

Synthesis and Thermal Behavior of Thermotropic Terpolymers Based on 8-(3-Hydroxyphenyl)octanoic Acid, 2,6-Naphthalenedicarboxylic Acid, and Substituted Hydroquinones

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Received 30 September 1999; accepted 11 April 2000

ABSTRACT: Aromatic–aliphatic thermotropic liquid crystalline terpolyesters derived from 2,6-naphthalenedicarboxylic acid, hydroquinones, and 8-(3-hydroxyphenyl)octanoic acid (HPOA), a monomer with built-in kink and flexible moieties, were prepared by a melt polycondensation reaction. These polymers were characterized for their thermotropic liquid crystalline properties. The effect of variation in the composition of the polyester on the liquid crystalline behavior and thermal properties was also studied. Increasing the content of kinked units increased the amount of structural irregularity and decreased the isotropization temperature. The T_m and thermal stability of the polyesters were found to decrease with increase in the HPOA content. The formation of the liquid crystalline phase was not prevented by the introduction of up to 40 mol % of HPOA in the copolyester. The effect of substituents on the thermal properties of the terpolyesters was also studied. Introduction of a phenyl substituent on the hydroquinone ring was found to lower the transition temperature compared to substituents such as methyl or methoxy. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1021–1029, 2001

Key words: liquid crystalline terpolyesters; synthesis; substituent effect; thermal behavior

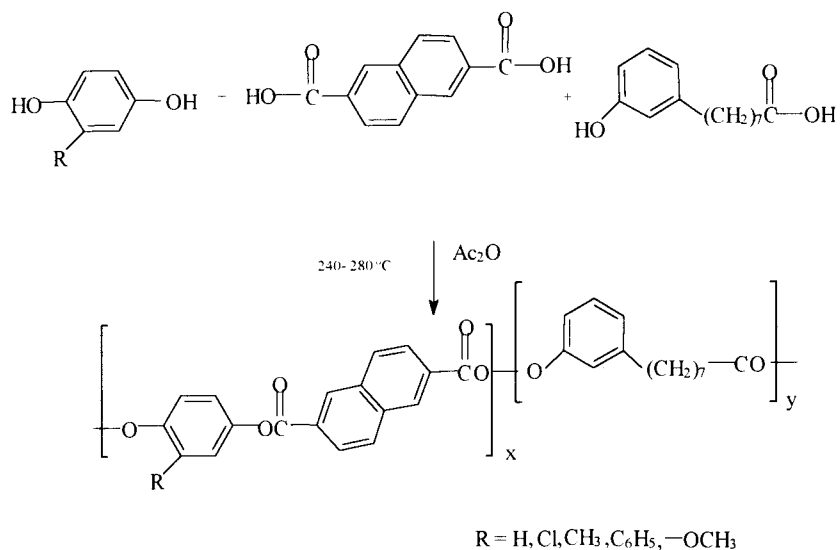
INTRODUCTION

Thermotropic main-chain liquid crystalline polymers have been intensively studied over the last two decades, primarily to extend the range of the physical properties of high-performance polymers such as thermal stability, processability, and mechanical properties.^{1–4} The thermal properties of these polymers can be altered through varying the backbone rigidity by judiciously choosing the linkage groups between the mesogens, by inserting nonlinear or kinked monomers or by introduc-

ing flexible spacers.^{5–8} In addition to many nonlinear monomers such as isophthalic acid, resorcinol, or *m*-hydroxybenzoic acid, many viable nonlinear monomers have been exploited to improve the tractability of liquid crystalline polymers.^{9–14} Previous work by Pillai et al.^{15,16} confirmed that poly(1,4-oxybenzoate-*co*-8-(3-oxyphe-nyl)octanoate prepared from *p*-hydroxybenzoic acid and a kinked monomer 8-(3-hydroxyphenyl)octanoic acid exhibits anisotropic properties in the range 200–400°C. This indicates that the core angle defect of 8-(3-hydroxyphenyl)octanoate along with the flexible spacers hinders the extensive molecular parallelism required for liquid crystalline polymers. Since introduction of a flexible aliphatic group in liquid crystalline poly-

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Journal of Applied Polymer Science, Vol. 82, 1021–1029 (2001)
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Scheme 1 Synthesis of terpolyesters.

ters reduces the polymer relaxation time and rigid kinks reduce the degree of extended-chain orientation, modification of copolyesters with these units can permit the generation of novel liquid crystalline polymers.

