table 1. The absence of a T_m and the presence of a T_g in the DSC thermogram clearly demonstrated that this copolymer was essentially noncrystalline. Its T_f value was much lower than the T_m values of both the homopolymer of MPBP with TA and its copolymer with 30 mol % HBA.[17,26] Furthermore, its T_f value was much lower than the T_m value of a copolyester based on BP, TA, and 33 mol % HBA, which is a member of the Xydar family of copolyesters. Presumably, the low T_f value of this copolymer is caused by three principal reasons: (a) the internal copolymerization effect of unsymmetrically substituted MPBP unit, (b) the external copolymerization effect of 6-oxy-2-naphthoate unit, and (c) the linear offset structure of HNA moiety.

In contrast to copolymer **I-1**, each of the copolyesters **I-2** (a copolymer of symmetrically substituted DPBP with TA and 30 mol % HNA) and **I-3** (a copolymer of symmetrically substituted DPBP with NDA and 30 mol % HNA) showed a T_m in the first heating cycle of its DSC thermogram, shown in Figure 2, although neither of them had a T_m in the second heating cycle of its DSC thermogram. These results suggested that on cooling from the LC phase no measurable development of crystallinity occurred under the conditions used for these two copolymers. This lack of crystallinity could well have resulted from the mismatching of 6-oxy-2-naphthoate units with 3,3′-diphenyl-4,4′-biphenylene terephthalate units in the former copolymer and that of 6-oxy-2-naphthoate units with 3,3′-diphenyl-4,4′-biphenylene 2,6-naphthalenedicarboxylate units in the latter copolymer. Their T_m values were lower than those of the respective homopolymers because of the copolymerization effect of 6-oxy-2-naphthoate unit. Furthermore, the T_m value of polymer **I-2** was slightly higher than that of the copolymer of DPBP with TA and 30 mol % HBA. In contrast, the T_m value of polymer **I-3** was essentially identical with that of the copolymer of DPBP with NDA and 30 mol % HBA.[17,26,27] Their T_m values were considerably lower than the T_m value of the equivalent Xydar copolymer containing BP.

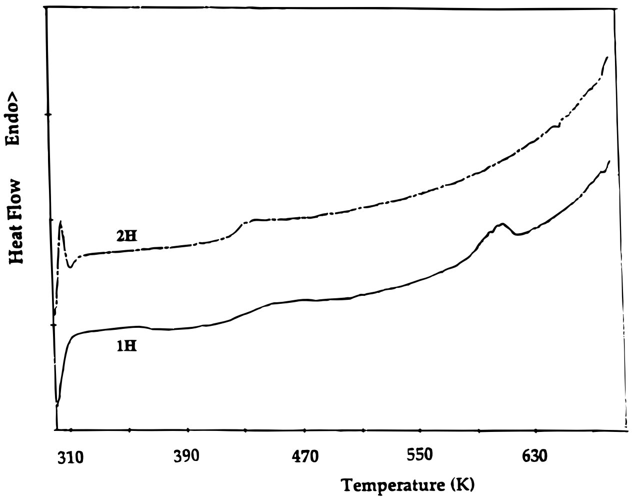


Figure 2. DSC thermograms of copolymer **I-3** in the first and second heating cycles, 1H and 2H, respectively.

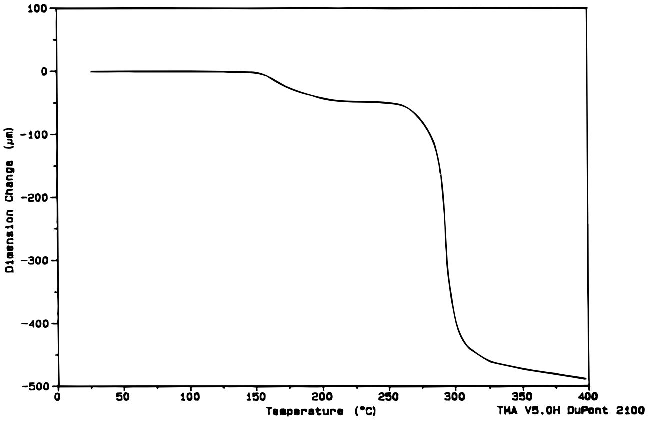


Figure 3. TMA plot of copolymer **I-3** with a heating rate of 20 °C/min and a load force of 100 mN.

