Fully Aromatic Liquid Crystalline Polyesters of Phenyl-Substituted 4,4′-Biphenols and 1,1′-Binaphthyl-4,4′-diol with either 2-Bromoterephthalic Acid or 2-Phenylterephthalic Acid

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ABSTRACT: Fully aromatic, thermotropic homopolyesters, derived from either phenyl-substituted 4,4′-biphenols or 1,1′-binaphthyl-4,4′-diol and 2-bromoterephthalic acid or 2-phenylterephthalic acid, were prepared by acidolysis condensation polymerization reactions and characterized for their liquid crystalline (LC) properties. The solubility behavior of these substituted homopolyesters in common organic solvents had also been investigated. The two homopolymers of substituted biphenols with 2-phenylterephthalic acid were soluble in common organic solvents. All of the polyesters had lower T_m/T_f values than those of respective unsubstituted homopolymers, as expected, and formed nematic LC phases which persisted up to 400 °C, except those of phenyl-substituted biphenols with 2-phenylterephthalic acid. The homopolymer of 3-phenyl-4,4′-biphenol with 2-phenylterephthalic acid formed a nematic phase at or above 150 °C and showed a T_i at 290 °C. That of 3,3′-bis(phenyl-4,4′-biphenol with 2-phenylterephthalic acid also formed a nematic phase at or above 200 °C and also showed a T_i at 280 °C. They had glass transition temperatures, T_g, in the range of 133–151 °C and high thermal stabilities in the range of 445–485 °C, respectively.

Introduction

Fully aromatic, thermotropic polyesters are one of the most important classes of liquid crystalline polymers (LCPs) because of their ease of processing in the nematic liquid crystalline (LC) phase to obtain either high strength fibers or engineering thermoplastics. In general, however, they have high melting transitions, T_m, because of their high enthalpy change and low entropy change at the crystal-to-nematic LC phase transition. Moreover, they have very low solubility in all but aggressive solvents.

There are several kinds of structural modifications to decrease the T_m values of this class of polymers to a convenient[1] level in order to prevent thermal degradation during the melt processing including (a) the introduction of a bulky substituent group in either aromatic diacid or aromatic diol or both to disrupt lateral packing,[2-4] (b) copolymerization of different sizes of LC forming units to lower the symmetry of the polyester primary structure,[5-7] (c) the use of bent (nonlinear) monomers to lower the persistent length of the polymer chain in the LC phase and to disrupt lateral interactions in the solid state,[8-10] and (d) the incorporation of flexible linkages or spacers between the LC forming units giving rise to semiflexible thermotropic polyesters.[11,12]

Furthermore, several structural modifications of this class of polymers have been developed to increase their solubility in common organic solvents, such as $CHCl_3$, CH_2Cl_2, and THF.

(a) The first approach is to incorporate 2,2′-bis(trifluoromethyl)-substituted biphenylene in combination with trifluoromethyl)-substituted phenylene units in the copolyester chain, resulting in an unusual solubility in common organic solvents.[13]

(b) The second approach is to incorporate 2,2′-bis(methyl)-substituted biphenylene along with methyl-, bromo-, and *tert*-butyl-substituted phenylene units in the polyester chain in order to have solubility in common organic solvents.[14]

(c) The third approach is to incorporate a bulky substituents, such as *tert*-butyl, phenyl, phenoxy, phenylalkyl, and 4-biphenyl, in both the aromatic diacid and aromatic diol moiety in the polyester chain.[15-17]

(d) The fourth approach is to incorporate a high percentage (>25%) of *o*-phenylene units from 1,2-dihydroxybenzene (catechol) into the copolyester chain in order to have solubility in $CHCl_3$.[18,19]

Recently, we reported[20-22] the synthesis and characterization of a series of both homopolyesters of phenyl-substituted 4,4′-biphenols with either terephthalic acid (TA) of 2,6-naphthalenedicarboxylic acid (2,6-NDA) alone and their copolyesters with either 30 mol % of *p*-hydroxybenzoic acid (HBA) or 50 mol % of each of the two aromatic dicarboxylic acids. In this report, we describe the preparation and characterization of a series of homopolyesters of these types of monomers, including 3-phenyl-4,4′-biphenol (MPBP), 3,3′-bis(phenyl)-4,4′-biphenol (DPBP), and 1,1′-binaphthyl-4,4′-diol (BND) with either 2-bromoterephthalic acid (BrTA) or 2-phenylterephthalic acid (PhTA). These polyesters, that is, disubstituted poly(4,4′-biphenylene terephthalates) and monosubstituted poly(1,1′-binaphthyl-4,4′-ylene terephthalates) having a bulky substituent group in each of the aromatic diacid and aromatic diol moieties, may have solubility in common organic solvents. Furthermore, the bulky substituents present in both the diacid and diol moieties can decrease substantially the crystallinity and the T_m value of a homopolymer as compared to that of the respective unsubstituted homopolyester.