This study reports the synthesis and properties of copolyesters and terpolyesters based on 2,6-naphthalenedicarboxylic acid (NDA), hydroquinone (HQ), and 8-(3-hydroxyphenyl)octanoic acid (HPOA). Since introduction of lateral substituents decreases the mesophase transition temperature (T_m) by frustrating chain packing,¹⁷ the effect of substituted hydroquinones on the properties of these polyesters was studied. In addition to introducing flexible spacers, since HPOA introduces molecular kinks by virtue of its 1,3-connectivity on the aromatic ring, copolyesters based on 3-hydroxybenzoic acid and 2-hydroxybenzoic acids were also prepared for comparison.

EXPERIMENTAL

Materials

1,4-Dihydroxybenzene (HQ), 1,1'-biphenyl-2,5-diol, 97% (PhHQ), 1,4-dihydroxy-2-methylbenzene, 99% (MeHQ), 2-chloro-1,4-dihydroxybenzene, 85% (ClHQ), 1,4-dihydroxy-2-methoxybenzene, 98% (MeOHQ), NDA, 3-hydroxybenzoic acid (3-HBA), and 2-hydroxybenzoic acid (2-HBA) were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as received. HPOA was prepared according to a previously reported pro-

cedure.¹⁵ Dowtherm® is a mixture of dibenzylbenzenes obtained from Spectrochem (Mumbai, India).

Preparation of HPOA

HPOA was prepared by phase-transfer catalyzed permanganate oxidation of cardanol according to Pillai et al.¹⁵ Cardanol (1 mol) was acetylated using acetic anhydride (1.2 mol) and oxidation was performed in the presence of a phase-transfer agent, Aliquat 336, in methylene chloride at 40°C. The nonaqueous layer was extracted with 10% sodium hydroxide and heated to deacetylate the product. The alkaline extract was neutralized with concentrated HCl, extracted with ether, and dried. The product was recrystallized from water. The melting point was 62°C.

Synthesis of Polymers

In a typical polymerization, the requisite amount of NDA, HQ, and 3-HBA monomers with an excess of acetic anhydride were heated to reflux for 2 h. After this period, the temperature of the resulting slurry was gradually increased in steps of 240°C (60 min), 260°C (60 min), 280°C (30 min), and 280°C (60 min) under a vacuum (Scheme 1). The acetic acid formed both in the acetylation and acidolysis reactions was simultaneously distilled off. After polymerization, the melt was cooled to form a solid product which was ground into a fine powder. The polymer was successively washed with an isopropanol/acetone mixture to remove the residual monomers.

CHARACTERIZATION

Inherent viscosity values were determined using a Ubbelohde viscometer at room temperature for the polymer solutions (0.5 g/dL) in a mixed solvent of *p*-chlorophenol (PCP):1,1,2,2-tetrachloroethane (TCE) (60:40). Transition temperatures were determined using a TA Instruments differential scanning calorimeter Model 2010. DSC thermograms were recorded at a heating rate of 20°C/min under a nitrogen flow. Thermogravimetric analysis (TGA) was carried out with a DuPont TGA 950 attached to a Thermal Analyst 2000 system at a heating rate of 20°C/min in air or nitrogen. Identification of mesophases was performed by the observation of optical textures of polymer melts on a hot stage (Linkam 600) attached to a Nikon polarizing microscope. Wide-angle X-ray diffraction patterns were recorded on a Rigaku D_{max} powder diffractometer using Ni-filtered CuK α radiation.

