

Main-Chain Liquid-Crystalline Polymers Containing Azobenzene Mesogen Having Long Lateral Aliphatic Side Chain: Effect of Copolymerization on Thermal and Phase Behaviors

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ABSTRACT: Homo- and copolyesters of derivatives of hydroxyazobenzenecarboxylic acid with various percentage compositions of *m*-hydroxy benzoic acid (*m*-HBA)/*p*-hydroxy benzoic acid (*p*-HBA) were synthesized and characterized. The properties of the copolyesters were compared with their corresponding homopolyesters. The solubility of the copolyesters with *m*-HBA increased because of the decrease in the rigidity of the polymer chain attributed to the introduction of nonlinear molecules, whereas the solubilities of the copolyesters with *p*-HBA changed only slightly compared to their corresponding homopolyesters. Thermal and phase behaviors of the polymers were characterized by TGA, DSC, and polarizing light microscopy (PLM) methods. Above 30% composition of *m*-HBA, the thermal stability of

the copolyesters with *m*-HBA decreased compared to that of the homopolyester **P1**, whereas the copolyesters of *p*-HBA possessed greater thermal stability than that of their homopolyesters at all compositions. The introduction of the long, flexible alkyl side chain laterally to the backbone of the azobenzene moiety drastically reduced the transition temperature of the homopolyester, but without destroying the mesophase. The effect of copolymerization on liquid-crystalline behavior and transition temperature of the copolyesters was discussed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1976–1982, 2004

Key words: liquid-crystalline polymers (LCP); copolymerization; viscosity; thermal properties; chain

INTRODUCTION

Liquid-crystalline polymers (LCPs) containing azobenzene mesogen are interesting because they combine the properties of anisotropy with photoresponsive behavior in a single molecule. Although the rigidity and the planarity of azobenzene group provide anisotropy of shape required for LC property, it has structural features that can be modified to incorporate property profiles for photoresponsive behavior. Thus, azobenzene-based LCPs have a number of applications in areas such as LC displays, nonlinear optics (NLO) materials, and information-storage devices.^{1–3} It was shown in earlier works^{4–8} that the transition temperature of the polymer could be lowered by introducing long flexible alkyl side chain laterally to the backbone of azobenzene moiety.^{4–8} The polymer also showed better solubility in common organic solvents. It was also observed that the lateral side chain induces polymorphic behavior and the stabilization of the mesophase was ascribed to the alignment of the long alkyl side chain parallel to the long axis of the mole-

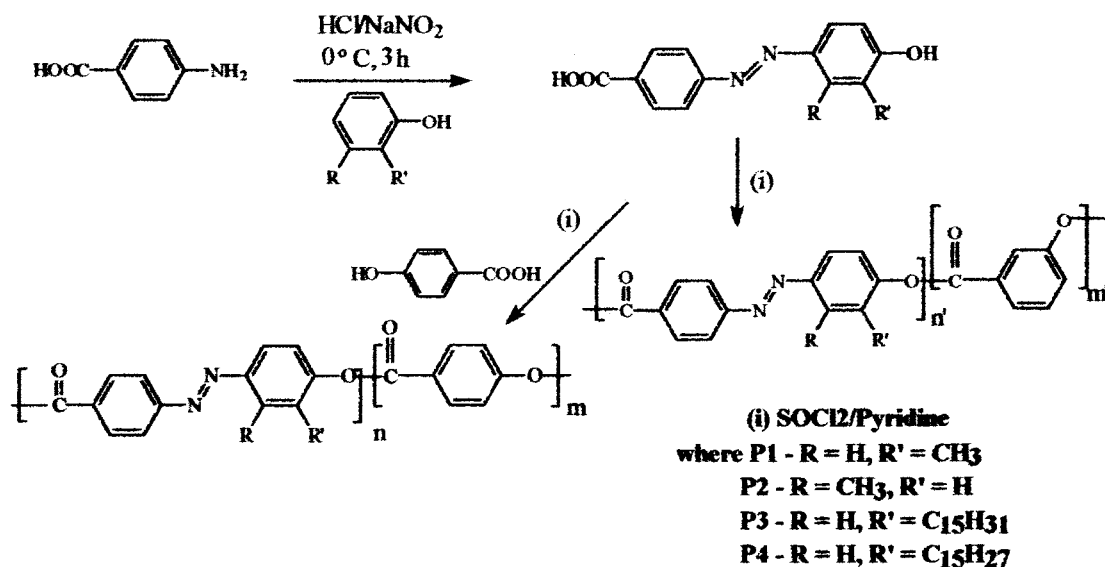
cule; however, the polymers were thermally labile and could not be poled for studies on NLO application. The method of copolymerization with aromatic hydroxy acids such as *p*-hydroxy benzoic acid (*p*-HBA)/*m*-hydroxy benzoic acid (*m*-HBA) was adopted to enhance the thermal stability of the azobenzene polymers. The results on the synthesis and characterization of eight main chain copolyesters having azobenzene mesogens with and without methyl/C₁₅ aliphatic lateral side chain attached to the azobenzene moiety are presented in this article.

