Crystalline and Liquid Crystalline Polyesters of Phenyl-Substituted 4,4′-Biphenols. 5. Copolymers with 4,4′-Oxybis(benzoic acid)

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Received December 8, 1995; Revised Manuscript Received March 18, 1996[⊗]

ABSTRACT: Wholly aromatic, thermotropic copolyesters, derived from either 3-phenyl-4,4′-biphenol (MPBP) or 3,3′-diphenyl-4,4′-biphenol (DPBP) with either terephthalic acid (TA) or 2,6-naphthalenedicarboxylic acid (NDA) and 50 mol % 4,4′-oxybis(benzoic acid) (OBBA), were prepared by the melt polycondensation reaction, and their liquid crystalline properties were characterized by a number of experimental techniques. The solubility of these polyesters in common organic solvents had also been studied. They had lower fusion temperatures, T_f, than the T_m values of the copolyesters of 4,4′-biphenol, TA, and 4-hydroxybenzoic acid. Their low T_f values were because of increased entropy of the respective monomers. Each of them exhibited a nematic phase above its T_f value that contained both the threaded and schlieren texture. The two copolyesters of MPBP and hand-drawn fibers therefrom showed a banded texture that could be preserved for a prolong period of time. Each of them showed a nematic-to-isotropic transition as determined by the polarizing light microscope studies. The copolyesters of MPBP had a much broader range of mesophase than those of DPBP. The two copolyesters of DPBP exhibited a biphase behavior at lower temperatures than those of the copolyesters of MPBP. Their random microstructures were confirmed with the WAXD studies of oriented fibers and the ^{13}C-NMR spectroscopy, whenever possible. No development of crystallinity occurred in these copolyesters even on annealing. They had relatively high glass transition temperatures, T_g, in the range of 149−171 °C when compared with other liquid crystalline polyesters and good thermal stability, T_d, in the range of 413−436 °C. Since they had no detectable crystallinity, the copolyesters of either MPBP or DPBP with TA and OBBA were soluble in common organic solvents, but those with NDA and OBBA were not soluble in these solvents.

Introduction

The possibility that wholly aromatic, thermotropic polyesters might be spun from the melt to obtain fiber properties similar to those of Kevlar fibers, which are solution-spun fibers based on aromatic polyamides that can not be melt processed, created a special interest in this class of polymers. Several reviewers have discussed the reasons for this growing interest in thermotropic nematogenic polymers,[1−4] and the principles underlying the chemical design of such polymers are now resonably well understood.[5−7] While wholly aromatic, homopolyesters, generally, have very high crystal-to-nematic transitions, T_m, it is possible to obtain such polymers with considerably low T_m values by the use of several types of chemical structural modifications[5−20] including: (i) the introduction of bulky substituents in either the aromatic diacid, aromatic diol, or both to disrupt lateral packing, (ii) copolymerization of different sizes of mesogenic (liquid crystalline forming) monomers to lower the symmetry of the polyester primary structure, (iii) the incorporation of noncoplanar 2,2′-disubstituted 4,4′-biphenylene unit in combination of a monosubstituted 1,4-phenylene unit in order to reduce the interchain interactions, and (iv) the use of nonlinear or bent monomers lower the persistence length of the polymer chain in the liquid crystalline (LC) phase and disrupt lateral interactions in the solid state.

Many studies have been devoted to wholly aromatic, thermotropic polyesters, which form a nematic LC phase in the melt, based on modifications i−iii. The common monomers used, generally, are hydroquinones (HQs), terephthalic acids (TAs), 4,4′-biphenols (BPs), 4-hydroxybenzoic acids (HBAs), 6-hydroxy-2-naphthoic acid (HNA), naphthalenediol isomers (ND), and naphthalenedicarboxylic acid isomers (NDA). However, in the case of modification iv, resorcinol (RE), isophthalic acid (IA), *m*-hydroxybenzoic acid (*m*-HBA), 2,5-thiophenedicarboxylic acid (T), and other nonlinear monomers have been used as comonomers to decrease the T_m values of this class of polymers. In general, when the concentration of nonlinear monomer is increased in a copolyester beyond a certain critical value, its liquid crystallinity is lost. For example, Erdemir et al.[21] reported that the IA/HQ/HBA forms an isotropic melt if the percentage of IA is >67%. Jin et al.[22] observed that the TA/RE/HBA loses the liquid crystallinity if the percentage of RE exceeds 33%. Lenz et al.[23] reported that the ClHQ/TA/RE loses LC properties when the percentage of RE exceeds 60%. Jackson[6] reported that the HQ/TA/*m*-HBA containing in excess of 50% *m*-HBA forms an isotropic melt. Rosenau-Eichin et al.[24] studied the HBA/*m*-HBA system and found that the copolyester with more than 50% *m*-HBA forms an isotropic melt. Cai and Samulski[25] reported that the HQ/TA/IA containing more than 85% IA loses the liquid crystalline properties. These results suggest that the incorporation of nonlinear unit in the aromatic polyester causes to decrease the T_m, to decrease the range of LC phase, and eventually to destroy the LC phase with a high percentage of this unit in the copolyester, that is, with a critical

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

S0024-9297(95)01809-2 CCC: $12.00

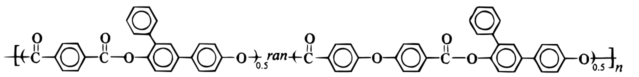
amount. The critical amount of a nonlinear monomer in a copolyester depends not only on its chemical structure but also on the chemical structures of other mesogenic comonomers.

A large number of studies[6,21−25] have been devoted to wholly aromatic, thermotropic polyesters based on common nonlinear monomers, but a few studies have been performed on this class of polymers based on the nonlinear 4,4′-oxybis(benzoic acid) (OBBA).[26−29] Interestingly, the homopolyester of this nonlinear diacid and ClHQ was reported by Kleinschuster et al.[26] to give fibers having tenacities in the range of 10−16 g/denier and modulii of 170−230 g/denier, which are the values expected for fibers that are obtained by melt spinning in the nematic LC phase. McIntyre et al.[27] reported the results of a series of thermotropic copolyesters derived from ClHQ, TA, and OBBA, all of which are nematogenic over the entire compositional range. They have a minimum T_m at 275 °C for the 50/50 copolymer composition of the two aromatic diacids. Recently, Skovby et al.[28] reported the results of another series of thermotropic copolyesters derived from phenylhydroquinone (PhHQ), TA, and OBBA. Each of the copolymers, except the copolymer containing 70 mol % OBBA, forms a nematic LC phase in the temperature range of 225−318 °C, suggesting that OBBA unit is capable of decreasing the T_m considerably for the preparation of this class of polymers.