RESULTS AND DISCUSSION

The solubility of the copolyesters was poor in common organic solvents. The best results were obtained in a *p*-chlorophenol:1,1,2,2-tetrachloroethane mixture, although in some instances, the polymers were not fully soluble. While HPOA-based copolyesters had an intrinsic viscosity in the range 0.4–0.5 dL/g, those that incorporated 3-HBA had intrinsic viscosity values in the range of 0.6–0.7 dL/g (Tables I, II, and V). As the replacement of HPOA with 3-HBA or 2-HBA increases the intrinsic viscosity values, it is difficult to ascertain that a low intrinsic viscosity value of an HPOA-based polyester indicates a low molecular weight. Since it has been reported that incorporation of angular units and flexible spacers interferes with the rodlike character of the molecules and decreases the chain rigidity, an HPOA-based copolyester can also decrease the rigidity of the polymer chain and, hence, the low intrinsic viscosity values at an equivalent molecular weight.¹⁷

The FTIR spectra showed the 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. The NMR measurements of these copolyesters were not feasible because samples prepared

by the above melt method were insoluble in common organic solvents.

Thermal Properties

The thermal stability of all copolyesters was determined by TGA. The thermal stability limit, which is taken as the temperature at which a 5% weight loss (T_5) occurred, varied from 354 to 305°C (Table III) when the HPOA content was increased from 10 to 40 mol %. The TGA trace of the terpolyester containing 20 mol % HPOA, Terpolyester 2, under nitrogen at 20°C/min is given in Figure 1. When the compositions of these copolymers were gradually changed by increasing the proportion of nonlinear 8-(3-oxyphenyl)octanoate units, the thermal stability of these polymers were found to decrease. Incorporation of greater amounts of flexible aliphatic segments inherently weakens the structure and promotes thermal degradation.

Rigid polyesters consisting of unsubstituted 1,4-phenylene groups are not melt-processable because they do not melt below the onset of thermal decomposition.^{18,19} The melting temperature can be lowered by intentionally reducing the rodlike character of the chain, either through introduction of units having noncollinear bonds or by copolymerization with flexible units. Compared to the copolymer, the random introduction of a third monomer to form a terpolymer introduces the disruption of chain regularity. This reduces the crystallinity and is effective in disrupting the chain packing when incorporated in small amounts. The DSC thermogram of the polyester prepared from NDA, HQ, and 20 mol % of HPOA (Terpolyester 2) is shown in Figure 2. It includes a crystal-to-nematic transition at about 220°C and a nematic-to-isotropic transition at 320°C in the first heating cycle, which was further confirmed by polarized light microscopic (PLM) studies. For characterization of the melt morphology, the polyesters were evaluated by visual observation on a hot stage by a PLM study. Terpolyester 2 exhibited a broad transition, during which they formed a birefringence liquid crystalline phase and an isotropic phase. They exhibited a characteristic nematic appearance with either a threaded or a schlieren texture depending on the nature of the comonomer above their respective melting transition (Fig. 3).

The mesophase transition temperature was also found to decrease with increase in the HPOA content (Table III). The DSC thermogram of the