As was similar to polymer **I-1**, but unlike copolymers **I-2** and **I-3**, polymer **I-4** did not show any T_m in each of its heating cycles of the DSC thermograms. However, it fused to form a LC phase at low temperature, shown in Table 1. The absence of T_m and the presence of T_g only indicated that this copolymer was also essentially noncrystalline. The noncrystallinity of this copolymer resulted from the copolymerization effect of 6-oxy-2-naphthoate unit. As expected, its T_f value was much lower than the T_m values of both the homopolymer of BND with TA and its copolymer with 30 mol % HBA. Its T_f value was also much lower than the T_m of its respective homopolymer of BND with NDA. In fact, the homopolymer has a T_m above 400 °C.[28] The low T_f value of this copolymer clearly demonstrated that the copolymerization with as low as 30 mol % HNA caused to form a LC phase at 250 °C from >400 °C of its homopolymer. This observation is in fact reminiscent of the copolymerization effect of 42 mol % HNA with 58 mol % HBA, which causes a decrease in T_m to 245 °C[11,12] from 600 °C[29] (445[30] and 510−530[31] °C) of the respective homopolymer of HBA.

Additionally, polymer **I-2** had an isotropization transition, T_i, determined by PLM studies, at about 450 °C having a biphasic (at which anisotropic and isotropic phases coexist) temperature range of about 30 °C. Although the biphasic system is common to many lyotropic LCPs over a range of concentrations when an anisotropic phase occurs in conjunction with an isotropic phase, it is less common to thermotropic LCPs, particularly the wholly aromatic, thermotropic polymers. In this class of LCPs, the LC-to-isotropic transition, T_i, is so high that polymer degradation sets in before the isotropic phase forms so that the observation of the coexistence of anisotropic and isotropic phases is relatively rare.[3] Moreover, the origin and mechanisms through which a phase separation between the isotropic and anisotropic phases occurs in LCPs are still not clear. Nonetheless, a biphasic behavior is observed in the case of a chemically disordered (irregular), semiflexible thermotropic LC polyester.[32] Recently, a similar phenomenon is also observed in several wholly aromatic, thermotropic homopolyesters and copolyesters.[23,33]

In contrast to copolymer **I-2**, other copolymers in the series had T_i values over 450 °C. Therefore, it was observed that copolymerization increases the stability of LC phase to a large extent by both decreasing the T_m values and increasing the T_i values of the respective homopolymers. The observed broad range of LC phase for each of the copolymers is in excellent agreement with this statement.[3] Moreover, this observation is in excellent agreement with the recent results of a series of thermotropic copolyesters, which have a broad range of LC phase, reported by Khan et al.[34] All of these polyesters are based on 2-phenylhydroquinone (87.5 mol %), TA with either symmetrically substituted hydroquinones (13.5 mol %), such as 2,5-diphenylhydroquinone, 2,6-diphenylhydroquinone, and 2,5-dimethylhydroquinone, or hydroquinone (25 mol %). As discussed earlier, the nematic-to-isotropic transition, T_i, is rarely observed in a wholly aromatic, thermotropic polyester because it usually occurs at such a high temperature that thermal degradation precedes the T_i transition. However, the two homopolymers of DPBP with either TA or NDA had T_m values at 341 and 362 °C, respectively, and also had T_i values at 398 and 423 °C, respectively.[26] The homopolymer of BND with TA, prepared by the melt polycondensation reaction, had a T_m at 353 °C and a T_i at 380 °C, respectively, and in contrast, that with NDA did not melt below 400 °C, as mentioned earlier.[28]