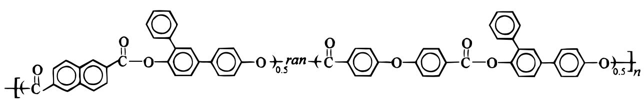
In this article, we describe the preparation and characterization of a series of thermotropic copolyesters based on substituted 4,4′-biphenols, 3-phenyl-4,4′-biphenol (MPBP) and 3,3′-diphenyl-4,4′-biphenol (DPBP), with either TA or 2,6-NDA and 50 mol % OBBA. On copolymerization with this nonlinear OBBA, a random distribution of 4,4′-oxybis(benzoate) units with either terephthalate or 2,6-naphthalenedicarboxylate units along the polyester chain would be expected to disturb the packing of the polymer chains giving rise to a low-T_m polyester. The structures and designations of the copolyesters I, which were prepared and characterized in this study, are shown below:

Copolymer No. **Polymer Structure**

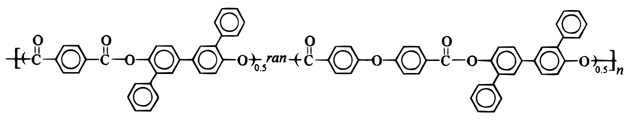
I-1 (MPBP-TA/OBBA)



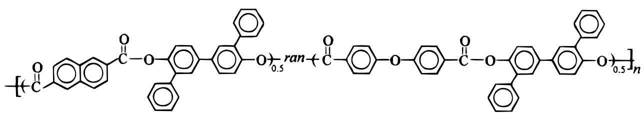
I-2 (MPBP-NDA/OBBA)



I-3 (DPBP-TA/OBBA)



I-4 (DPBP-NDA/OBBA)



All of these wholly aromatic, thermotropic copolyesters were characterized by a variety of experimental techniques, including solution viscometry, gel-permeation chromatography (GPC), Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, 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 copolyesters, whenever possible. Their solubility in various common organic solvents had also been investigated.

Experimental Section

Monomers. The two phenyl-substituted 4,4′-BPs, MPBP and DPBP, were received as diacetates from Schnectady Chemicals Inc., NY. The three aromatic dicarboxylic acids, TA, 2,6-NDA, and 4,4′-OBBA, were received from Amoco Chemicals and used without further purification.

Polyester Synthesis. All of the copolyesters were prepared from the copolymerization of 50 mol % OBBA with the requisite amounts of the other two comonomers by the melt polycondensation reaction without an added catalyst. The temperature program for the polycondensation reaction was typically at 250−275 °C (12 h) during which acetic acid began to distill out from the reactor gradually and then at 300 °C (12 h) under vacuum.[19] At the end of polymerization reaction, the solidified polyester was dissolved in a mixture of *p*-chlorophenol−1,1,2,2-tetrachloroethane (60/40 by wt), 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 typically 92−97%.

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. Those of two polymers, **I-1** and **I-3**, were also measured in chloroform at 35 °C at the same concentration with the same type of viscometer. Their molecular weights were determined using a Waters 804E gel-permeation chromatography devise calibrated with monodisperse polystyrene standards through Ultrastyragel columns with 500, 10^3, 10^4, and 10^6 Å pore sizes at room temperature by using $CHCl_3$ as a solvent. IR spectra were recorded with a Nicolet FTIR analyzer using neat films of polyesters in KBr pellets. The ^1H- and ^{13}C-NMR spectra were recorded with a Brüker AM 500 FT-NMR spectrometer operating at 500 and 125.8 MHz, respectively, in $CDCl_3$ using TMS as an internal standard.

The phase transition 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 glass transition temperature, T_g, was taken as the onset of this transition in 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 all of the polyesters there were no phase transition temperatures in either the first or second heating cycle of the DSC thermogram. Therefore, a fusion temperature, T_f, was used for comparison of the melt behavior of the different copolymers. It was defined as the temperature of onset of flow as observed for each of the copolyesters on a hot-plate melting point apparatus and verified by the use of a hot stage on PLM studies from the observation of a typical nematic texture on the edge of the sample, that is, at the thinnest part. Moreover, the isotropization transition, T_i, for each of the copolymers was determined at a temperature on the hot stage of a PLM instrument at which the disappearance of both the birefringence and the threaded texture occurred. The LC texture of each of the copolyesters was observed on a PLM instrument (Leitz, Model Ortholux) equipped with a pair of crossed polarizers and Mettler hot stage. TGA was obtained on a DuPont TGA 951 with a Thermal Analyzer 2100 system at a heating rate of 20 °C/min under a nitrogen flow.

Table 1. Properties of Thermotropic Copolyesters of MPBP and DPBP

copolymer no.	monomer[a]	IV[b] (dL/g)	M_n[c]	M_w/M_n	T_g[d] (°C)	T_f[e] (°C)	T_i[f] (°C)	T_d[g] (°C)	texture by PLM
I-1	MPBP + TA + OBBA	1.31 (1.51)	20 000	2.57	149 (158)	210	450	419	nematic
I-2	MPBP + NDA + OBBA	0.72			153 (150)	180	455	420	nematic
I-3	DPBP + TA + OBBA	0.83 (0.94)	17 700	2.26	159 (169)	200	260	413	nematic
I-4	DPBP + NDA + OBBA	2.40			171 (183)	310	380	436	nematic

[a] Monomer designation: MPBP = 3-phenyl-4,4′-biphenol, TA = terephthalic acid, OBBA = 4,4′-oxybis(benzoic acid), NDA = 2,6-naphthalenedicarboxylic acid, and DPBP = 3,3′-diphenyl-4,4′-biphenol; 50 mol % OBBA was included in each of the copolymers. [b] IV, inherent viscosity, was measured in *p*-chlorophenol at 50 °C, and the value in parentheses was measured in $CHCl_3$ at 35 °C at a polymer concentration of 0.2 g/dL. [c] M_n, number-average molecular weight (M_w, weight-average molecular weight) was measured in $CHCl_3$ against polystyrene standards. [d] Glass transition temperature, T_g, was recorded from the DSC thermogram, and the value in parentheses was determined with a thermomechanical analyzer. [e] 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. [f] Isotropization temperature, T_i, was determined on the hot stage of a polarizing light microscope at which the disappearance of both the birefringence and the threaded texture occurred. [g] Thermal stability, T_d, was determined in nitrogen at a heating rate of 20 °C/min at a temperature at which a 5% weight loss of the sample occurred.