Table I Composition of the Terpolyesters

Monomers Used		Terpolyesters Prepared		
Acronym	IUPAC Name	Acronym	IUPAC Name	Composition (% Mol Ratio)
Hydroquinone (HQ)	1,4-Dihydroxybenzene	Terpolyester 1	Poly[1,4-phenylene naphthalene-2,6-dicarboxylate-co-8-(3-oxyphenyl)-octanoate]	NDA : HQ : HPOA 45 : 45 : 10
2,6-NDA (NDA)	2,6-Naphthalene dicarboxylic acid	Terpolyester 2	Poly[1,4-phenylene naphthalene-2,6-dicarboxylate-co-8-(3-oxyphenyl)-octanoate]	NDA : HQ : HPOA 40 : 40 : 20
HPOA	8-(3-Hydroxyphenyl) octanoic acid	Terpolyester 3	Poly[1,4-phenylene naphthalene-2,6-dicarboxylate-co-8-(3-oxyphenyl)-octanoate]	NDA : HQ : HPOA 30 : 30 : 40
PhHQ	1,1'-Biphenyl-2,5-diol	Terpolyester 4	Poly[2-phenyl-1,4-phenylene naphthalene-2,6-dicarboxylate-co-8-(3-oxyphenyl)-octanoate]	NDA : PhHQ : HPOA 40 : 40 : 20
ClHQ	2-Chloro-1,4-Dihydroxybenzene	Terpolyester 5	Poly[2-chloro-1,4-phenylene naphthalene-2,6-dicarboxylate-co-8-(3-oxyphenyl)-octanoate]	NDA : ClHQ : HPOA 40 : 40 : 20
MeHQ	1,4-Dihydroxy-2-methylbenzene	Terpolyester 6	Poly[2-methyl 1,4-phenylene naphthalene-2,6-dicarboxylate-co-8-(3-oxyphenyl)-octanoate]	NDA : MeHQ : HPOA 40 : 40 : 20
MeOHQ	1,4-Dihydroxy-2-methoxybenzene	Terpolyester 7	Poly[2-methoxy-1,4-phenylene naphthalene 2,6-dicarboxylate-co-8-(3-oxyphenyl)-octanoate]	NDA : MeOHQ : HPOA 40 : 40 : 20
2-HBA	2-Hydroxybenzoic acid	Terpolyester 8	Poly[1,4-phenylene naphthalene-2,6-dicarboxylate-co-3-oxybenzoate]	NDA : HQ : 3-HBA 45 : 45 : 10
3-HBA	3-Hydroxybenzoic acid	Terpolyester 9	Poly[1,4-phenylene naphthalene-2,6-dicarboxylate-co-3-oxybenzoate]	NDA : HQ : 3-HBA 40 : 40 : 20
		Terpolyester 10	Poly[1,4-phenylene naphthalene-2,6-dicarboxylate-co-3-oxybenzoate]	NDA : HQ : 3-HBA 30 : 30 : 40

Table II Synthesis of Terpolyesters

Polyester	Polymerization Conditions: Temperature (°C)/Time (min)	Elemental Analysis (%)				Yield (%)	Inherent Viscosity (dL/g)	Solubility
		Calcd		Observed				
		C	H	C	H			
Terpolyester 1	240/60, 260/60(N), 280/30(D), 280/60(V)	67.39	3.68	67.42	3.63	88	0.4	sol. PCP/TCE
Terpolyester 2	240/60, 260/60(N), 280/30(D), 280/60(V)	67.87	3.36	68.01	3.39	80	0.5	sol. PCP/TCE
Terpolyester 3	240/6, 260/60(N), 280/30(D), 280/60(V)	68.82	5.02	69.03	5.23	70	0.5	sol. PCP/TCE

PCP, 4-chlorophenol; TCE, 1,1,2,2-tetrachloroethane; N, nitrogen gas purge; V, vacuum; D, Dowtherm®.

terpolyester with 50 mol % HPOA, showed a T_g , but neither a crystal-to-liquid crystalline transition, T_m , nor an isotropization temperature, T_i . The absence of a T_m and the presence of a T_g clearly indicate that the polymer is noncrystalline. The nonlinear monomer with flexible segments decreases the persistence length of the polymer chain and makes extended close packing and crystallization difficult. Moreover, the presence of flexible spacers can result in a dilution of the aromatic number density, which, in turn, results in a lower melting temperature.²⁰ Consequently, the T_m decreases when the concentration of the nonlinear monomer is increased.