The structures and designations of the homopolyesters, I, which were prepared and characterized in this study,

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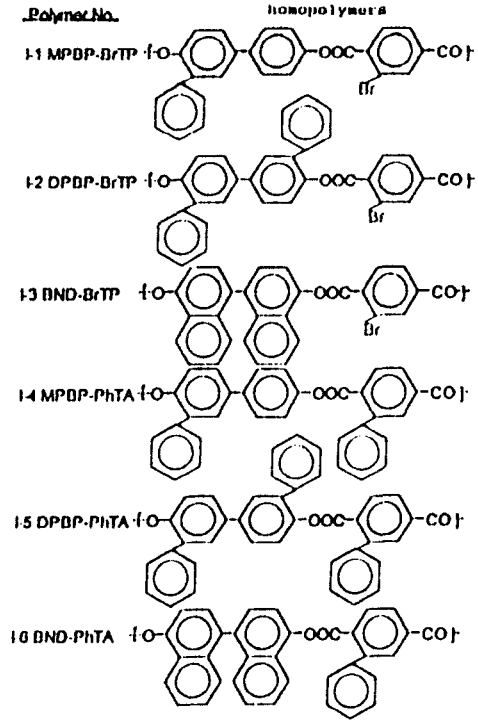
are shown:



These fully aromatic homopolyesters were characterized by a variety of experimental techniques, including solution viscosity, gel-permeation chromatography (GPC), nuclear magnetic resonance (NMR) spectroscopy, polarized light microscopy (PLM), differential scanning calorimetry (DSC), transmitted light intensity measurement (LTI), and thermogravimetric analysis (TGA). Furthermore, their solubility in various common organic solvents had been investigated.

Experimental Section

Monomers. The two substituted biphenols, MPBP and DPBP, and BND were received as diacetates from Schnectady Chemical Co., Inc., Schnectady, NY, and used without further purification because of their satisfactory elemental analyses. The 2-bromoterephthalic acid (BrTA) was received from Aldrich Chemical Co. and recrystallized from a mixture of water and ethanol (80/20 by volume). The synthesis of 2-phenylterephthalic acid (PhTA) was performed according to a previously reported procedure.[23]

Homopolyesters. All homopolyesters were prepared by melt polycondensation reactions, without an added catalyst, from the individual diacetate derivatives of the substituted biphenols and BND with either BrTA or PhTA. The polycondensation reactions were carried out in a specially designed one-neck-stoppered and 3-mm-thick-walled glass reactor (10.5 × 6.4 cm) equipped with a narrow glass tube outlet with two stopcocks. In this design the entire reactor was kept in a molten salt bath during polymerization to provide a solution to sublimation usually encountered in the polycondensation reaction. At 5–10-min intervals the acetic acid formed from the reaction was removed from the reactor into a trap by successively opening the bottom stopcock, closing the bottom one, and opening the top one by the pump. Finally, at the end of the polymerization reaction the solidified polyester was processed by either one of two procedures as follows: (1) the product (polymers I-2 and I-3) was chipped out of the reactor, ground, and washed successively with xylene, *n*-propanol, and acetone several times to remove any residual monomers, or (2) the product (polymers I-1 and I-4 to I-6) was dissolved in a mixture of *p*-chlorophenol and 1,1,2,2-tetrachloroethane, precipitated from the solution with a 10-fold excess of ethanol, and washed several times with boiling ethanol. The polyesters were either dried under vacuum at 95 °C for 24 h in the former case or dried for 72 h in the latter case. The usual polymerization time was 24 h (except polymer I-3 for which the polymerization time was 9 h), and the yield of the polymerization reaction varied between 90 and 95%.

Polymer Characterization. Inherent viscosities of the polymers, when possible, 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-4 and I-5) were also measured in chloroform at 30 °C at the same concentration with the same type of viscometer. Their molecular weights were also determined using a Waters 804E gel-permeation chromatography device calibrated with monodisperse polystyrene standards through "Ultrastyragel" columns with 500-, 10^3-, 10^4-, and 10^6-Å pore sizes at 50 °C with THF as the solvent. The H^1 and C^{13} NMR spectra were recorded with a Bruker AM 300 spectrometer, operating at 300 and 75.48 MHz, respectively, in $CDCl_3$ using TMS as the internal standard.

Phase transition temperatures were measured with a Perkin-Elmer DSC-2 under a nitrogen flow with both heating and cooling rates of 20 °C/min. The temperature axis of the DSC thermogram was calibrated prior to use with reference standards of high-purity indium, tin, and lead. Polymer samples usually weighing 5-10 mg were used for this analysis. The peak maximum of the phase transition temperature, when possible, was recorded from the first heating cycle only for a sample. The glass transition temperature was taken as the onset of that transition from either the first or second heating cycle, whichever was more prominent. For three samples there were no phase transition temperatures in either the first or second heating cycle of the sample. For these samples, a fusion temperature, T_f, was reported as the temperature of onset of flow as observed for the sample on a hot-plate melting point apparatus. This property was verified by use of a Mettler hot stage on a Leitz Ortholux polarizing microscope from observation of the formation of a typical nematic texture at the edge of the sample, that is, at the thinnest part of the sample. For one sample an isotropization temperature, T_i, was also determined on a hot-plate melting point apparatus as the temperature where stir opalescence was no longer observed. This transition was also confirmed by observation of a "black" background when viewed through the polarizing light microscope equipped with a pair of crossed polarizers and a Mettler hot stage. The liquid crystalline textures for all of the polyesters were observed on an optical microscope equipped with a pair of crossed polarizers and a hot stage. Thermogravimetric analyses (TGA) were obtained with a Du Pont 2100 instrument at a heating rate of 20 °C/min in nitrogen.