For wide-angle X-ray diffraction studies, each of the polyesters was heated to well above its T_f and allowed to cool to fixed temperature 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 pump pressure (10^{-2} Torr). The radiation used was Cu Kα using a nickel filter, and the X-ray pattern was recorded on a photographic film. 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 for this analysis on heating the sample well above its T_f, pulling with tweezers, and quenching in air.

Results and Discussion

Solution Properties. The copolymers of MPBP and DPBP with equimolar amounts of TA and OBBA, **I-1** and **I-3**, namely, showed a very useful property that the former was soluble in chloroform (ca. 0.5 g/dL) and partly soluble in methylene chloride and the latter was soluble in a number of common organic solvents, including chloroform, methylene chloride, dioxane, and tetrahydrofuran (ca. 0.5 g/dL that was not the highest achievable concentration). They were also soluble in the usual solvents including *p*-chlorophenol (PCP), dichloroacetic acid (DCA), and 1,1,2,2-tetrachloroethane (TCE). In contrast, their copolyesters with equimolar amounts of NDA and OBBA, **I-2** and **I-4**, respectively, were not soluble in these common organic solvents but soluble in PCP. It is important to note that each of these copolyesters **I-1**−**I-4**, as discussed below, had no crystalline order or perfection at all. Despite the absence of crystallinity in these two copolyesters **I-2** and **I-4**, their insolubility in common organic solvents clearly demonstrates that the solubility of this class of polymers is a complex consequence of crystallinity and main-chain solvation and, hence, is difficult to predict from their chemical architectures. A similar result has been reported in the case of homopolymer of MPBP with 4,4′-benzophenone dicarboxylic acid and its various copolymers, which are also insoluble in common organic solvents despite the absence of crystallinity in each of these polyesters.[30] However, a large number of wholly aromatic, thermotropic polyesters have been prepared and characterized, but a limited number of polyesters of this type have been reported to have solubility in common organic solvents. Their structural modifications that are required in order to increase the solubility in common organic solvents typically include:[9,11,19,31−33] (a) the incorporation of noncoplanar 2,2′-bis(trifluoromethyl)-4,4′-biphenyldicarboxylate in combination with (trifluoromethyl)terephthalate in the copolyester chain, (b) the incorporation of 2,2′-dimethyl-4,4′-biphenyldicarboxylate in combination with bromo- and *tert*-butyl-1,4-phenylenes, (c) the incorporation of bulky substituent(s), such as *tert*-butyl, phenyl, phenoxy, phenylalkyl and 4-biphenyl in both the aromatic diacid and aromatic diol moieties, (d) the incorporation of high percentage (>50 mol %) of nonlinear 1,2-phenylene moiety, and (e) the incorporation of bulky substituent(s) in aromatic diol moiety, such as MPBP and DPBP, in combination with 3,4′-benzophenone dicarboxylate moiety. Therefore, the incorporation of either MPBP or DPBP in combination with equimolar amounts of TA and OBBA moieties provides structural variants of these polyesters having solubility in common organic solvents. It is important to note that all other thermotropic copolyesters including terpolyesters containing OBBA, which have been reported in the literature,[27,29,34,35] are not soluble in common organic solvents. Some of these polyesters are soluble either in *p*-chlorophenol[27,29] or in a mixture of *o*-chlorophenol and chloroform (1/3);[34] others are neither soluble even in an aggressive solvent or a mixture of aggressive solvents.[35]

Because of the solubility properties of polymers **I-1** and **I-3**, it was possible to measure their molecular weights by using $CHCl_3$ as a carrier solvent at room temperature by GPC. A GPC plot of polymer **I-1** indicated that a monomodal distribution with a weight-average molecular weight (M_w) of 69 000, compared with polystyrene standards, was obtained. Similarly, the GPC plot of polymer **I-3** also indicated that a monomodal distribution with M_w of 40 000, compared with the same standards, was obtained. The molecular weight distributions, as indicated by the ratio of weight-average to number-average molecular weights, M_w/M_n, were 2.57 and 2.26, respectively, for these polymers. It was also observed that a high-M_w polymer had a higher molecular weight distribution than that of a low-M_w polymer, which is in agreement with the result as reported by Heitz and Niessner.[36] The M_n and M_w values of these polymers were in agreement with their inherent viscosity, IV, values. Their measured IV values in $CHCl_3$ at 35 °C were 1.51 and 0.94 dL/g, respectively, and those in *p*-chlorophenol at 50 °C were 1.31 and 0.83 dL/g, respectively, collected in Table 1. Their essentially identical IV values in both the solvents suggested that the hydrodynamics chain properties of these polymers were essentially identical in these solvents. The length of statistical Kuhn segment of each of these polymers, which characterizes the equilibrium rigidity of the polymer chain, was presumably similar in these two solvents. In this context, reference can be made to the results by Tsvetkov et al.[37] on the hydrodynamic properties of poly(phenyl-1,4-phenylene phenylterephthalate) in DCA and dioxane, which show that these properties remain essentially identical in these solvents, even on passing from a polar to a nonpolar solvent. Its length of statistical Kuhn segment is also identical in both polar and nonpolar solvents and is close to 260 Å.

All of the copolyesters, **I-1**−**I-4**, were prepared by the melt polycondensation reaction of the appropriate monomers in the absence of a catalyst. All of them were soluble in the usual solvent, such as *p*-chlorophenol. The data in Table 1 show that, for this series of polymers, IV values in this solvent at 50 °C were in the range of 0.72−2.40 dL/g despite the inclusion of a flexible 4,4′-oxybis(benzoate) moiety as a nonlinear component; these values suggest that all of the polymers have sufficiently high molecular weights so that their thermal properties, optical textures, and other properties can be compared neglecting the effect of molecular weight on these properties. Generally, the flexible and nonlinear moiety may cause a decrease in rigidity of the polymer chain and, therefore, a decrease in the solution viscosity at equivalent molecular weight.[8]

FTIR Spectra. The IR spectra of the copolymers exhibited the following characteristic absorption bands that are indicative of aromatic polyesters: 3439−3458 (overtones of C═O), 3032−3064 (═C−H aromatic), 1736−1740 (C═O), 1595, 1477 (C═C aromatic), 1244−1254, 1191−1193, and 1067−1071 (C−O from ester and ether linkage of OBBA), and 700 cm^{-1} (═C−H out of plane bending of phenyl ring).