EXPERIMENTAL

Materials

p-Amino benzoic acid was obtained from Aldrich Chemicals (Milwaukee, WI), sodium nitrite and thionyl chloride from S.D. Fine Chemicals (Mumbai, India), and cresols from E-Merck (Bombay, India). Cardanol was obtained by distillation of cashew nutshell liquid (CNSL; 228–235°C, at 3.5 mm Hg). Hydroxy benzoic acids were obtained from Fluka Chemicals (Buchs, Switzerland) and pyridine from Ranbaxy Laboratories. Solvents were of reagent grade and purified by standard methods.

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Scheme 1 Synthesis and structure of monomers and polymers.

Preparation of monomers

The synthesis of the monomers was carried out according to the modified procedure of Pansare et al.¹⁰ and Saminathan et al.^{4,5} and is represented in **Scheme 1**.

4-[(4-Hydroxy-3-methylphenyl)azo]benzoic acid (1). Yield 81%, red crystals, MW 256.2, m.p. 245–246°C; IR (KBr, cm⁻¹): 3525, 3374 (Ar—OH), 1695 (Ar—COOH), 1595, 1545 (Ar—C=C-), 2990, 1437, 1364 (—CH₃), 1140 (—N=N-). ¹H-NMR (DMSO-*d*₆): δ 6.8–8.3 (7H, m, Ar), 2.1–2.4 (3H, s, —CH₃) ppm.

4-[(4-Hydroxy-2-methylphenyl)azo]benzoic acid (2). Yield 83%, red crystals, MW 256.2, m.p. 240–241°C; IR (KBr, cm⁻¹): 3240 (Ar—OH), 1680 (Ar—COOH), 1600 (Ar—C=C-), 2980, 1480, 1380 (—CH₃), 1115 (—N=N-). ¹H-NMR (DMSO-*d*₆): δ 6.6–8.3 (7H, m, Ar), 2.6–2.8 (3H, s, —CH₃) ppm.

4-[(4-Hydroxy-2-pentadecylphenyl)azo]benzoic acid (3). Yield 81%, red/orange powder, MW 452.6, m.p. 151–152°C; IR (KBr, cm⁻¹): 3320 (Ar—OH), 2927, 2855 (—CH₂-), 1690 (Ar—COOH), 1603, 1575, 1545 (Ar—C=C-), 1153 (—N=N-). ¹H-NMR (acetone-*d*₆): δ 0.7–3.4 (31H, m, —CH₂-), 6.7–8.5 (7H, m, Ar) ppm.

4-[(4-Hydroxy-2-pentadecadienyl)azo]benzoic acid (4). Yield 80%, red/orange powder, MW 449.6, m.p. 134–135°C; IR (KBr, cm⁻¹): 3290 (Ar—OH), 2930, 2850 (—CH₂-), 1690 (Ar—COOH), 1600, 1580 (Ar—C=C-), 3020, 780 (*cis*-CH=CH-), 1155 (—N=N-).