All of the copolymers in this study showed T_g values in the range of 128−180 °C, collected in Table 1, by DSC measurements, which were much higher than those (103−112 °C) of the Vectra family of copolyesters of HBA/HNA.[3] Additionally, their T_g values were also measured with a thermomechanical analyzer and are collected in Table 1. A typical TMA plot of polymer **I-3** is shown in Figure 3. There were two regions of softening: the first one corresponded to the T_g and the second one to the T_m of the copolymer. It is worth mentioning that many thermotropic LC polyesters, generally, have lower T_g values than conventional, nonliquid crystalline polyesters. The nonliquid crystalline polyesters consist of nonlinear units that are comparatively resistant to rotation themselves, resulting in their high T_g values. In this regard, it is a disadvantage for this class of polymers because their useful service temperatures are determined predominantly by their T_g values for various industrial applications. The high T_g values of the copolymers in the present study are presumably related to the phenyl-substituted 4,4′-biphenylene terephthalate, phenyl-substituted 4,4′-biphenylene 2,6-naphthalenedicarboxylate, and 1,1′-binaphthalene 2,6-naphthalenedicarboxylate units. The bulky phenyl substituent(s) in the 4,4′-biphenylene units and the annellated aromatic rings in 1,1′-binaphthalene units caused considerably increase in chain rigidity of the polyester chains resulting in the decrease of free volume and in the increase of cohesive energy density. Both these effects contrib-

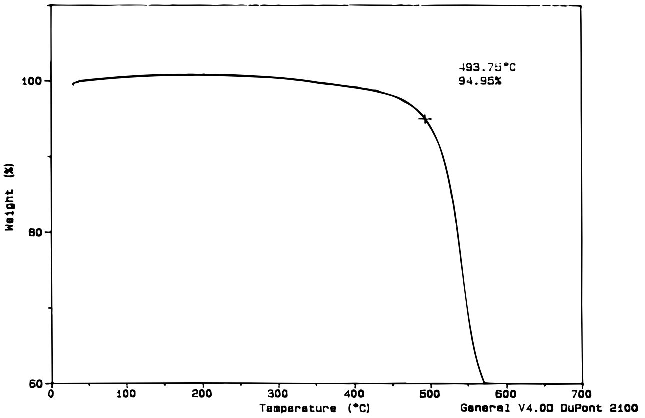


Figure 4. TGA plot of copolymer **I-1** in nitrogen at a heating rate of 20 °C/min.

uted to a high T_g.[35] The highest T_g of copolymer **I-4** among all of the copolymers is in excellent agreement with our recent results of other thermotropic LC polyesters containing 1,1′-binaphthalene units.[9,28] This observation is presumably related to resistance of the 1,1′-binaphthalene units in the polyester chain to backbone rotation. The lowest T_g of copolymer **I-1** is related to the asymmetric MPBP units, in contrast to symmetric DPBP and BND units present in other copolymers. The phenyl substituents of asymmetric MPBP units could be incorporated in head-to-tail and head-to-head fashions along the copolyester chain resulting in a large amount of free volume in the polymer matrix and, consequently, contributing to a low T_g.[36]

The thermal stabilities of all of the copolyesters were determined in nitrogen by TGA, and the results are collected in Table 1. A typical TGA plot of polymer **I-1** is shown in Figure 4. The thermal stability limit, which is taken as the temperature (°C) at which 5% weight loss occurred, varied from 417 to 494 °C in nitrogen, indicating that all of them had excellent thermal stabilities for melt processing in their nematic LC phases, as discussed in the following section, at elevated temperatures. They had higher thermal stability than that (ca. 400 °C) of an analogous series of copolyesters of PhHQ, TA and 2,5-diphenylhydroquinone, 2,6-diphenylhydroquinone, or hydroquinone.[34] The higher stability may be related to the incorporation of the more rigid and aromatic moiety of MPBP, DPBP, and BND units in the present series of copolyesters than that of phenyl-substituted hydroquinones. Additionally, their thermal stability was essentially identical with that of the Vectra family of thermotropic copolyesters under similar experimental conditions.[37] These results, as expected, indicate that wholly aromatic, thermotropic LC polyesters, generally, have high thermal stability because of the presence of aromatic moieties in these polymer chains.