Thermal Properties. The DSC thermogram of copolymer **I-1**, prepared from MPBP, TA, and 50 mol % OBBA, showed a T_g but neither a crystal-to-LC transition, T_m, nor a LC-to-isotropic transition, T_i. However, it fused to form a LC phase at low temperature, T_f, at 210 °C and underwent LC-to-isotropic transition at a relatively high temperature of about 450 °C as determined by PLM studies. Although at this high T_i value thermal decomposition occurred to some extent, it did not hinder the observation of this transition. The absence of a T_m and the presence of a T_g in its DSC thermogram clearly demonstrated that this copolymer was amorphous, which is in contrast to the copolymers both of ClHQ, TA, and 50 mol % OBBA and of PhHQ, TA, and 50 mol % OBBA. The T_f value of this copolymer was much lower than the T_m (275 °C) of the former copolymer and slightly lower than the T_m (225 °C) of the latter copolymer.[27,34] The T_i for the copolymer of PhHQ, TA, and 50 mol % OBBA is 288 °C, and therefore, it has a mesophase range of 63 °C.[34] In contrast, the copolymer **I-1** had a range of mesophase (240 °C), which was much higher than that of the copolymer of PhHQ. Its high range of mesophase was related to the greater length of MPBP when compared to the length of PhHQ moiety. The contrasting behavior of amorphous vs semicrystalline nature for these copolymers presumably occurred because of the difference in length of MPBP unit when compared with ClHQ and PhHQ units. This difference in length could cause a mismatch in the position of ester linkages of neighboring polymer chain and, therefore, reduce the interchain interactions. Furthermore, the incorporation of MPBP unit in the polyester chain had an effect of introducing a torsional deformation of the polymer chain, which arose because of the noncoplanarity of two phenyl groups of this unit. Furthermore, its T_f value was also much lower than the T_m values of both the homopolymer of MPBP with TA and its copolymer with 30 mol % HBA.[17,18,20] The amorphous nature and, hence, low T_f value of this copolymer were caused mainly by the following reasons: (a) internal copolymerization effect of asymmetrically phenyl-substituted 4,4′-biphenol moiety and (b) external copolymerization effect of both the aromatic dicarboxylates, TA and OBBA. Both the copolymerization effects of the respective monomers along the polyester chain were verified with ^{13}C-NMR spectroscopy.

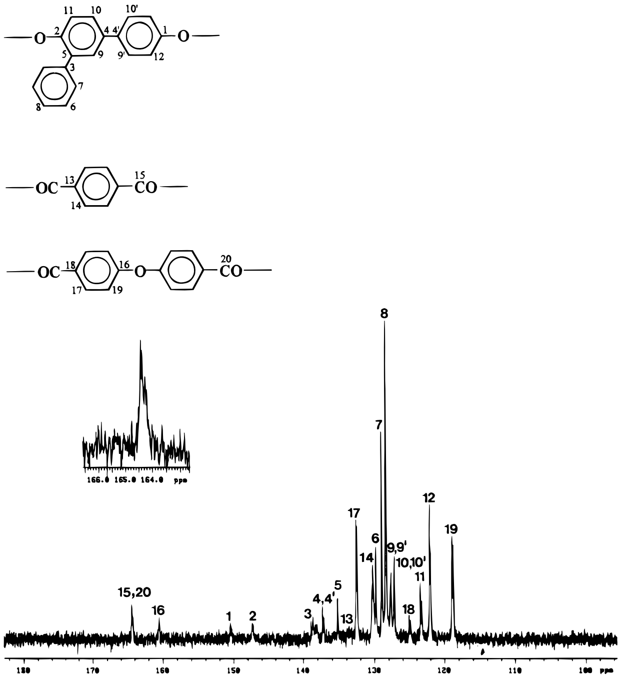


Figure 1. ^{13}C-NMR spectrum of copolymer **I-1** in $\mathrm{CDCl_3}$.

Figure 1 shows the ^{13}C-NMR spectrum of polymer **I-1** taken in $\mathrm{CDCl_3}$. The carbonyl carbons of the ester groups gave rise to four distinct resonances at ca. 164.4 ppm covering a total chemical shift of 0.7 ppm, which can be attributed to both the head-to-head and head-to-tail arrangements of asymmetric MPBP unit with the two symmetric aromatic dicarboxylates, TA and OBBA. This observation is in excellent agreement with the fact that the carbonyl carbon of ester group is sensitive not only to the nature of the next neighboring rings but also to that of the more distant ones. Moreover, its sensitivity to the sequence effects of aromatic copolyesters has been well documented in the literature.[9,24,38] The nonequivalent C4 and C4′ of the asymmetric MPBP unit showed resonances at ca. 147.6 and 150.5 ppm, respectively, and their line shapes suggested that these carbons, as is the carbonyl of the ester group, are also sensitive not only to the nature of the next neighboring rings but also to that of the more distant ones. This observation is also indicative of the random arrangements of MPBP units with TA and OBBA units. The C2 of TA unit showed resonance at ca. 130.0 ppm, and its line shapes are indicative of the random sequences of this unit with MPBP unit. Furthermore, the equivalent C4 and C4′ of OBBA unit had a resonance at ca.

160.4, and its line shapes are consistent with the random arrangements of MPBP units with this unit. These random arrangements of MPBP units also caused the distinct line shapes for the C1(C1′), C2(C2′), and C3(C3′) of OBBA unit, as expected. In other words, all of the carbons of this unit are sensitive to the head-to-head and head-to-tail arrangements of an asymmetric unit, MPBP. All of the aromatic carbon resonances of MPBP, TA, and OBBA units were consistent with their calculated ones and are shown in Figure 1. The ^{1}H-NMR spectrum of this polymer appeared rather broad and unstructured, except that the four hydrogens of TA moiety and those of OBBA moiety, which are connected to C2 and C2′, appeared distinctly at 8.1−8.4 ppm. The other four hydrogens of OBBA, which are connected to C3 and C3′, appeared at slightly high field at ca. 7.0 ppm.