The transmitted light intensity scan of a thin film (prepared by placing the sample between two cover glasses, heating up to a temperature where it flowed very well, and finally quenching in ice-cooled water) of polymer I-5 as a function of temperature at a heating rate of 2 °C/min was recorded.

Results and Discussion

All of the homopolyesters were prepared by the melt polycondensation reactions, and all homopolymers, except polymers I-2 and I-3, were soluble in *p*-chlorophenol. The data in Table I show that, for this series of homopolyesters, inherent viscosity (IV) values were in the range of 0.58–3.24 dL/g, suggesting that they had sufficiently high molecular weights so that their thermal properties, optical textures, and other properties can be compared without concern for the secondary effects of molecular weight on those properties.

Polymer I-1 was soluble in *p*-chlorophenol, but polymers I-2 and I-3 were soluble neither in *p*-chlorophenol nor in a mixture of *p*-chlorophenol/1,1,2,2-tetrachloroethane (60/40 by weight). The symmetric structures of the DPBP and BND moieties in contrast to the asymmetric structure of the MPBP moiety probably may increase the rigidity of polyester chain, resulting in a complete loss of solubility. It is important to note that Krigbaum and co-workers[2] and others[24] reported that the homopolymer of 2-phenylhydroquinone and 2-bromoterephthalic acid had solubility in a mixture of phenol/1,1,2,2-tetrachloroethane (60/

Table I. Inherent Viscosities and Solubilities of Homopolyesters in Various Solvents

polymer no.	monomer[a]	IV[b] (dL/g)	solubility[d] in PCP	DCA	TCE	$CHCl_3$	CH_2Cl_2	dioxane	THF
I-1	MPBP–BrTA	3.24	+	–	–	–	–	–	–
I-2	DPBP–BrTA		–	–	–	–	–	–	–
I-3	BND–BrTA		–	–	–	–	–	–	–
I-4	MPBP–PhTA	0.58	+	+	+	+[e]	+	+	±
		0.63[c]							
I-5	DPBP–PhTA	1.50	+	+	+	+[f]	+	+	+
		1.68[c]							
I-6	BND–PhTA	1.68	+	–	–	–	–	–	–

[a] Monomer designation: MPBP, 3-phenyl-4,4′-biphenol; DPBP, 3,3′-bis(phenyl)-4,4,′-biphenol; BND, 1,1′-binaphthyl-4,4′-diol; BrTA, 2-bromoterephthalic acid; PhTA, 2-phenylterephthalic acid. [b] Measured in *p*-chlorophenol at 50 °C. [c] Measured in chloforom at 30 °C. [d] Investigated at ca. 0.1 g/dL at room temperature (not the highest achievable concentration): +, soluble; ±, soluble on heating; –, insoluble; PCP, *p*-chlorophenol; DCA, dichloroacetic acid; TCE, 1,1,2,2,-tetrachloroethane; THF, tetrahydrofuran. [e] Investigated up to 0.5 g/dL. [f] Investigated up to 0.2 g/dL.

Table II. Molecular Weights of Polymers I-4 and I-5 by GPC Measurements

polymer	monomer[a]	M_n[b]	M_w[c]	M_z[d]	M_p[e]	M_w/M_n
I-4	MPBP–PhTA	9 200	30 800	88 100	27 100	3.35
I-5	DPBP–PhTA	26 700	133 000	301 000	162 000	4.98

[a] See footnote *a* in Table I for monomer identification. [b] M_n: number-average molecular weight. [c] M_w: weight-average molecular weight. [d] M_z: *z*-average molecular weight. [e] M_p: peak molecular weight.

40 by weight). In other words, these homopolyesters are insoluble in common organic solvents.

Furthermore, Table I shows a very useful property for polymers I-4 and I-5, namely, that both the polymers were soluble in many common organic solvents, including chloroform, methylene chloride, and dioxane. This property is desirable for ease of characterization, for ease of preparation of a film by solution casting, and for investigation of polymer blends. The solubility of these polymers presumably arises because of the presence of bulky substituent(s), a phenyl group, in both the 4,4′-biphenol and terephthalic acid moieties which reduces the interaction between the polyester chain, suppresses the crystallization tendency, and, therefore, improves the solubility considerably. This structural modification for these two polymers in order to have solubility in common organic solvents is in excellent agreement with the results reported by Heitz and co-workers.[16,17] Their IV values in chloroform at 30 °C were almost essentially identical to those in *p*-chlorophenol at 50 °C, suggesting that the hydrodynamic chain properties of the polymers were essentially identical in these two solvents. The length of the statistical Kuhn segment of each of these polymers, which characterizes the equilibrium rigidity of the chain, is presumably similar in both the solvents. In this context reference is made to the results by Tsvetkov and coworkers[25] on the hydrodynamic properties of diphenyl-substituted poly(*p*-phenylene terephthalate) in dichloroacetic acid and dioxane, which showed that those properties remained essentially identical in these two solvents, even on passing from a polar to a nonpolar solvent. The length of the statistical Kuhn segment is also identical in both solvents and close to 260 Å.