Synthesis of polymers

Polymerization reactions were carried out using thionylchloride and pyridine at room temperature. The polymers were precipitated in methanol, washed thor-

oughly with acetone, and dried in vacuum for 12 h at 60°C. Synthesis of the polymers is given in **Scheme 1**.

A typical procedure for the synthesis of the polymers is given below:

Thionylchloride (1 mL) was charged to a round-bottom flask fitted with a guard tube and kept in an ice bath. Pyridine (2 mL) was added dropwise with constant stirring and stirred for another 30 min. Appropriate amounts of monomers were taken and dissolved in pyridine. This solution was slowly added dropwise to the pyridine-thionyl chloride mixture. The contents were stirred for 40 h at room temperature. The polymer was precipitated by addition of methanol and purified by Soxhlet extraction.

Copolymer of p-HBA and 4-[(4-hydroxy-3-methylphenyl)azo]benzoic acid (P1a). Yield 80%, orange powder; FTIR (KBr, cm⁻¹): 1742 (ArCOOAr), 2960, 1420, 1500 (—CH₃), 1600 (Ar—C=C-), 1160 (—N=N-); viscosity: 0.48 dL/g.

Copolymer of p-HBA and 4-[(4-hydroxy-2-methylphenyl)azo]benzoic acid (P2a). Yield 60%, orange powder; FTIR (KBr, cm⁻¹): 1748 (ArCOOAr), 2960, 1418 (—CH₃), 1607, 1512 (Ar—C=C-), 1182 (—N=N-); viscosity: 0.59 dL/g.

Copolymer of p-HBA and 4-[(4-hydroxy-2-pentadecylphenyl)azo]benzoic acid (P3a). Yield 50%, orange powder; FTIR (KBr, cm⁻¹): 1742 (ArCOOAr), 2854, 1470, 1425 (—CH₃), 1600, 1519 (Ar—C=C-), 1169 (—N=N-); viscosity: 0.48 dL/g, UV-vis (λ_{max}): 360 nm.

Copolymer of 4-HBA and 4-[(4-hydroxy-2-pentadecadienyl)azo]benzoic acid (P4a). Yield 50%, brown/orange powder; FTIR (KBr, cm⁻¹): 1754 (ArCOOAr), 2927, 2862, 1413 (—CH₂-), 1602, 1512 (Ar—C=C-), 1160 (—N=N-); viscosity: 0.48 dL/g, UV-vis (λ_{max}): 360 nm.

TABLE I
Inherent Viscosities of the Polymers

Polymer	η_{inh} (dL/g)		
	Homopolymers	<i>p</i> -HBA	<i>m</i> -HBA
P1	0.606	0.48	0.795
P2	0.789	0.59	0.58
P3	0.505	0.52	0.629
P4	—	—	0.565

Copolymer of 3-HBA and 4-[(4-hydroxy-3-methylphenyl)-azo]benzoic acid (**P1b**). Yield 70%, orange powder; FTIR (KBr, cm^{-1}): 1754 (ArCOOAr), 2960, 1420, 1500 ($-\text{CH}_3$), 1610 (Ar—C=C-), 1155 ($-\text{N}=\text{N}-$); viscosity: 0.795 dL/g.

Copolymer of 3-HBA and 4-[(4-hydroxy-2-methylphenyl)-azo]benzoic acid (**P2b**). Yield 55%, orange powder; FTIR (KBr, cm^{-1}): 1734 (ArCOOAr), 2968, 1423 ($-\text{CH}_3$), 1610, 1503 (Ar—C=C-), 1177 ($-\text{N}=\text{N}-$); viscosity: 0.55 dL/g.