The second series of polymers, Terpolyesters 4–7, prepared in this study are listed in Table IV. All polymers contained therein have essentially the same chemical structure but differ only in the type of the substituent on the hydroquinone ring. There are several reports on rigid copolyesters incorporating substituted HQ to control the transition temperature.^{21–24} It was suggested by earlier workers^{2,3} that substituents act to increase the interchain distance and hinder effective packing. Moreover, the random arrangement of a sub-

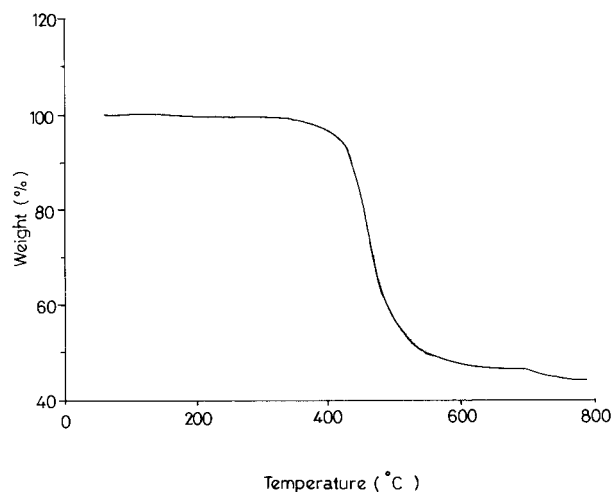
stituted monomer in both head-to-head and head-to-tail fashion along the polyester chain causes the melting temperature and isotropization temperature to be lower than is the decomposition temperature.²⁵

Introduction of a substituent on the hydroquinone moiety caused the melting temperature and isotropization temperature to be lower than the decomposition temperature. The DSC thermogram of Terpolyester 6, prepared from NDA, MeHQ, and 20 mol % HPOA, exhibits a rather complex DSC thermogram. It undergoes a glass transition at about 125°C and melts into a nematic phase at 250°C. The endothermic peak, which appears before the melting transition, seems to be related to a crystal–crystal transition. Upon copolymerization with ClHQ instead of

Table III Thermal Properties of Polyesters Containing Different Mol Percent of HPOA in NDA/HQ/HPOA Copolyester

Polyester	T_5 (°C)	T_g (°C)	T_m (°C)	T_i (°C)
Terpolyester 1	354	—	239	380 ^a
Terpolyester 2	344	110	223	337
Terpolyester 3	305	100	200	280

^a Observed with fast heating rate.

**Figure 1** TGA trace of the Terpolyester 2 (20°C/min in nitrogen).

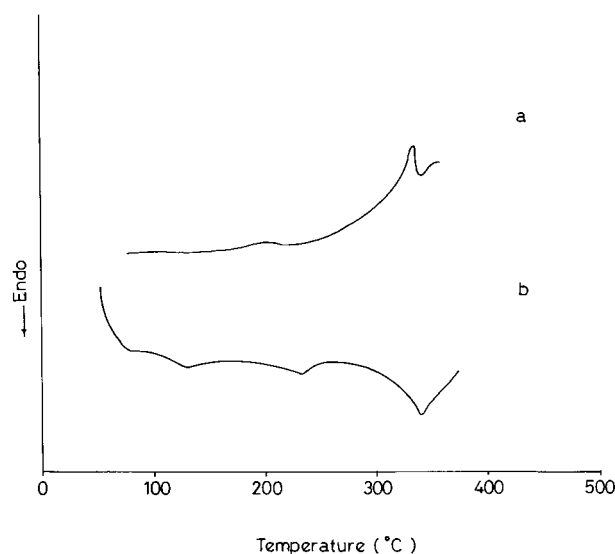


Figure 2 DSC trace of the Terpolyester 2 (20°C/min in nitrogen): (a) heating; (b) cooling.