Because of the solubility properties of polymers I-4 and I-5, it was possible to evaluate their molecular weights by gel-permeation chromatography (GPC), and the data obtained are collected in Table II. A GPC plot for polymer I-5, as shown in Figure 1, indicates that a single peak with an average molecular weight (M_w) of 133 000, compared with polystyrene standards, was obtained. Similarly, the GPC plot for polymer I-4 also indicates that a single peak

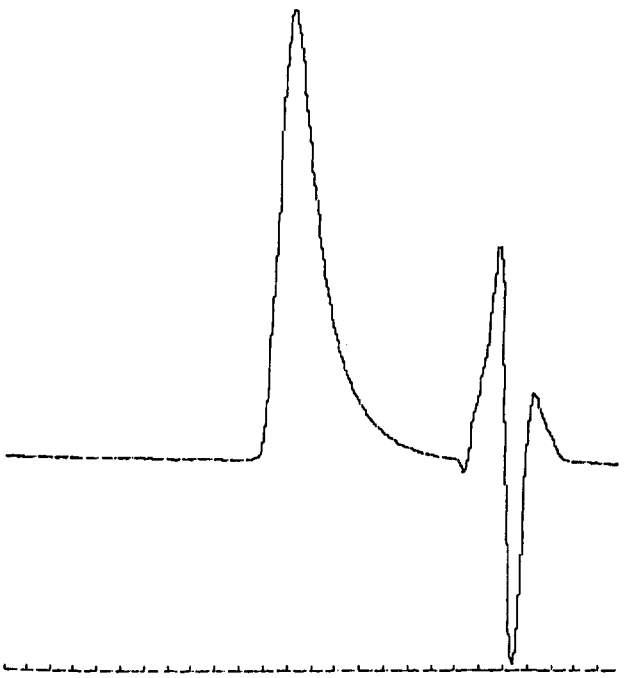


Figure 1. GPC plot of polymer I-5 in THF at 50 °C.

with M_w of 30 800, compared with polystyrene standards, was obtained. Both M_n and M_w values of these polymers are in agreement with their IV values. The molecular weight distributions, as indicated by the ratio of the weight- to number-average molecular weights, M_w/M_n were 3.35 and 4.98, respectively, for these polymers. It was observed that a high M_w sample has higher molecular weight distributions than those of a low M_w sample, which is in agreement with the results as reported by Heitz and Nissner.[17]

The homopolymer of BND with PhTA, I-6, prepared by the melt polycondensation reaction, was soluble in *p*-chlorophenol but not in common organic solvents. In contrast, this homopolymer prepared by the solution polycondensation reaction in diphenyl ether was soluble in chloroform up to a concentration of 5 g/dL as reported by Hohlweg and co-workers.[26] The reason for a dramatic change in the solubility of this polymer because of polymerization reaction conditions has remained unexplained, and no further attempts were made to investigate this anomalous behavior. However, it is worth mentioning that the IV value of polymer I-6 was 1.68 dL/g in *p*-chlorophenol at 50 °C and that of Howleg's polymer was 1.90 dL/g in chloroform at 30 °C.

A large number of fully aromatic, thermotropic polyesters has been prepared and characterized, but a few polyesters of this type have been reported to have solubility

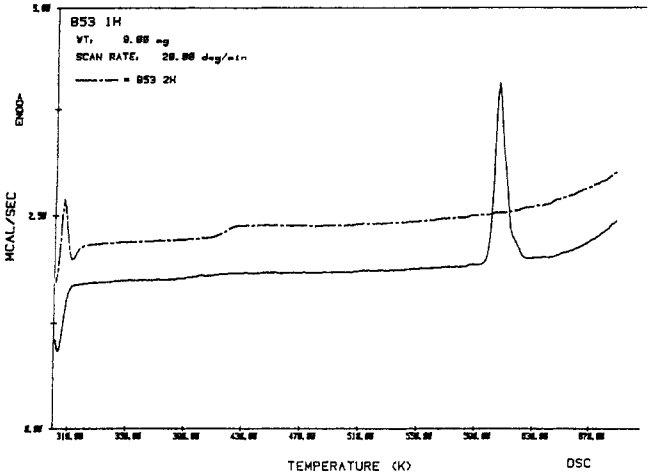


Figure 2. DSC thermograms of polymer I-2 in the first and second heating cycles, 1H and 2H, respectively.

in common organic solvents. The structural modifications, as discussed in the Introduction, which are required in order to have solubility of this class of polymers in common organic solvents, can be easily recognized from Table III which is a compilation of other fully aromatic, thermotropic polyesters having solubility in chloroform.

The homopolymer of MPBP with BrTA, I-1, showed a glass transition temperature, T_g, at 151 °C, and there was neither a melting endotherm, T_m, nor an isotropization endotherm, T_i, in either the first heating or second heating cycle of the DSC thermogram. However, it had a fusion temperature, T_f, at 170 °C presumably because of very little or no crystallinity in this sample. The amorphous nature of this polymer may arise from the random distributions of bulky substituents, phenyl and bromine atoms, in consecutive repeating units along the polyester chain. Krigbaum and co-workers[2] reported that the homopolymer of PhHQ with BrTA had a T_m at 222 °C, a T_i at 376 °C, and a mesophase range of 154 °C. The low T_f and presumably inaccessible T_i values of polymer I-1 may be related to the long rigid 4,4′-biphenylene unit as compared to that of a 1,4-phenylene unit in the polyester chain. It had a much lower crystallinity and T_f than the T_m of poly(4,4′-biphenylene terephthalate), which undergoes decomposition before its transformation into the LC state.