Copolymer of 3-HBA and 4-[(4-hydroxy-2-pentadecylphenyl)azo]benzoic acid (**P3b**). Yield 50%, orange powder; FTIR (KBr, cm^{-1}): 1738 (ArCOOAr), 2964, 1570, 1415 ($-\text{CH}_3$), 1610, 1539 (Ar—C=C-), 1158 ($-\text{N}=\text{N}-$); viscosity: 0.63 dL/g, UV-vis (λ_{max}): 360 nm.

Copolymer of 3-HBA and 4-[(4-hydroxy-2-pentadecadienyl)-azo]benzoic acid (**P4b**). Yield 55%, brown/orange powder; FTIR (KBr, cm^{-1}): 1736 (ArCOOAr), 2965, 2882, 1443 ($-\text{CH}_2-$), 1612, 1517 (Ar—C=C-), 1166 ($-\text{N}=\text{N}-$); viscosity: 0.57 dL/g, UV-vis (λ_{max}): 360 nm.

Characterization

The solid monomer dyes obtained were purified by column chromatography and recrystallized from the methanol–water mixture. The color of the monomers was red/orange, which is a characteristic feature of azobenzene compounds. The monomers obtained were characterized using spectral methods; the polymers were characterized by viscosity, thermal, and spectral methods. Viscosity measurements were done using a Ubbelohde viscometer (Cannon-Ubbelohde, State College, PA). UV-vis spectra of the films were measured on a Shimadzu model UV-2101PC spectrophotometer (Shimadzu, Kyoto, Japan). The FTIR spectrum of the polymer was taken using a Nicolet-Magna 560 spectrophotometer (Nicolet Analytical Instruments, Madison, WI). The ^1H - and ^{13}C -NMR spectra were recorded with a Bruker 300-MHz FTNMR spectrometer (Bruker Instruments, Billerica, MA). Tetramethylsilane was used for internal shift referencing in all cases. Sample tubes (5 mm o.d.) were used for the ^1H and 10 mm o.d. sample tubes for the ^{13}C -NMR spectra. Thermogravimetry analysis (TGA) was performed with Dupont 951 thermogravimetric analyzer

(Dupont, Boston, MA), and differential scanning calorimetry (DSC), using TA Instruments DSC 2010 (TA Instruments, New Castle, DE). Melting point determinations were done using Mel-Temp II apparatus. Optical polarized microscopic observations were done with a hot-stage polarized light microscope (PLM) using a Leitz-1350 heating stage (Leitz, Wetzlar, Germany) coupled with PLM. The samples were kept on the heating stage, which was mounted below the microscope, and thus the phase transitions were observed at different temperatures.

RESULTS AND DISCUSSION

Polymer structure

The polymer formation was ascertained by the ester carbonyl stretching vibrations at 1740–1750 cm^{-1} range in the FTIR spectrum. Simultaneously, the peaks at 3550–3300 cm^{-1} of the hydroxyl groups and peaks at 1700–1670 cm^{-1} of the carbonyl groups of monomers vanished or largely decreased on polyester formation. The $-\text{N}=\text{N}-$ stretching vibrations were observed at about 1150 cm^{-1} . In the case of polymer **P4**, the peaks at 3020 and 790 cm^{-1} , attributed to the unsaturation of the side chain, decreased largely, indicating the possibility of crosslinking. This was supported by the fact that polymer **P4** was insoluble in all the solvents tried. The UV-vis spectra of the polymers showed characteristic peaks at the azobenzene region (~ 360 nm) showing the presence of azobenzene groups. The inherent solution viscosities (η_{inh}) of the polymers were measured using a Ubbelohde suspended-level viscometer at 28°C using *N*-methyl-2-pyrrolidinone as solvent. Viscosities of polymers were in the range 0.5–1 dL/g. The viscosity values of the polymers are provided in Table I.