As was similar to copolymer **I-1**, the copolymer **I-2**, prepared from MPBP, NDA, and 50 mol % OBBA, also showed a T_g but neither a T_m nor a T_i in the heating cycles of DSC thermograms. However, it also fused to form a LC phase at relatively low T_f (180 °C) and underwent isotropization at relatively high temperature (455 °C) as determined by PLM studies. Its isotropic transition at this high temperature was accompanied with the thermal decomposition to some extent that did not hinder the observation of this transition. The absence of a T_m and the presence of a T_g in the DSC thermogram clearly indicated that this copolymer was also amorphous. The amorphous nature of this copolymer could have resulted from the internal copolymerization effect of asymmetric MPBP unit and the external copolymerization effect of each of the aromatic dicarboxylates, NDA and OBBA. Both the copolymerization effects of the respective monomers eliminated the crystallinity completely in this copolymer, which is in contrast to the copolymers of ClHQ, TA, and 50 mol % OBBA and of PhHQ, TA, and 50 mol % OBBA. As expected, its T_f value was much lower than the T_m values (275 and 225 °C) of the copolyesters of ClHQ and PhHQ.[27,34] Furthermore, its mesophase range (275 °C) was much higher than that (63 °C) of the copolymer of PhHQ.[34] The high range of its mesophase was related to both the greater length of MPBP unit when compared with that of PhHQ and the greater length of NDA when compared with that of TA. The presence of NDA in this copolymer, instead of TA in copolymer **I-1**, also caused a higher mesophase range than the copolymer **I-1**. It had a lower T_f than copolymer **I-1**, which was presumably related to the linear offset structure of NDA moiety. This linear offset structure can provide an additional factor for the reduction of interchain interactions. Additionally, its T_f value was much lower than those (260 and 235 °C) of the homopolymer of MPBP with NDA and its copolymer with 30 mol % HBA.[17,18]

As were similar to copolymers **I-1** and **I-2**, the copolymer **I-3**, prepared from DPBP, TA, and 50 mol % OBBA, did not exhibit a T_m and a T_i in the heating cycles of DSC thermograms. However, it formed a LC phase as low as 200 °C and underwent isotropization at relatively low temperature (260 °C), both of which were determined by the use of hot-stage PLM studies. The presence of a T_g and the absence of a melting endotherm in the DSC thermogram suggested that this copolymer was essentially amorphous. This observation was also in contrast to the copolymers of ClHQ and PhHQ, each of which contained equimolar amounts of TA and OBBA. As expected, the T_f value of this copolymer was lower than the T_m values (275 and 225 °C) of the copolymers of ClHQ and PhHQ having identical chemical compositions.[27,34] Its T_f value was also lower than the T_m values of the homopolymer of DPBP with TA and its copolymers with either 30 mol % HBA or 30 mol % HNA. The T_m values of the homopolymer of DPBP with TA and its copolymers (with either 30 mol % HBA or 30 mol % HNA) are 341, 318, and 332 °C, respectively.[17,18,39] Therefore, it was observed that the crystallinity in the homopolymer of DPBP, a symmetric monomer, with TA (whose degree of crystallinity[40] is 44%) could be eliminated completely with the copolymerization of 50 mol % OBBA. However, it had a mesophase range of 60 °C, which was essentially similar to that (63 °C) of the copolymer of PhHQ, TA, and 50 mol % OBBA.[34] Furthermore, its mesophase range was much lower than those (240 and 275 °C) of copolymers **I-1** and **I-2**, each of which contained the MPBP unit. This result was presumably related to the additional phenyl substituent in DPBP unit. This additional phenyl substituent in DPBP could cause the reduction of the axial ratio (*L*/*D*) considerably and, hence, the T_i for this copolymer. It is important to note here that the homopolymers of DPBP with either TA or NDA exhibit T_i values at 398 and 423 °C, respectively, which are in contrast to the respective homopolymers of MPBP.[17] The amorphous nature and, hence, low T_f of this copolymer were caused mainly by the copolymerization effect of TA and OBBA units. The copolymerization effect of these dicarboxylates was attributed to their random placements along the polyester chain, which was also verified with the ^{13}C-NMR spectroscopy.

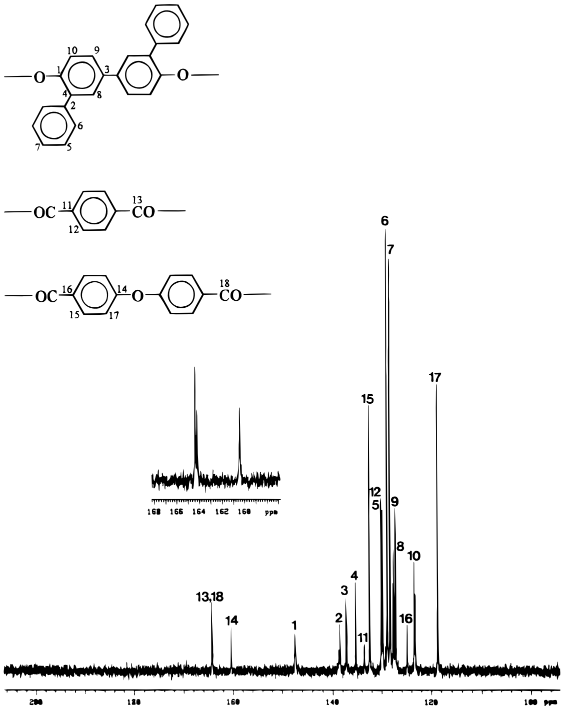


Figure 2. ^{13}C-NMR spectrum of copolymer **I-3** in $CDCl_3$.

Figure 2 shows the ^{13}C-NMR spectrum of polymer **I-3** taken in $CDCl_3$. In contrast to the copolymer **I-1**, the carbonyl carbons of ester groups of this copolymer gave rise to two distinct resonances at 164.2 and 164.4 ppm, which can be attributed to the presence of two non-equivalent ester carbonyls present in this copolymer. The equivalent C4 and C4′ of the symmetric DPBP unit showed a resonance at 147.4 ppm, but its line shapes indicated that these carbons are connected to the esters groups of two aromatic dicarboxylic acid moieties, TA and OBBA. Therefore, these carbons, as is the carbonyl of ester, are sensitive to the microstructures of the copolyester. The C1(C4) and C2(C3) of TA unit showed resonances at 133.5 and 130.1 ppm, as expected. Similarly, the C4(C4′), C3(C3′), C2(C2′), and C1(C1′) of OBBA unit also showed resonances at their appropriate chemical shifts, as expected. All of the aromatic carbon resonances of DPBP, TA, and OBBA units were consistent with their calculated ones and are shown in Figure 2. The ^{1}H-NMR spectrum of this copolymer appeared rather broad and unstructured, except that the four hydrogens of TA moiety and those of OBBA moiety, which are attached to C2 and C2′, appeared distinctly at 8.0 ppm. The other four hydrogens, which are connected to C3 and C3′, appeared at slightly high field at ca. 7.1 ppm.