In contrast, the homopolymers of DPBP and BND with BrTA (I-2 I-3, respectively) showed T_g values at 139 and 144 °C and melting endotherms, T_m, at 332 and 351 °C, respectively, in the first heating cycle of the DSC thermogram. A typical DSC thermogram of polymer I-2 is shown in Figure 2. The absence of both a crystallization exotherm in the first cooling cycle and a melting endotherm in the second heating cycle suggested that crystallization did not occur at a rate of 20 °C/min. Furthermore, the T_m values of polymers I-2 and I-3 were lower than those[20,24] of the respective homopolymers with TA which may arise from the random distributions of bromine atoms in consecutive repeating units along the polyester chain. The higher T_m values of these two polymers than the T_f value of polymer I-1 presumably may be related to the symmetric structural moieties of both DPBP and BND in contrast to the asymmetric structural moiety of MPBP. These two polymers also did not exhibit T_i values up to the temperature of 400 °C as is similar to polymer I-1. The presumably high T_i values again may be related to the presence of long rigid 4,4′-biphenylene and 1,1′-binaphthyl-4,4′-ylene units, respectively, in these polymers.

The homopolymer of MPBP with PhTA, I-4, showed a broad isotropization endotherm, T_i, at 290 °C in the first heating cycle but no isotropization endotherm in the second heating cycle. However, it had a T_f at 150 °C presumably because of very little or no crystallinity. Its lower crystallinity than that of the homopolymer with TA, as expected, may be attributed to the random arrangements of the bulky phenyl groups in consecutive repeating units along the polyester chain, which can severely disrupt the packing in the crystal lattice of this homopolymer. These random arrangements of the phenyl groups along the polyester chain were confirmed with C^{13} NMR spectroscopy. Figure 3 shows the C^{13} NMR spectrum of the carbonyl carbon region of this homopolyester. The carbonyl carbons of the polymer gave rise to four distinct resonances covering a total chemical shift range of 3.0 ppm, as expected. In addition, there were two resonances of carbonyl carbons at 170 and 173 ppm which were attributable to the chain end groups CH_3COO– and –COOH, respectively. The H^1 NMR spectrum appeared broad and unstructured, except that the four hydrogens of one of the rings of MPBP unit showed crudely a four-line pattern in the range of 8.0–8.5 ppm.

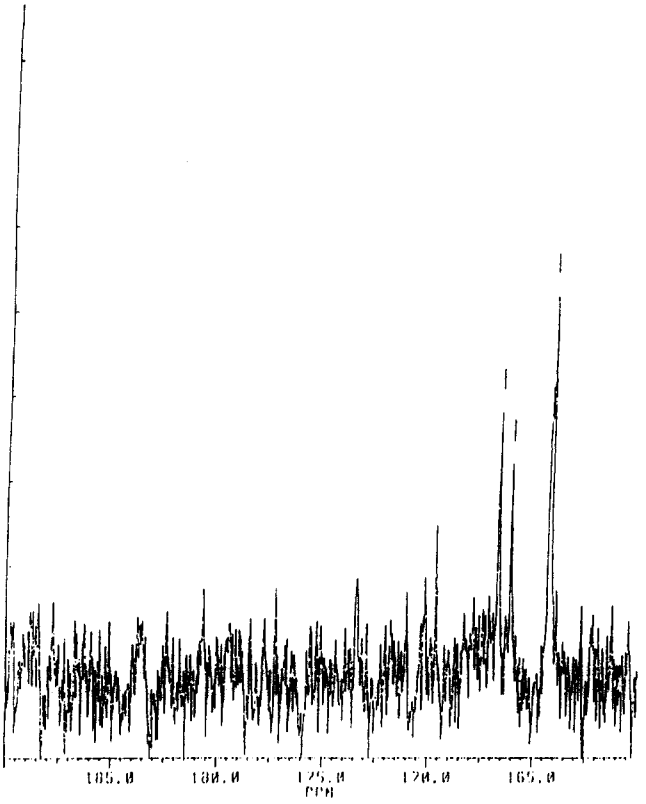
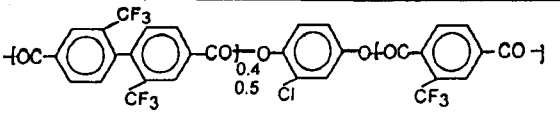
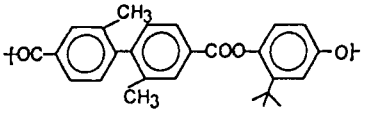
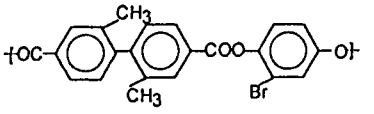
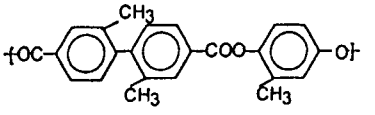
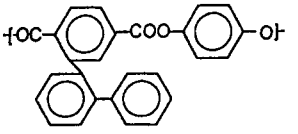
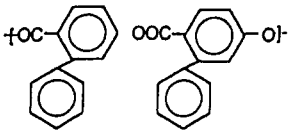
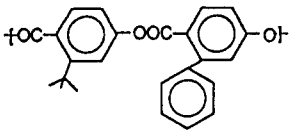
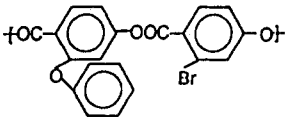
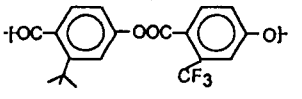
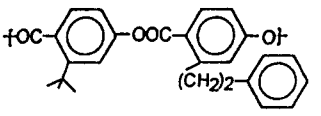
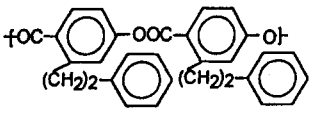
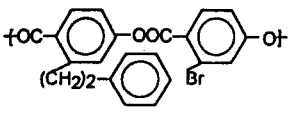
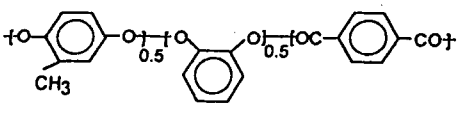
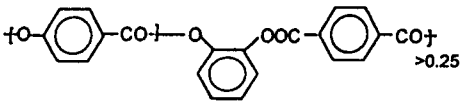
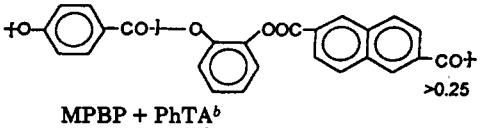