Variation of phase behavior with molecular weight on copolymers of *p*-HBA

Homopolyesters **P1** and **P2** and copolyesters **P1b** and **P2a** of different viscosities (molecular weights) were

TABLE II
Solubility of the Polymers

Polymer	Conc. H_2SO_4	CHCl_3	THF
P1	+	–	–
P2	+	–	–
P3	–	+	+
P4	–	–	–
P1B	+	+ / –	+ / –
P2B	+	+ / –	–
P3B	+	+	+
P4B	+	+ / –	+

+, soluble; –, insoluble; + / –, partially soluble.

TABLE III
 T_m Values of Homopolymer P1 and Its Copolymer P1b
 Containing Varying Amounts of *m*-HBA

	Polymer			
	P1	P1b 20%	P1b 30%	P1b 50%
T_m (°C)	253	228.2	226.9	221.7

synthesized and characterized using polarizing light microscopy (PLM) and DSC analysis. During the course of the polymerization reaction, a small portion of polymer sample was withdrawn and precipitated using 50 mL methanol. This was done at intervals of 15, 25, 30, 35, 40, and 45 h. The precipitates thus obtained were purified by Soxhlet extraction and dried at 60°C for 12 h and examined for their transition temperatures (T_m). From the results obtained it was found that T_m increases with the time of reaction and reaches a plateau after a particular time of reaction for each polymer. (Further studies were carried out with polymers that attained this plateau.) This can be explained as follows: the liquid-crystalline property is mainly attributed to the anisotropic orientation of molecular rigid units. This optimum rigidity is obtained at a particular range of molecular weight and further increases in molecular weight do not affect the packing order of the polymer chain. The T_m thus becomes independent of molecular weight after a particular value. Any increase in molecular weight after that time is ascertained by the increase in solution viscosity values.

Solubility studies

Synthesized homopolyesters and copolyesters containing *m*-HBA units were found to possess different solubilities. As expected, the decrease in the rigidity of the copolyester chain attributed to the nonlinear molecules (*m*-HBA) increased the solubility of the copolymer. The solubilities of the homopolyesters and copolyesters are compared for three solvents, as given in Table II. It was found that homopolymer **P4** is insoluble in all solvents tried, whereas its copolymer with

m-HBA (**P4b**) was found to be soluble in conc. H_2SO_4 and partially soluble in chloroform and THF. Polymers having the pentadecyl side chain were highly soluble in common solvents. Also, it was observed that the copolymers of *m*-HBA possessed better solubility than that of the corresponding homopolymers in all solvents tried. This can be easily explained: the decrease in rigidity of the main chain is attributed to the introduction of "kink" molecules. At the same time the solubility studies of copolymers of *p*-HBA revealed that the solubility of the copolymers of *p*-HBA does not change significantly compared to that of their homopolyesters, although there was a slight decrease in solubility for the copolymers.

Effects of copolymerization: copolymers of *m*-hba

Thermal and phase behavior studies

The effect of introducing *m*-HBA into the main chain of the homopolymer of **P1** and *p*-HBA into the main chain of the homopolymer of **P2** were studied. Polymers **P1** and **P2** differ, in structure, only in the position of their methyl groups. The homopolymer **P1** with methyl group *meta* to the azo group possesses a higher T_m (see Tables III and IV) when compared with that of the polymer **P2** with the methyl group in the *ortho* position to the azo group. Thus, we copolymerized polymer **P1** with *m*-HBA to obtain copolymer **P1b**, so that there was a considerable decrease in the T_m for the resulting copolymers. At the same time homopolymer **P2** with a low T_m compared to that of **P1** was copolymerized with *p*-HBA and the resulting copolymer **P2a** obtained was characterized; the results obtained are now discussed.

The TGA thermograms of homopolymer **P1** and its copolymers (**P1b**) with *m*-HBA are shown in Figure 1, which shows that the copolymers degrade in two steps, the first of which may be attributable to the azo-containing unit. The TGA curves of the polymers show that the thermal stability is only slightly affected because of the increase in percentage of *m*-HBA. In fact, the thermal stability of the copolymer with *m*-HBA composition above 30% decreased.