The DSC thermogram of copolymer **I-4**, prepared from DPBP, NDA, and 50 mol % OBBA, contained neither a T_m nor a T_i, as was similar to those of copolymers **I-1**–**I-3**. However, it showed a LC phase at 310 °C (T_f) that then transformed into an isotropic phase at 380 °C (T_i). In this case, both the T_f and T_i were also determined by the PLM studies. The presence of a T_g and the absence of a T_m for this copolymer were indicative of its amorphous state, which is also in contrast to the copolymers of ClHQ and PhHQ, each of which contained equimolar amounts of TA and OBBA. Despite the absence of its crystallinity, the T_f value of this copolymer was higher than the T_m values of the copolymers of ClHQ and PhHQ.[27,34] However, its T_f value was lower than the T_m values of the homopolymer of DPBP with NDA and its copolymers with either 30 mol % HBA or 30 mol % HNA, as expected. The T_m values of the homopolymer of DPBP with NDA and its copolymers are 362, 338, and 334 °C, respectively.[17,18,39] This result indicated that the copolymerization with 50 mol % OBBA would enable one for the elimination of crystallinity in the homopolymer of DPBP, a symmetric monomer, with NDA (whose degree of crystallinity[40] is 47%). Additionally, its mesophase range was 70 °C, which was slightly higher than those of copolymer **I-3** and the copolymer of PhHQ, TA, and 50 mol % OBBA,[34] but much lower than those of copolymers **I-1** and **I-2**, each of which contained MPBP unit. Therefore, it was observed that the DPBP unit in this copolymer also caused a dramatic decrease in T_i, presumably because of the reduction in axial ratio, as was similar to the copolymer **I-3**. The amorphous state and, hence, relatively low T_f of this polyester were also caused by the copolymerization effect of NDA and OBBA.

The T_g values for all of the copolymers are in the range of 149–171 °C (Table 1) as determined by DSC measurements. Additionally, their T_g values were measured with a thermomechanical analyzer and are in the range of 150–183 °C (Table 1). The TMA plot of each of the copolymers exhibited two distinct regions of softening: The first one was related to the T_g and the second to the T_f of this copolymer. Their T_g values were higher than those (103–112 °C) for the Vectra family of copolyesters (HBA/HNA).[41] They were also much higher than those (97 and 128 °C) for the copolymers of ClHQ and PhHQ.[27,34] The high T_g values of these copolymers, in the present study, were presumably related to the 3-phenyl-4,4′-biphenylene and 3,3′-diphenyl-4,4′-biphenylene units. These units caused a significant increase in the chain rigidity of the respective polyester chains resulting in the decrease of free volume and in the increase of cohesive energy density. Both the effects contributed to a high T_g. Furthermore, it was observed that the copolymers containing an asymmetric MPBP unit had lower T_g values than those of the copolymers containing a symmetric DPBP unit. The phenyl substituent of asymmetric MPBP unit could be incorporated in the head-to-head and head-to-tail fashions along the polyester chain resulting in an increased free volume and, consequently, contributing to a low T_g.[42] However, for the various industrial applications of wholly aromatic, thermotropic polyesters, a relatively low T_m and a low level crystallinity, on the one hand, are highly desirable so that they can be processed at convenient temperatures without their thermal degradation. On the other, the absence of a significant amount of crystallinity can result in poor mechanical properties above the T_g. In this case, the useful service temperature limit of a polymer is effectively determined by the T_g. Generally, it is a disadvantage that many thermotropic polyesters have lower T_g values than those of nonliquid crystalline polyesters.[41] In this regard, the new series of copolyesters **I-1**–**I-4** having relatively high T_g values is of considerable practical interest.

The thermal stabilities of the copolymers were determined in nitrogen by TGA, and the results are collected in Table 1. The thermal stability limit, T_d, which was taken as the temperature (°C) at which a 5% weight loss of a sample occurred, varied from 413 to 436 °C in nitrogen indicating that each of them had an excellent thermal stability for the melt processing in its nematic LC phase, as discussed below, at the elevated temperature. Their thermal stability was essentially similar to that of either the copolymer of ClHQ or the copolymer of PhHQ, each of which contained equimolar amounts of TA and OBBA.[27,34] Additionally, their thermal stability was lower than that (490–500 °C) of the Vectra family of copolyesters (HBA/HNA) under identical experimental conditions.[43] This lower thermal stability when compared with HBA/HNA copolyesters was presumably related to the presence of flexible OBBA unit present in each of the copolyesters. However, this result is in good agreement with the fact that the phenyl substituent in the aromatic diol moiety or in the aromatic dicarboxylic acid moiety does not affect the thermal stability of a thermotropic polyester. In contrast, other substituents including halogen, alkyl, alkoxy, phenoxy, and phenylalkyl are known to decrease the thermal stability of the respective polyesters considerably.[8,19,31]

Optical Properties. All of the copolymers, listed in Table 1, formed turbid melts above their T_f values that exhibited stir opalescence. However, the copolymers **I-1** and **I-2** showed a strong stir opalescence; in contrast, the copolymers **I-3** and **I-4** showed a pronounced decrease in the intensity of stir opalescence. For further characterization of their melt morphology, they were evaluated by visual observations on a PLM instrument. All of the copolyesters formed a typical nematic appearance with either a schlieren (disclination strength, $S = \pm^1/_2$ and $S = \pm 1$) or a threaded texture depending on the thickness or the temperature of the sample. Each of the copolyesters of MPBP formed a banded texture above its T_f value, which on further heating disappeared in the temperature range of 330–350 °C. On cooling, it reappeared and could be preserved at room temperature for an extended period of time, since there was no interference from the crystallization process of each

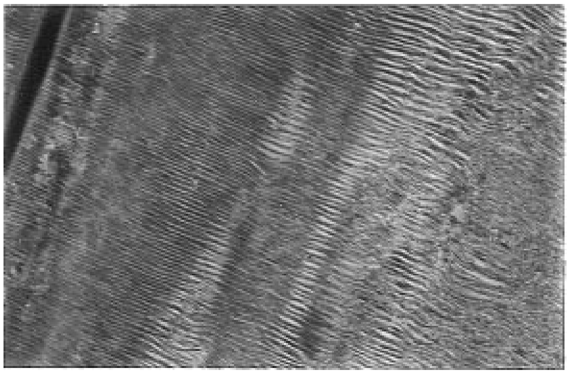


Figure 3. Photomicrograph of copolymer **I-1** taken at 250 °C displaying a banded texture (magnification 400×, reproduced at 65% of original size).