MeHQ, Terpolyester 5, the transition temperature associated with the crystalline melting decreased to about 22°C due to disturbance in chain packing. The large electronegativity, low polarizability, and Cl—Cl repulsion among the polymer chains decreases the phase transition.²⁶

The mesophasic transition temperature was further decreased to 204°C when a bulky phenyl group was introduced into the hydroquinone moiety. On melting, it formed a liquid crystalline phase, but there appeared to be no development of crystallinity as observed by the absence of a melting endotherm on the second heating cycle. In the first cooling cycle, it showed only a very broad and

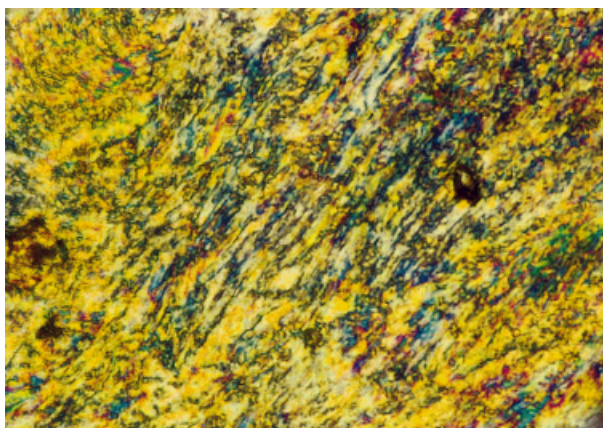


Figure 3 PLM study of Terpolyester 2 ($\times 250$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table IV Thermal Properties of NDA and HPOA with Substituted HQ

Polyester	T_5 (°C)	T_m (°C)	T_i (°C)
Terpolyester 4	357 (358)	204	> 400
Terpolyester 5	356 (361)	223	337
Terpolyester 6	384 (356)	—	—
Terpolyester 7	409 (354)	260	320

Values given in parentheses are obtained for the polyesters without HPOA.

small crystallization exotherm. In the second cycle, no such exotherms were observed, presumably because the bulky phenyl group on the hydroquinone ring and the nonlinear HPOA units greatly reduce the rate of crystallization from the melt state. In contrast, the copolymer with methyl-substituted hydroquinone exhibited neither a crystal-to-nematic nor a nematic-to-isotropic transition in the DSC thermogram, probably due to its noncrystalline nature. The increased T_m value of methoxy-substituted hydroquinone may be due to an increase in the intermolecular force of attraction. Hence, MeHQ-based copolyesters exhibit an increased T_m and thermal stability. The thermal stability of these polyesters was found to be comparable with those of the copolyesters containing HQ. But the presence of these unsymmetrically substituted hydroquinones hinders the three-dimensional packing of the polymer chain and these copolyesters exhibit only a low degree of crystallinity.

In the present study, when HPOA was replaced by 3-HBA, Terpolyesters 8–10, the melting point of the terpolyesters as determined by DSC were usually much less well defined than were those of the terpolyesters based on HPOA with broad and small melting endotherms. This is understandable because these copolyesters have a low degree of crystallinity or are completely amorphous. Introduction of an increasing amount of 3-HBA units decreases the chain stiffness and linearity, eventually resulting in a polymer that melts into an isotropic state. The thermal properties of these polymers are given in Table V. The terpolyesters based on 3-HBA, Terpolyesters 8–10, are able to maintain the rigidity of the polymer chain compared to HPOA-based polyesters having long alkyl spacers, Terpolyesters 1–3. But its presence induces a bend along the polymer chain, destroying their linearity. This nonlinearity is expected to reduce the parallel association of the polymer

Table V Properties of NDA/HQ/3-HBA Terpolyesters Containing Different Mol Percent of 3-HBA

Polyester	Inherent Viscosity (dL/g)	T_g (°C)	T_g (°C)	T_m (°C)	T_i (°C)
Terpolyester 8	—	332	—	210	360
Terpolyester 9	0.6	337	90	240	310
Terpolyester 10	0.7	370	85	—	320

chain in the nematic state and thereby decreases the stability of the mesophase. In contrast to HPOA-based polyesters, the thermal stability of the polymers with 3-HBA were found to increase with increase in the hydroxybenzoic acid content due to the formation of a blocklike sequence of 3-oxybenzoate.²⁷