Optical Properties. All of the copolymers, listed in Table 1, formed turbid melts above their T_m/T_f values that exhibited strong stir opalescence. This property was taken as the first indication of their LC behavior. For further characterization of their melt morphology, they were evaluated by visual observations on hot-stage PLM studies. All of them formed a typical nematic appearance with either a marbled texture or a Schlieren texture depending on the thickness or temperature of the sample. In some cases, a LC texture was observed that was predominantly populated with surface inversion walls[38] (also called inversion walls of the first kind by Nehring and Saupe[39]), emerging and ending at $\pm^1/_2$ point singularities. There is a $\pi/2$ turn of the molecular director at the center of the wall.[39] From the $\pm^1/_2$ point singularities, it is possible to indentify unambiguously that the LC phase is nematic.

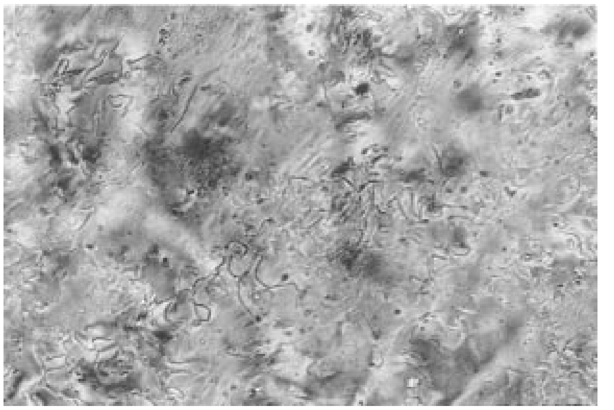


Figure 5. Photomicrograph of copolymer **I-1**, taken at 200 °C on heating, displaying a marbled texture (magnification 400×; reproduced at 70% of original size).

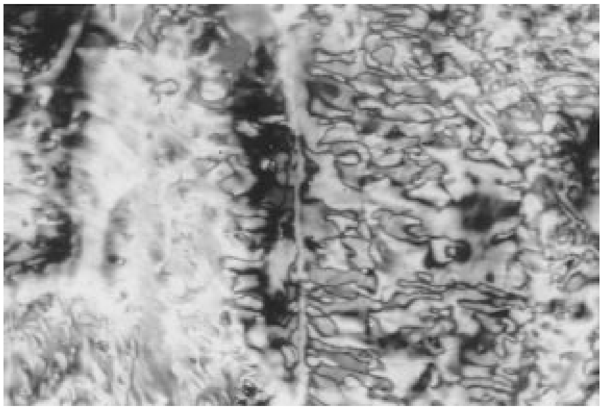


Figure 6. Photomicrograph of copolymer **I-1**, taken at 240 °C on annealing at this temperature for 24 h, displaying a Schlieren texture (magnification 400×; reproduced at 70% of original size).

Figure 5 shows a photomicrograph of copolymer **I-1** taken at 200 °C displaying a marbled texture, which is often found in the nematic phase. Marbled textures often appear with glass surfaces that have not been especially treated. The boundaries which separate different areas usually consist of threads, twist disclinations, and inversion walls of various types. There was a considerable movement of the LC phase, and the closed loops, shown in Figure 5, could be seen floating in the LC phase. These were unstable and disappeared after some time. The birefringent regions arose from regions with a nearly defect-free planar alignment.[38]