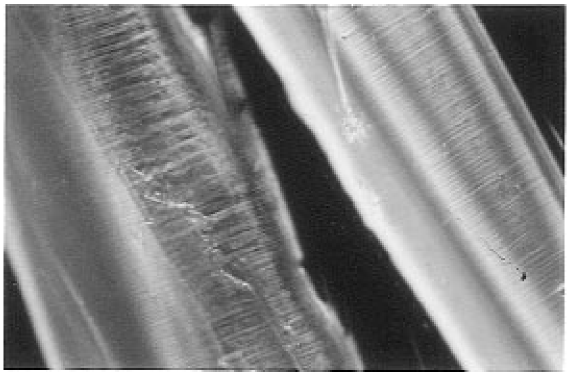


Figure 4. Photomicrograph of two strands of hand-drawn fiber obtained from copolymer **I-1** displaying a banded texture (magnification 400×, reproduced at 65% of original size).

of the respective copolymers. Figure 3 shows the photomicrograph of copolymer **I-1**, prepared by shearing the sample between the two microscope cover glasses and taken at 250 °C, displaying a banded texture. The bands have a width of the order a 1 μm, and they can be easily observed by PLM. They always lie perpendicular to the prior shear direction and are associated with a periodic variation in director orientation about the flow axis.[41]

Interestingly enough, a hand-drawn fiber from each of the copolymers of MPBP (**I-1** and **I-2**) also exhibited distinctly a banded texture as shown in Figure 4 for the copolymer **I-1**. This banded texture in the fiber could also be preserved for an extended period of time, since there was no interference from the crystallization process of this copolymer. The banded texture has also been reported in the other oriented thermotropic polyesters that are studied by both TEM and PLM.[44,45] The formation of a banded texture occurs, generally, on shearing of either a lyotropic or thermotropic LCP. It has been reported in the literature[46−48] that its formation in a LCP is associated with a transient phenomenon on the one hand, namely, it typically occurs after the cessation of flow in shear or elongation, presumably as a result of some relaxation process, but there is some evidence that under certain circumstances it may appear during the flow itself. On the other, Han et al.[49] observed the development of a banded texture in a melt-spun fiber (no domain structure) of a semiflexible thermotropic polyester on isothermal annealing at 130 °C for a period of over 24 h, but it disappeared only after the isothermal annealing continued for a period of over 48 h. They attributed the disappearance of the banded texture to the formation of high-temperature melting crystals. They suggested that the formation of this texture in this polyester was not related to the transient phenomenon. Although a banded texture is a universal phenomenon in LCPs in general, the origin and mechanisms of its formation have not been yet well understood and require further studies. Another intriguing property of a LCP is its biphase structure over a range of concentrations, common to a wide number of lyotropic polymers, at which an anisotropic and an isotropic phase coexist. Similarly, a thermotropic polymer may also undergo phase separation at high temperature into a birefringent LC and an isotropic phase.[41] Generally, a wholly aromatic, thermotropic polyester has a high T_i, and therefore, the coexistence of an anisotropic and an isotropic phase has rarely been observed.[30,50] However, each of the copolymers had the accessible T_i (Table 1), and therefore, it was possible to observe its biphasic behavior. The biphasic thermal range for each of the copolymers of MPBP, **I-1** and **I-2**, was 30−50 °C broad. However, each of the copolymers of DPBP, **I-3** and **I-4**, exhibited the biphasic state at a relatively low temperature, which was 20−30 °C above its T_f value. The presence of this biphasic property in these two polyesters caused qualitatively the decrease in intensity of stir opalescence.

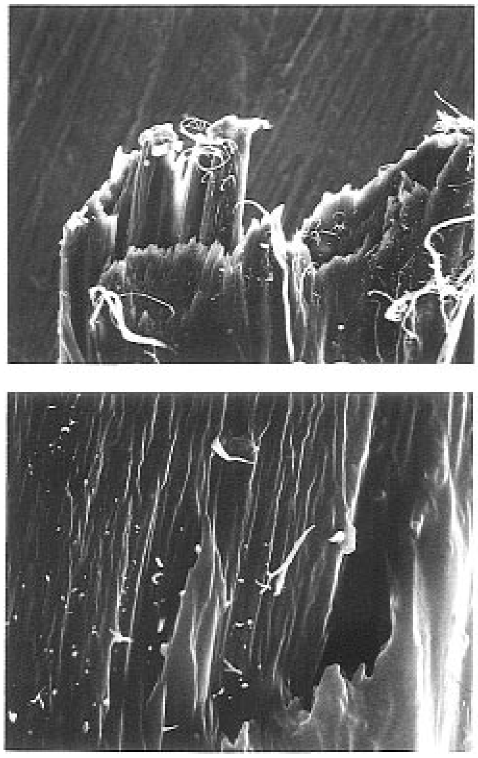


Figure 5. SEM micrographs of a fractured fiber drawn from copolymer **I-1** exhibiting a skin−core morphology: top, magnification 300×, and bottom, magnification 2500× (reproduced at 65% of original size).

Scanning Electron Microscopy. The SEM studies of hand-drawn fiber for each of the copolymers of MPBP, **I-1** and **I-2**, were performed in order to understand their morphologies. Figure 5 shows the typical micrographs at low and high magnifications of the tip of a fiber drawn from copolymer **I-1**. It shows distinctly a surface skin and a regular fibrillar internal structure with a characteristic size of a few microns, the well-known skin−core morphology, indicating the orientation of the polymer chain. The fibrillar, ribbon-like structures, which consist of uniaxially oriented sheets, are also present in the micrograph. The skin (high degree of orientation)−core (low degree of orientation) is a con-

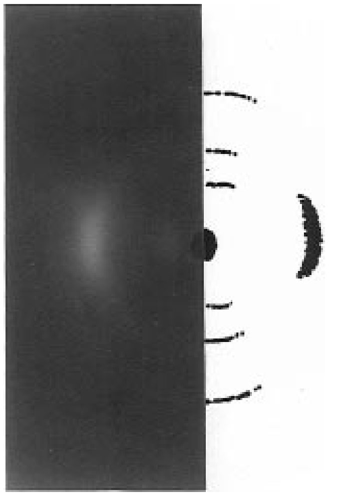


Figure 6. X-ray diffraction pattern obtained from copolymer **I-1** by drawing a fiber from its nematic melt. Because of the low intensity of the pattern obtained, the right-hand side is reproduced with a drawing showing the positions of the meridional arcs (fiber direction vertical).