Many viable nonlinear monomers have been exploited to improve the tractability of liquid crystalline polymers, but the core angle subtending the exocyclic bond in these kinked monomers dictate how much the backbone deviates from linearity. When NDA and MeOHQ were terpolymerized with 20 mol % of another kinked monomer such as 2-HBA, for the same composition, the transition temperatures were found to decrease to 240 and 300°C. The isotropization temperature of the polyester with a high proportion of *o*-linked units could be determined only by a polarizing microscope because the endotherm of isotropization was very broad and could not be determined precisely. The isotropic transition was also accompanied by thermal decomposition. The copolyesters with more than 25 mol % of 2-HBA were amorphous, and during slow cooling, the nematic texture remained in the nematic solid glasses at room temperature. Although an increase in the content of 2-oxybenzoate units decreased the melting transition, it decreased the mesophasic range. Replacement of angular units with rodlike hydroxybenzoate units causes an increase in the melting temperature, indicating that the effect of increased chain rigidity is more important than is randomization.

The DSC thermogram of the terpolymer prepared from NDA, MeOHQ, and 20 mol % of 4-hydroxybenzoic acid contained neither a T_m nor T_i in the heating cycle. The DSC trace exhibited only a glass transition, implying that the polymer is amorphous in nature. However, it showed a liquid crystalline phase around 270°C that then transformed into an isotropic phase around 390°C. The T_m and T_i values were determined by PLM studies. The PLM studies of the copolyester showed birefringence even at ambient temperature, indi-

cating a possible frozen LC phase. The temperatures of fusion of these terpolyesters were higher than the T_m values of the terpolymers of HPOA but lower than those of the copolymer of NDA and HQ. These results are in accordance with those of Kricheldorf and Erxleben²⁸ in that the bond angle around the central atom of a nonlinear monomer rather than its size is an important factor in determining the critical amount of each of these monomers. The isotropization temperature was found to decrease with decrease in the core angle.

The X-ray diffraction powder pattern of all the polymers indicates that they are semicrystalline in nature. The linear offset motion of 2,6-naphthalene units, together with the random incorporation of kink units, provides a disturbance in chain packing and, hence, lowers its crystallinity. The WAXD analysis of a terpolymer containing different mol percents of HPOA is shown in Fig-

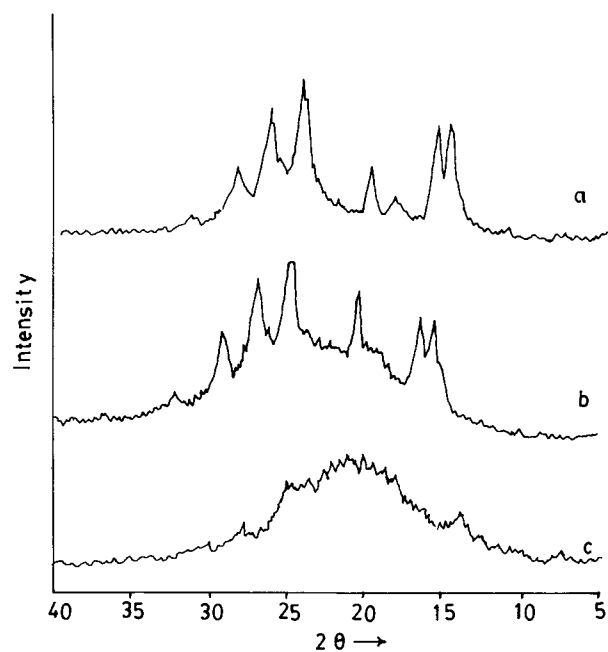


Figure 4 WAXD pattern of the NDA/HQ/HPOA terpolyesters: (a) Terpolyester 1; (b) Terpolyester 2; (c) Terpolyester 3.