Figure 6 shows a second type of texture, which is called Schlieren texture, obtained with the copolymer **I-1**. This texture was micrographed on annealing the sample at 240 °C for 24 h. It shows clearly that point singularities with disclination strength $S = \pm^1/_2$ and ±1 are both present, and this observation is sufficient to indentify the LC phase unambiguously as nematic. Usually, point singularities with disclination strength $S = \pm^1/_2$ are greater in number than those with disclination strength $S = \pm1$ in the nematic phase because of energetic consideration.[39] It is important to note that Schlieren textures are characteristics of smectic LC phases; however, in these textures, disclination strength $S = \pm^1/_2$ does not occur, and only those with $S = \pm1$ are observed.[39]

Figure 7 shows the photomicrograph of copolymer **I-3**, taken at room temperature on heating the sample to a

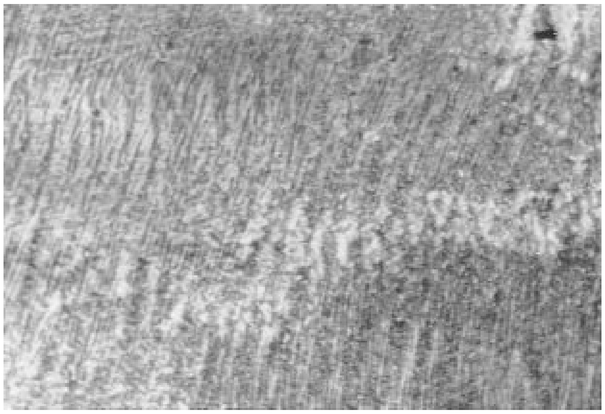


Figure 7. Photomicrograph of copolymer **I-3**, taken at room temperature on heating to a temperature of 385 °C and then cooling, displaying a banded texture (magnification 400×; reproduced at 70% of original size).

temperature of 385 °C and then cooling with a rate of 20 °C/min, displaying a banded texture. The banded texture was first observed in the lyotropic Kevlar fiber by transmission electron microscopy (TEM), but in recent years, it has also been observed in a wide range of LCPs both, rigid and semiflexible, thermotropic and lyotropic polymers by PLM studies.[3] The bands have a width of the order of 1 μm, and therefore, they can be easily observed with the PLM studies. The formation of a banded texture occurs, generally, on shearing of either a lyotropic or thermotropic LCP. It has been reported in the literature[40−42] that its formation in a LCP is associated with a transient phenomenon, namely, it typically occurs after the cessation of flow in shear or elongation. On the other hand, Han et al.[43] observed the banded texture by PLM studies in a melt-spun fiber of a semiflexible main-chain thermotropic polyester. This texture persisted during the isothermal annealing for over 24 h but disappeared only after the isothermal annealing continued for a period of over 48 h. The disappearance of this texture was attributed to the formation of high-temperature melting crystals in this polyester, which began only after the annealing continued for 48 h. In our case, when the copolymer **I-3** was heated to about 385 °C from its nematic melt, neighboring disclinations of opposite signs in their disclination strength interacted and annihilated to form new disclinations. Consequently, the ordered domain size grew and reached an optimum size with the simultaneous development of a banded texture, shown in Figure 7, without being subjected to shear. This texture remained unchanged on cooling down to room temperature. This observation was presumably related to the fact that there was no interference from the crystallization process of this polymer. As discussed earlier, the crystallization of this copolymer did not occur on cooling at a rate of 20 °C/min from the nematic melt, which was supported from the absence of cooling exotherm in its DSC thermogram. The observation of this banded texture for this polymer **I-3** is essentially similar to that of a semiflexible main-chain thermotropic polyester reported by Chen et al.[44] They found a banded texture in this semiflexible polyester on annealing in the nematic melt for 10 min to induce the growth of ordered macromolecular chains and then quenching to room temperature, without being subjected to shear. Although, a banded texture is a universal phenomenon in LCPs in general, the origin and mechanisms of its formation have not been well understood and require further studies.