Figure 3. Carbonyl region of the C^{13} NMR spectrum of polymer I-4.

The homopolymer had a mesophase range of 140 °C. It is important to note that the homopolymer of PhHQ with PhTA had also a mesophase range of 74 °C considering the calculated crystal-to-nematic transition at 158 °C and the nematic-to-isotropic transition at 231 °C, which was experimentally observed. It also did not exhibit a T_m in the DSC thermogram because of its amorphous nature or glassy state.[2] The observed high mesophase range of polymer I-4 may be attributed to the long rigid 4,4′-biphenylene units in this polymer.

The homopolymer of DPBP with PhTA, I-5, showed neither a melting endotherm, T_m, nor an isotropition transition, T_i, in the DSC thermogram. However, it had a T_f at 200 °C and a T_i at 280 °C as determined with the polarizing light microscope studies. The absence of a melting endotherm, T_m, and the presence of a T_g clearly demonstrated that this polymer was amorphous. In

Table III. List of Other Fully Aromatic Thermotropic Polyesters Having Solubility in $CHCl_3$ at Room Temperature

polymer no.	polymer structure	ref
1		13
2		14
3		14
4		14
5		4
6		*a*
7		17
8		17
9		17
10		15
11		15
12		16
13		18
14		19
15		19
16	MPBP + PhTA[b]	this study
17	DPBP + PhTa[b]	this study

[a] The solubility of this polymer has been investigated in both dichloroacetic acid and dioxane.[26] Its solubility in chloforom (0.2 g/dL) has also been investigated in our laboratory. [b] For polymer structure, see Introduction.

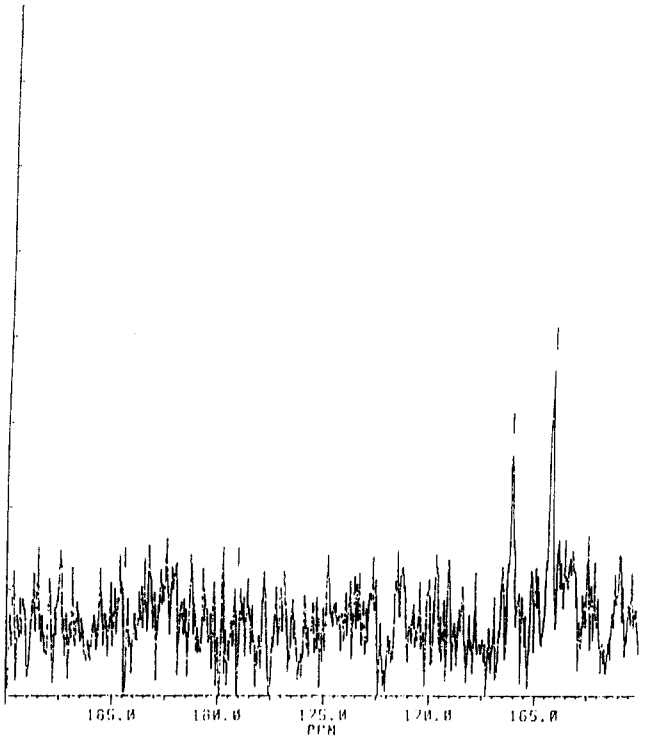


Figure 4. Carbonyl region of the C^{13} NMR spectrum of polymer I-5.