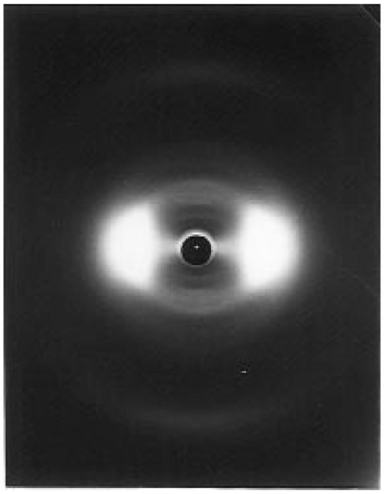


Figure 7. X-ray diffraction pattern obtained from copolymer **I-2** by drawing a fiber from its nematic melt (fiber direction vertical).

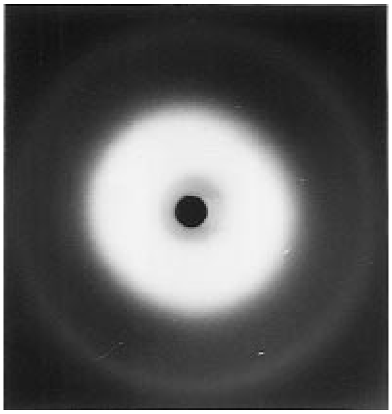


Figure 8. X-ray diffraction pattern obtained from copolymer **I-4** by drawing a fiber from its nematic melt. There was no orientation.

sequence of the very high molecular anisotropy of thermotropic polyesters.[51]

X-ray Diffraction. The X-ray diffraction pattern obtained for a fiber drawn from the nematic melt of copolymer **I-1** is shown in Figure 6. The temperature range in which fibers could be drawn was exceedingly narrow, and only very fine fibers were obtained. Even with a long exposure (ca. 2 days), its X-ray pattern was exeedingly weak, but three meridional arcs at 0.78, 0.53, and 0.34 nm could be seen on the original pattern, although they are too weak to be reproduced photographically. A composite diagram of this copolymer is shown in Figure 6. An equatorial diffraction spot, centered at a spacing of 0.45 nm, was clearly seen. The pattern has the hallmarks of the oriented nematic state with aperiodic layer line spacings consistent with those expected for a random copolyester.[52]

The copolymer **I-2** exhibited a sufficiently high melt viscosity that allowed fibers to be drawn from the nematic state with ease. A respectable, oriented nematic X-ray diffraction pattern was obtained, shown in Figure 7, which contained a series of aperiodic meridional spacings at 0.93, 0.76, 0.57, 0.36, 0.31, and 0.21 nm and a strong liquid-like diffraction signal on the equator at 0.45 nm. The replacement of the TA unit (copolymer **I-1**) with the linear offset geometry of a NDA unit seemed to improve the ability of this copolymer to form an oriented nematic state, which was contrary to our expectation. Fibers could not be melt-drawn from the copolymer **I-3**, most likely because of the relatively narrow range of LC phase along with the biphasic behavior at relatively low temperature of this polymer. Although polarized light microscopy studies indicated the existence of a nematic texture, it was not possible to study it further using X-ray diffraction.

Although it was possible to obtain fibers from the nematic melt of copolymer **I-4**, the fibers did not show any indication of orientation. The pattern shown in Figure 8 contains a strong, diffuse halo centered on a spacing of 0.45 nm and a prominent ring at spacing 0.21 nm. This pattern is the type to be expected from an unoriented nematic texture, although it should not be taken as firm proof. It is likely that the relatively narrow range of LC phase and the biphasic behavior at relatively low temperature of this polymer created difficulties in obtaining the orientation. The difficulty in obtaining the fibers from the copolyesters containing DPBP, **I-3** and **I-4**, prevented a complete comparison among the members of the family of four thermotropic polymers, in the present study, but all of the indications are that they were able to form nematic phases. The two copolyesters containing the MPBP unit exhibited oriented nematic phases. On annealing none of the samples developed any measurable amount of crystallinity. This behavior is in contrast to that of the homopolymers of MPBP with TA and of MPBP with NDA,[17] both of which developed crystallinity on annealing.

Conclusion

All of the copolyesters, derived from phenyl-substituted 4,4′-biphenols, terephthalic or 2,6-naphthalenedicarboxylic acid, and 50 mol % 4,4′-oxybis(benzoic acid), had much lower fusion temperatures, T_f, than the T_m values (400−470 °C[53]) of Xydar family of copolyesters (based on BP, TA, and HBA), which would facilitate their processing at temperature as low as 180 °C from their nematic melts. Each of them showed a nematic phase above its T_f value, which showed both the threaded and schlieren texture. Additionally, the two copolyesters of MPBP including their hand-drawn fibers exhibited a banded texture. Each of these two copolyesters had a broad range of LC phase (240 and 275 °C), which was in contrast to that (60 and 70 °C) of the copolyesters containing 3,3′-diphenyl-4,4′-biphenol. The low T_f values of the polyesters containing MPBP were related to both the internal copolymerization of MPBP and the copolymerization effect of the respective linear and nonlinear aromatic dicarboxylic acids. Those of the polyesters of DPBP were related to the copolymerization effect of the two diacids. They exhibited T_i values, determined by PLM studies, and showed a biphasic behavior. The biphase for each of the copolyesters containing DPBP occurred at a relatively much lower temperature than that of the polyesters containing MPBP. The microstructures of all of these copolymers had random monomer sequences that were determined by both the WAXD technique from the analyses of their oriented fiber diffraction patterns and ^{13}C-NMR spectroscopy, whenever possible. None of these copolymers could crystallize even on annealing. They had relatively high T_g values, up to 171 °C, and good thermal stability, up to 436 °C, respectively. These results suggested that noncrystalline polyesters having low T_f values could be prepared from either an asymmetrically or a symmetrically substituted 4,4′-biphenol on copolymerization with equimolar amounts of linear and nonlinear aromatic dicarboxylic acids, which have practical implications. Especially, the copolymerization of equimolar amounts of either TA or NDA and OBBA with DPBP, a symmetric monomer, could suppress the crystallinity completely in the respective homopolymers of either TA or NDA with DPBP. The copolymers of either MPBP or DPBP with TA and OBBA had solubility in common organic solvents including chloroform and methylene chloride, but those with NDA and OBBA had no solubility in these solvents. As expected, the copolymer of DPBP had higher solubility than that of MPBP.

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 gratefully acknowledge the Schnectady Chemical Co., New York, for supplying the MPBP and DPBP monomers. We are thankful to Mr. Keith Dodsworth for performing the SEM analysis.

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MA951809C