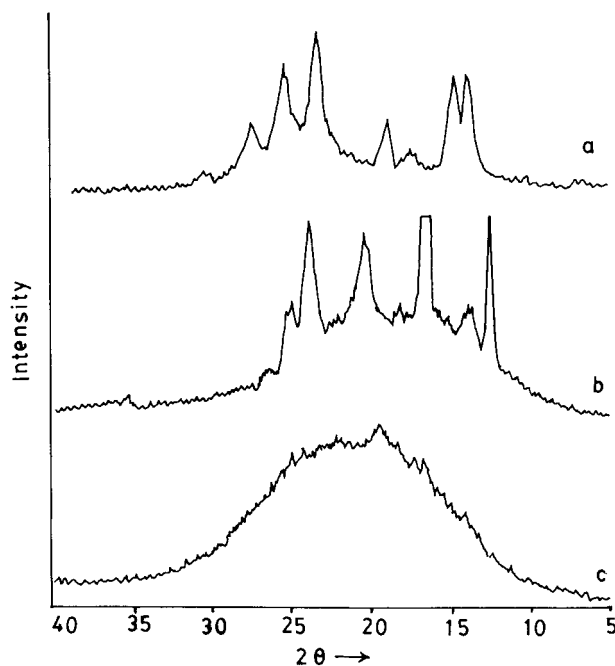


Figure 5 WAXD pattern of the NDA/HQ/3-HBA terpolyesters: (a) Terpolyester 8, (b) Terpolyester 9; (c) Terpolyester 10.

ure 4. The homopolymer of NDA and HQ showed diffraction peaks at $2\theta = 18.4, 25.5,$ and 27.5° and some other small peaks. The diffraction peaks of the copolyesters containing 10% HPOA were almost similar to that of the copolymer. But for terpolyesters with an HPOA content of 20–40 mol %, the peaks were found to shift slightly and a peak appeared at $2\theta = 20^\circ$. The peaks gradually became weak as the amount of HPOA was increased. The broadening of the peaks with an increase in HPOA content indicated a decrease in the crystallinity with an increase in the kink with flexible groups. This is because the length of the NDA/HQ chain blocks becomes shorter with increase of the HPOA unit. The kinky unit not only affected the degree of crystallinity but also the perfection of the crystal lattice by reducing the periodicity along the repeat units. A similar behavior was reported by Erdemir et al. for copolyesters prepared from 4-hydroxybenzoic acid, HQ, and isophthalic acid.²⁹

Careful inspection of the WAXD diagram (Fig. 5) of the 3-HBA-based terpolyester shows that incorporation 3-HBA results in changes in the diffraction pattern. Some reflections found in the powder diagram of the polymer were found to be less intense or missing in the WAXD diagram of the copolyester containing 20 mol % 3-HBA. The

presence of some reflection, either sharper or stronger, indicates that a different type of ordered structures are present in the sample, depending upon the composition. The percentage crystallinity value showed a decrease from 58 to 31% with an increase of 3-HBA from 10 to 20 mol % in these terpolyesters. As the mol % of 3-HBA increased to 50, the WAXD pattern showed a broad peak, indicating lowering of the periodicity along the chains, resulting in reduced crystallinity.

CONCLUSIONS

Aromatic–aliphatic main-chain liquid crystalline terpolyesters derived from various aromatic diols with 2,6-NDA and HPOA were prepared and characterized for their liquid crystalline properties. The polyesters exhibit thermotropic nematic phases as judged by their optical textures observed through a polarizing microscope. The formation of a liquid crystalline phase was not prevented by the introduction of up to 40 mol % of HPOA and the copolymer exhibited mesophases at relatively low temperatures. The T_m and thermal stability of the polyesters were found to decrease with increase in the HPOA content. An increase in the kinked monomer content also caused a loss of crystallinity of the copolyesters. Furthermore, the inclusion of a kinked monomer with flexible units is more effective than that of a kinked monomer in decreasing the melting transition. Introduction of a phenyl substituent on the hydroquinone ring was found to lower the transition temperature compared to substituents such as methyl or methoxy.

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