Figure 8. Photomicrograph of several strands of hand-drawn fiber of copolymer **I-1** displaying a highly oriented fibrillar morphology (magnification 400×; reproduced at 70% of original size).

Figure 9. SEM micrograph of a bundle of fibers drawn from copolymer **I-1** displaying a coherent surface skin and fribrillar morphology (magnification 300×; reproduced at 70% of original size).

Figure 8 shows a photomicrograph of several strands of fiber drawn from the nematic phase of polymer **I-1**, which clearly reveals that the polymer chain is highly oriented with no apparent fine structure. However, at very high magnification the oriented fiber of a thermotropic polyester shows a fine "domain" texture, that is, regions of high local order. These domains observed in oriented structures are typically in the order of a few microns across, elongated along the fiber axis.[45]

Scanning Electron Microscopy. The SEM studies of hand-drawn fibers of the copolymers were performed in order to gain insight into their morphologies. Figure 9 shows a typical micrograph of a bundle of fibers drawn from polymer **I-1**, which reveals a distinct surface skin and a regular fibrillar internal structure with a characteristic size of a few microns. At high magnification, and in another section of the same sample, ribbon-like structures, which appear to be uniaxially oriented sheets, are distinctly observed, shown in Figure 10. Furthermore, Figure 11 shows micrographs of a fractured fiber drawn from polymer **I-4** at low and high magnifications, which indicate that there exist a smooth surface skin and a sheetlike structure of the core for the fractured fiber of this polymer. Generally, as orientation is increased, the ratio of skin to core increases and longer, more fibrillar structures are observed. It is important to mention that the strength of the fiber correlates with fibrillarity of the fractured surface and the length of the fibril "pull out". However, similar structures have also been reported for both wholly aromatic, thermotropic polyesters and lyotropic Kevlar fibers.[45]

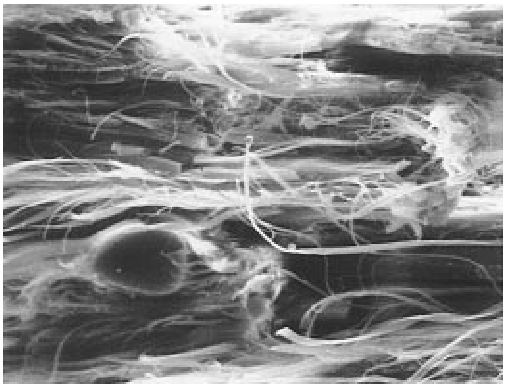


Figure 10. SEM micrograph of a bundle of fibers obtained from copolymer **I-1** displaying a ribbon-like morphology (magnification 1000×; reproduced at 70% of original size).

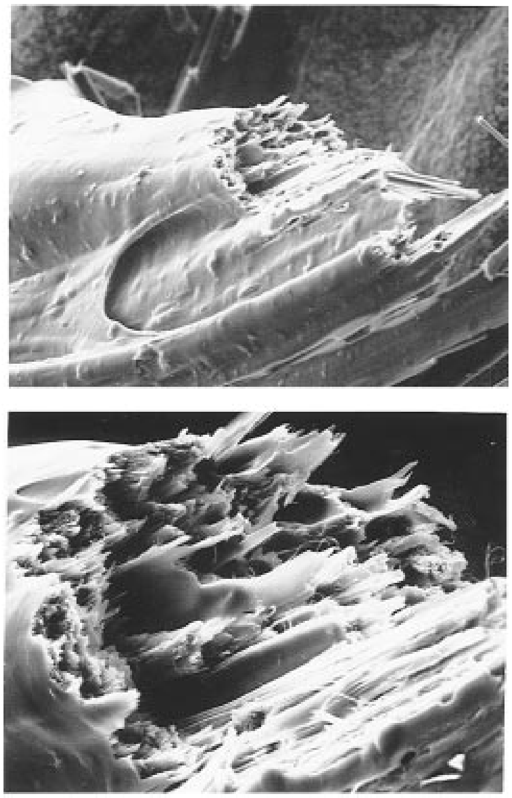


Figure 11. SEM micrographs of a fractured fiber drawn from copolymer **I-4** exhibiting a sheetlike, a fribrillar, and a coherent surface skin morphology: (top) magnification 100× and (bottom) magnification 300× (reproduced at 70% of original size).