contrast, the homopolymer of DPBP with TA[20] had a much higher crystallinity, a higher T_m, and a higher T_i than those properties of the homopolymer of DPBP with PhTA. The amorphous nature, low T_f, and low T_i of this polymer were expected because PhTA has an asymmetrical structure containing a single phenyl group which serves a dual role in the suppression of the crystallinity and T_f of this homopolymer. The first role is due to its large-size steric hindrance, and the second one is due to the random head-to-head or head-to-tail arrangements of this group in consecutive repeating units along the polymer chain, which is termed the "internal copolymerization effect". Both of these effects can severely disrupt the packing of the polymer chain, resulting in an amorphous sample having a low T_f value. The random head-to-head and head-to-tail arrangements of the phenyl group in PhTA were also confirmed with C^{13} NMR spectroscopy. Figure 4 shows the C^{13} NMR spectrum of the carbonyl carbon region of this homopolyester. The carbonyl carbons of the polymer gave rise to two distinct resonances covering a total chemical shift range of 2.5 ppm, as expected. The resonances of carbonyl carbons from the chain ends were not detected for this sample because of its higher molecular weight than that of polymer I-4. The H^1 NMR spectrum of this polymer also appeared broad and unstructured, except that the six hydrogens of the DPBP unit showed clearly a singlet at 8.1 ppm. This homopolymer had a mesophase range of 80 °C, which was essentially comparable to that of the homopolymer of PhHQ with PhTA.

The transmitted light intensity scan of a thin film of polymer I-5 as a function of temperature at a heating rate of 2 °C/min exhibited a T_g at 135 °C, a T_m at 195 °C, and a T_i at 278 °C, as shown in Figure 5. The T_m and T_i transitions for this polymer were also confirmed with the polarizing light microscope studies. It is worth mentioning that light transmission study is a valuable technique for those thermotropic polyesters whose DSC thermograms give very little or no information regarding the formation of the LC phase and nematic-to-isotropic transition.[27]

The homopolymer of BND with PhTA, I-6, showed only a T_g at 145 °C in the DSC thermograms. It did not exhibit

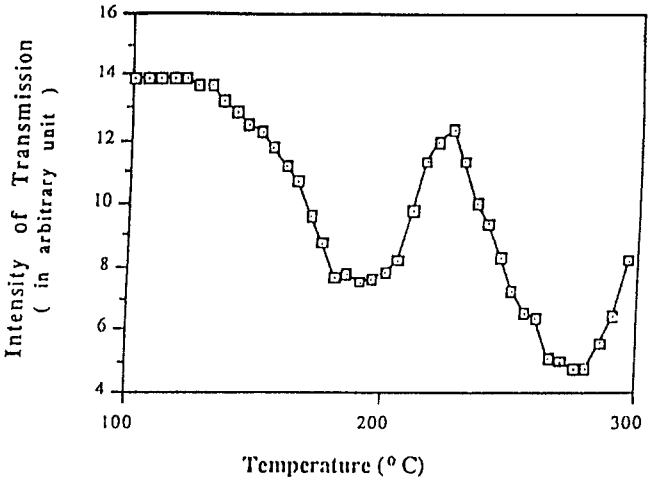


Figure 5. Transmitted light intensity as a function of temperature for polymer I-5 (heating rate 2 °C/min).

a melting endotherm, similar to polymer I-5, but had a fusion temperature, T_f, at 255 °C. The T_f value of this polymer is much lower than the T_m of the homopolymer with TA[26] which presumably arises because of both the random arrangements of the pendant phenyl group in PhTA, giving rise to an internal copolymerization effect and steric effect. The same homopolymer, prepared from the solution polycondensation reaction in diphenyl ether, had a T_g at 183 °C and a T_f at 243 °C as reported by Hohlweg and co-workers.[26] These differences in thermal transitions may be attributed to the different thermal histories of the polymer, as prepared by melt polycondensation vs solution polycondensation reaction.

All of the substituted homopolymers in this study showed glass transition temperatures, T_g, in the range of 133–151 °C, which were higher than those (108–122 °C) of disubstituted poly(*p*-phenylene terephthalates).[2] Furthermore, monosubstituted poly(*p*-phenylene terephthalates) had higher T_g values (130–220 °C) than those of disubstituted polymers.[2] The T_g is, generally, dependent on the kind of substituent present in a given polymer.

All of the homopolyesters listed in Table IV formed turbid melts that exhibited strong stir opalescence. This property was taken as the first indication of their liquid crystalline behavior. For further characterization of their melt morphology, the homopolyesters were evaluated by visual observations on a polarizing light microscope. Each of the polymers exhibited a typical nematic appearance with either the so-called polished marble texture or a threaded texture depending on the thickness of the sample. In contrast, the homopolymer of 4,4′-biphenol with BrTA formed a fan-shaped texture indicative of a smectic phase at or above its T_m, 270 °C, as reported by Heitz and coworkers.[28]

The thermal stabilities of all of the thermotropic polyesters were determined in nitrogen by TGA, and the results obtained are summarized in Table IV. A typical TGA plot is shown in Figure 6. The thermal stability limit, which is taken as the temperature at which a 5% weight loss occurred, varied from 445 to 485 °C in nitrogen, indicating that all of the polyesters had good thermal stabilities for melt processing at elevated temperatures. Hatke and co-workers[4] reported that the thermal stability of the Vectra family of copolyesters under identical conditions was in the range of 490–500 °C. Furthermore, Jackson[3] reported that a methyl or chloro substituent attached to a hydroquinone moiety in a LC aromatic polyester decreased the thermal oxidative stability of the polyester; however, the substituent permitted greater