TABLE IV
 T_m Values of the Polymers^a

Polymer	T_m (°C)		
	Homopolymers	Copolymer: <i>m</i> -HBA 30%	Copolymer: <i>p</i> -HBA 30%
P1	K253Ndec > 250	K227Ndec > 300	K263Ndec > 320
P2	K230Ndec > 220	K170Ndec > 260	K249Ndec > 320
P3	K154Ndec > 260	K146Idec > 290	K260Ndec > 310
P4	K153Idec > 210	—	—

^a dec, decomposition; K, refers to the sort of crystal state of polymers; N, nematic; I, isotropic.

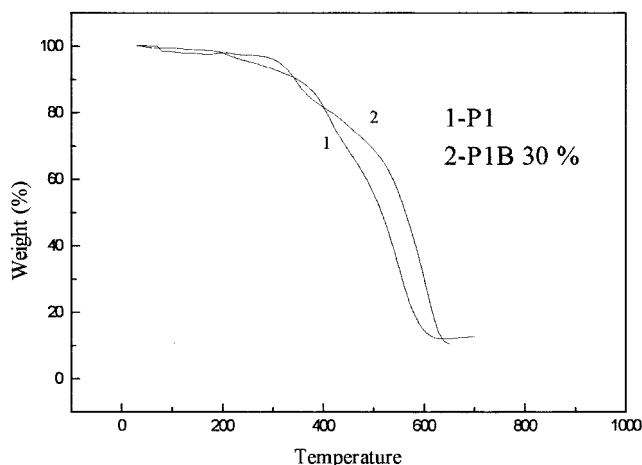


Figure 1 TGA curve of homopolymer of 4-[(4-hydroxy-3-methylphenyl)azo]benzoic acid and its copolymers with different percentages of *m*-HBA.

The TGA curves of polymers **P2** and **P2a** are shown in Figure 2. The T_g value of the homopolymer is 160°C, whereas that of the copolymer with 20% *p*-HBA is 278°C and that of 30% *p*-HBA is 316°C. This increase in thermal stability of the copolymer with the increase in *p*-HBA can be attributed to the increase in rigidity of the main chain resulting from the increase in *p*-HBA content.

The DSC curves of homopolymer **P1** and its copolymers containing various percentage compositions of *m*-HBA (**P1b**) are given in Figure 3. The T_m values of homopolymer **P1** and its copolymer **P1b** containing varying amounts of *m*-HBA are provided in Table III, from which it may be observed that the T_m value decreases with the increase in percentage of *m*-HBA,

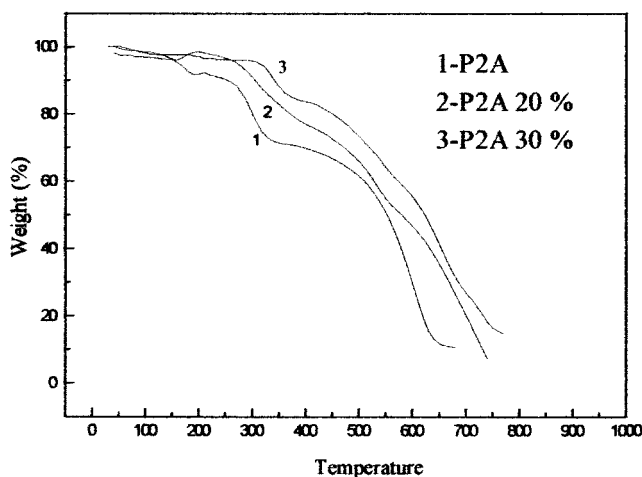


Figure 2 TGA curve of homopolymer of 4-[(4-hydroxy 2-methylphenyl)azo]benzoic acid and its copolymers with different percentages of *p*-HBA.