X-ray Diffraction. The X-ray diffraction pattern of polymer **I-1** obtained for a fiber drawn from the nematic melt is shown in Figure 12, left. The pattern exhibits a typical nematic character of layer lines and a strong diffuse diffraction peak on the equator, with spacing centered at 0.44 nm. The layer line spacings are aperiodic, as expected from a random copolymer, and their values are listed in Table 2. The polymer **I-2** had a sufficient high viscosity that allowed fibers to be drawn from the nematic state with ease. Oriented, nematic-like X-ray diffraction patterns were obtained, Figure 12, right, and Table 2, which showed a series of aperiodic layer lines consistent with a random copolymer and also an equatorial peak at 0.44 nm spacing.

The X-ray diffraction patterns, Figure 13, left, of fibers drawn from the nematic state of polymer **I-3** showed the expected features of the oriented nematic phase with aperiodic layer line spacings, Table 2, and an equatorial peak at 0.43 nm. In addition, its X-ray pattern contains some sharp diffraction arcs and circles from a crystalline impurity, which was not removed during the purification process. However, the observed oriented X-ray diffraction pattern of each of the copolyesters **I-1**−**I-3** is in good agreement with those of other wholly aromatic, thermotropic polyesters.[46] In fact, the random microstructures of this class of polymers have been established by this technique. The other technique such as ^{13}C NMR has its severe limitation in the determination of their microstructures because of the insolubility of these polymers in common organic solvents.

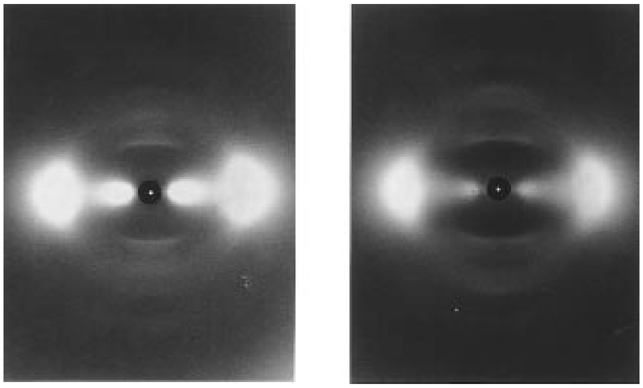


Figure 12. X-ray diffraction patterns obtained from (left) copolymer **I-1** and (right) copolymer **I-2** by drawing fibers from the nematic melt (fiber direction vertical). The spacings are listed in Table 2.

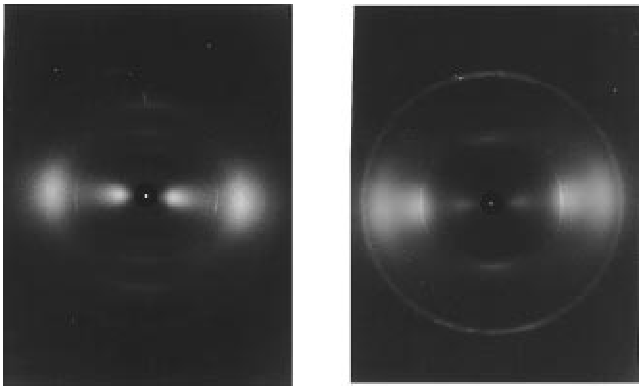


Figure 13. X-ray diffraction patterns obtained from (left) copolymer **I-3** and (right) copolymer **I-4** by drawing fibers from the nematic melt (fiber direction vertical). The spacings are listed in Table 2.