Table IV. Thermal Properties and Thermal Stability of Homopolyesters

polymer no.	monomer[a]	T_g (°C)	T_m[b] (°C)	T_f[c] (°C)	thermal (°C)	thermal stability	texture by optical microscopy
I-1	MPBP–BrTA	151		170		470	nematic
I-2	DPBP–BrTA	139	332			473	nematic
I-3	BND–BrTA	144	351			445	nematic
I-4	MPBP–PhTA	133		150	290	450	nematic
I-5	DPBP–PhTA	147		200[c]	280[d,e]	485	nematic
I-6	BND–PhTA	145		255		463	nematic

[a] See footnote *a* in Table I for monomer identification. [b] The crystalline melting transition, T_m, and isotropization temperature, T_i, were determined from the first heating cycle of the DSC thermogram and aso verified by polarizing light microscopy studies. [c] The fusion temperature, T_f, was determined from the temperature of onset of flow as observed on a hot-plat melting point apparatus and verified with a polarizing light microscope on observation of a typical nematic texture on the edge, the thinnest part of the sample. [d] The isotropization temperature, T_i, was determined in the hot-plate melting point apparatus at the temperature where stir opalescence was no longer observed and also verified by PLM studies. [e] Transition temperatures were also determined with the transmitted light intensity scan as a function of temperature. [f] Thermal stability,, the temperature (°C) at which a 5% weight loss occurred, was determined from TGA measurement in nitrogen at a heating rate of 20 °C/min.

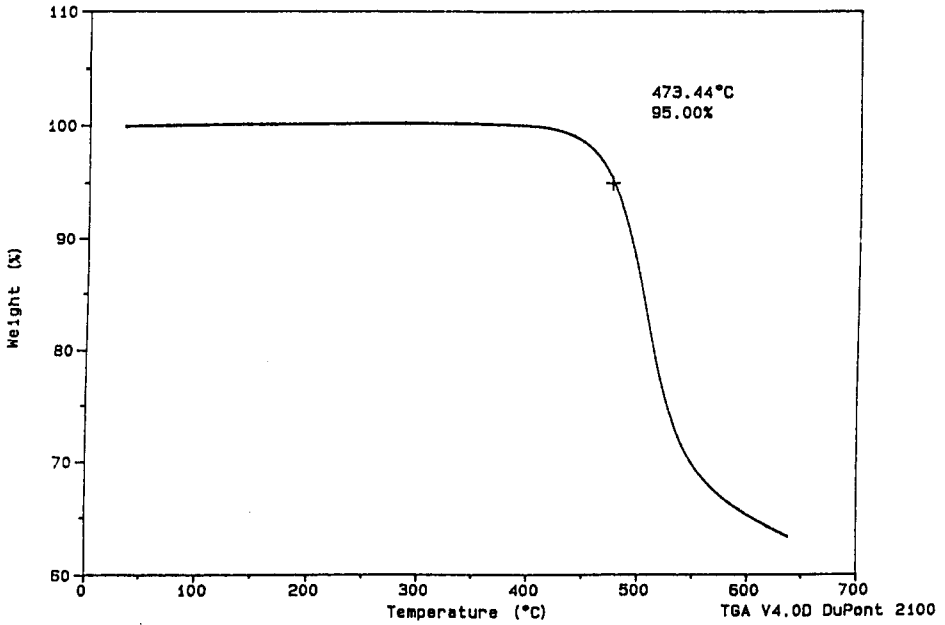


Figure 6. Thermogravimetric analysis (TGA) of polymer I-2 in nitrogen.

chemical resistance of a shaped object to be obtained by heat treatment in air at 300 °C. At 300 °C in air, the hydroquinone polyesters containing phenyl or *tert*-butyl substituents were the most stable. These results are in agreement with those of the polyesters in this study.

Conclusion

Fully aromatic, thermotropic polyesters, in general, have high melting transitions, T_m, and no solubility in common organic solvents because of their extended rigid structures and low melting entropies. To overcome these problems, a series of homopolyesters of this class of polymers derived from either phenyl-substituted biphenols or 1,1′-binaphthyl-4,4′-diol and 2-bromoterephthalic acid or 2-phenylterephthalic acid were prepared by the melt polycondensation reaction and characterized for their thermotropic behavior by a variety of experimental techniques.

The homopolymers of MPBP and DPBP with PhTA (I-4, and I-5, respectively) had solubilities in common organic solvents including chloroform, methylene chloride, and dioxane. The solubility of these polyesters may be attributed to the presence of a bulky substituent(s), a phenyl group, in each of the aromatic diol and diacid moieties.

All of the substituted polyesters had either lower T_m (332-351 °C) or lower T_f (150–255 °C) values than those of the respective unsubstituted homopolymers. The homopolymer of MPBP with PhTA, I-4, formed a nematic phase at or above 150 °C and showed a T_i at 290 °C, as determined from both the DSC and PLM studies. That of DPBP with PhTA, I-5, also formed a nematic phase at or above 200 °C and also exhibited a T_i at 280 °C, as determined from both the PLM and LTI studies. Other homopolyesters formed nematic LC phases at or above their T_m/T_f values which persisted up to 400 °C. They had also high thermal stabilities in the temperature range of 445–485 °C in nitrogen.

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