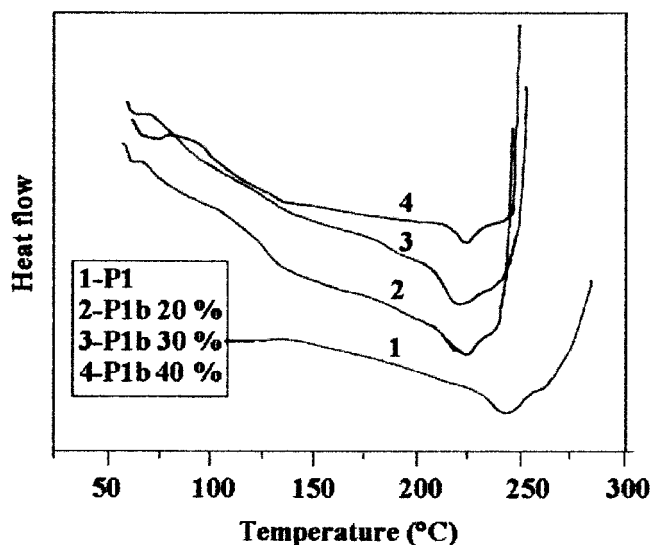
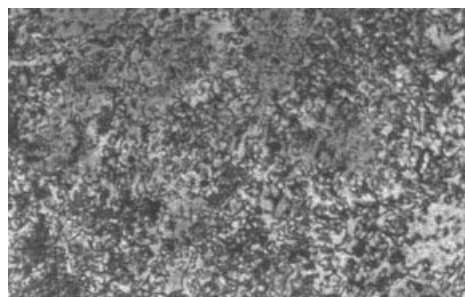
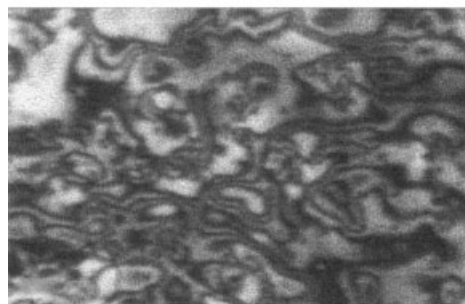


Figure 3 DSC curves of homopolymer **P1** and copolymers **P1b** with varying percentages of *m*-HBA.

as expected. This could be attributed to the introduction of "kink" molecules into the main chain. The PLM observations of the polymers showed nematic threaded LC textures [Fig. 4(a)]. It was found that up to 30% *m*-HBA composition the polymers showed LC phase and above 30% composition the polymers did



(a)



(b)

Figure 4 (a) Nematic schlieren texture of copolyester **P1b** 30% at 226.9°C. (b) Nematic schlieren texture of copolymer **P2a** 30% at 249°C.

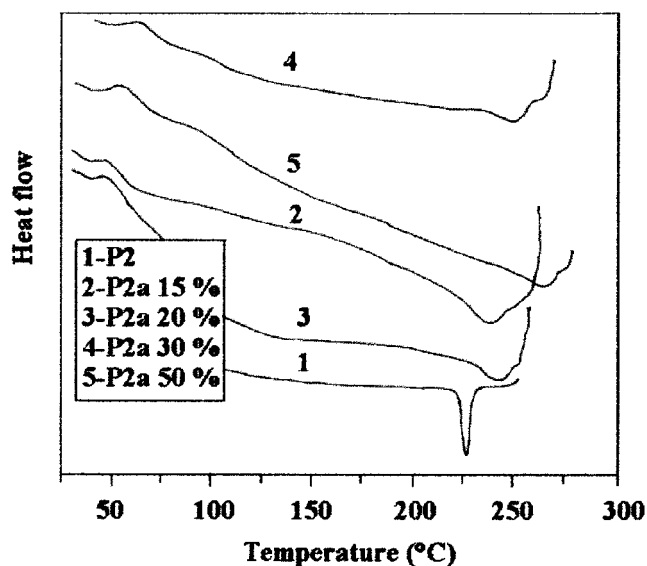


Figure 5 Curves of homopolymer of 4-[(4-hydroxy 2-methylphenyl)azo]benzoic acid and its copolymers with different percentages of *p*-HBA.

not show any clear LC phase. The polymer above this composition showed some unclear textures on shearing, which existed up to 50% composition, above which the polymer completely lost its LC character.