Table 2. X-ray Diffraction Spacings of Thermotropic Copolyesters of MPBP, DPBP, and BND

copolymer no.	spacing (nm ± 0.002)	description
I-1	0.810	off-meridional
Figure 12, left	0.562	meridional
	0.500	meridional
	0.412	meridional
	0.326	meridional
	0.440	equatorial
I-2	0.791	off-meridional
Figure 12, right	0.590	meridional
	0.474	meridional
	0.412	meridional
	0.326	meridional
	0.440	equatorial
I-3	0.850	off-meridional
Figure 13, left	0.621	meridional
	0.451	meridional
	0.430	equatorial
I-4	0.773	meridional
Figure 13, right	0.545	equatorial
	0.373	equatorial

The X-ray diffraction pattern of polymer **I-4** obtained from a fiber drawn from the nematic melt is shown in Figure 13, right, and the line spacings are listed in Table 2. Its X-ray pattern differs from those of the other three copolymers in this series: The usual equatorial strong, diffuse peak at spacing 0.43−0.45 nm is replaced by two separate peaks at spacings 0.55 and 0.37 nm, respectively. This feature indicates a two-dimensional character to the packing of these stiff macromolecular chains. The presence of BND units in this copolymer, Table 1, is expected to impact a ribbon-like shape to the macromolecule, and azimuthal rotation will be restricted giving rise to a localized sanidic or boardlike character, as discussed in detail in our previous publication of this series.[26]

Conclusions

The three copolyesters, derived from phenyl-substituted 4,4′-biphenols, terephthalic acid, or 2,6-naphthalenedicarboxylic acid and 30 mol % 6-hydroxy-2-naphthoic acid, had either lower fusion temperature, T_f, or lower crystal-to-nematic transitions, T_m, than those of the Xydar family of copolyesters based on 4,4′-biphenol, which would facilitate their processing at temperatures as low as 185 °C from their nematic melts. The fourth copolymer, derived from 1,1′-binaphthyl-4,4′-diol, 2,6-naphthalenedicarboxylic acid, and 30 mol % of the same comonomer, also had much lower T_f than T_m values of its respective homopolymers with TA and NDA. Each of them exhibited a nematic phase above its T_f/T_m values having both a marbled texture and a Schlieren texture. They had a wide range of LC phase; particularly, each of the copolymers containing either DPBP or BND had a much broader range of LC phase than those of its respective homopolymers because of the copolymerization effect of 6-hydroxy-2-naphthoic acid. The microstructures of these copolyesters had random monomer sequences as determined by WAXD technique from the analyses of their oriented fiber diffraction patterns. Additionally, the presence of 1,1′-binaphthalene units in the copolymer **I-4** created a conformation with the more ribbon-like character, which provided certain constraints on the local azimuthal rotations of the polymer chain about its axis. Generally, wholly aromatic, thermotropic polyesters have relatively low T_g values in the range of 110−150 °C, which is a major disadvantage for their high-temperature applications. However, all of the copolymers in the present series had relatively high T_g values, up to 180 °C. Thermogravimetric analyses indicated that they had excellent thermal stability up to about 500 °C. These results indicate that wholly aromatic, thermotropic copolyesters having low T_f/T_m can be prepared from phenyl- or diphenyl-substituted 4,4′-biphenols and 1,1′-binaphthyl-4,4′-diol on copolymerization with as low as 30 mol % 6-hydroxy-2-naphthoic acid, which have practical implications.

Acknowledgment. E. D. T. Atkins wishes to acknowledge the award of a Visiting Professorship to the Polymer Science and Engineering Department, University of Massachusetts at Amherst. We also gratefully acknowledge the Schnectady Chemical Co., NY, for supplying MPBP, DPBP, and BND monomers. We are thankful to Mr. Keith Dodsworth for performing SEM analysis.

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MA951330K