The DSC curves of the copolymers **P2a** containing different molar ratios of *p*-HBA are shown in Figure 5. From the DSC curves it was found that the transition temperature increased as the percentage composition of *p*-HBA increased. Up to 50% composition of *p*-HBA the copolymers showed T_m before decomposition temperature and above that composition the copolymers were found to have very high T_m , above its decomposition temperature. Figure 4(b) gives the nematic schlieren texture of the copolymer **P2a**. Table IV provides the T_m values of all the polymers mentioned. The difference in the T_m values of homopolymers and copolymers of **P1** and **P2** can be attributed to the reactivity difference of the monomers. It is obvious that the monomer **1** has more reactivity, considering the position of methyl group (which is *ortho* to the hydroxyl group), thus enhancing the reactivity of the hydroxyl group.

It is interesting to note that the introduction of a long aliphatic hydrocarbon side chain such as pentadecyl/pentadecenyl group laterally to the azobenzene moiety (**P3** and **P4** series polymers) did reduce the transition temperatures, but without disturbing the mesophase structures (Table IV). The thermal and phase behaviors of the homopolymers and copolymers could be explained on the basis of the presence of the saturated/unsaturated long hydrocarbon side chain and also on the linear/nonlinear nature of the

HBA used. A drastic reduction in the transition temperature was noticed for the homopolymer having the pentadecyl moiety as the lateral attachment. A stable nematic texture was noticed in PLM measurements. When the pentadecyl group was substituted with the unsaturated pentadecenyl group, the resulting polymer on heating started to decompose near 200°C, as observed by an exotherm in DSC and confirmed by TGA. However, a threaded nematic texture were obtained when the polymer was heated to below 200°C and rapidly quenched to room temperature and observed under PLM, thus confirming an earlier observation.⁶ This was attributed to the stabilization of mesophase under crosslinked network structures formed from the unsaturated pentadecenyl group.⁶ Copolymers with *m*-HBA did not show any liquid-crystalline behavior, as can be understood on the basis of its nonlinear structure. On the other hand, *p*-HBA-based copolyesters exhibited liquid-crystalline behavior, although the reduction in the transition temperature was only marginal. This can be understood on the basis of the higher thermal stability imparted by the copolymerization with *p*-HBA.

CONCLUSIONS

Copolymers of derivatives of (azophenyl)hydroxybenzoic acid with various percentage compositions of *m*-HBA and *p*-HBA were synthesized and characterized. The solubility of the copolymer with *m*-HBA, as expected, was found to be higher compared to that of the corresponding homopolymer. This can be attributed to the decrease in the rigidity of the polymer chain resulting from the introduction of nonlinear molecules. On the other hand, the solubilities of the copolymers with *p*-HBA changed only slightly compared to the corresponding homopolymer, although there was a slight decrease. Introduction of the *m*-HBA unit did not alter the thermal stability of the copolymer up to 30% composition, but above that it decreased the thermal stability. At the same time the copolymers of *p*-HBA were found to possess greater thermal stability than their homopolymers at all compositions. The T_m value of copolymers of *m*-HBA decreased as the percentage composition of *m*-HBA increased. The copolymer of *m*-HBA lost its liquid-crystalline property above 30% composition of *m*-HBA, whereas the copolymers of *p*-HBA possessed the liquid-crystalline property up to 50% composition of *p*-HBA. The long alkyl side chain attached laterally to the azobenzene moiety drastically reduced the transition temperature of the homopolyesters while maintaining the mesogenic order. In the case of the corresponding copolyesters (with *p*-HBA), only a marginal reduction in transition temperature was observed, indicating better thermal

stability. The copolyesters of *m*-HBA did not exhibit any liquid-crystalline behavior, possibly because of its nonlinear shape.

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