

Semiflexible Random Thermotropic Copolymers from 8-(3-Hydroxy phenyl) Octanoic Acid and 3-Chloro-4-Hydroxy Benzoic Acid/3,5-Dibromo-4-Hydroxy Benzoic Acid

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ABSTRACT: Two series of semiflexible random thermotropic copolymers containing 8-(3-hydroxy phenyl) octanoic acid (HPOA) with either 3-chloro-4-hydroxy benzoic acid or 3,5-dibromo-4-hydroxy benzoic acid were prepared by melt polycondensation techniques. The copolyesters were characterized with Fourier transform infrared spectroscopy, dilute solution viscometry, hot-stage polarized light microscopy, differential scanning calorimetry, thermogravimetric analysis, and wide-angle X-ray diffraction. Studies revealed that the amount of HPOA as a disruptor incorporated into the backbone of substituted 4-hydroxy

benzoic acids had a detrimental effect on the liquid-crystalline behavior. Mesophase-transition temperatures were observed between 210 and 250°C, and the optical textures were of typical nematic phases. The degree of crystallinity decreased with an increase in the HPOA content. The thermal stability of the copolymers was in the range of 310–370°C. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 778–783, 2008

Key words: halogenated; liquid-crystalline polymers (LCP); polyesters; synthesis; thermal properties

INTRODUCTION

The design and synthesis of main-chain thermotropic polymers have been an attractive approach in both fundamental and technological fields because of their unique semicrystalline and liquid-crystalline morphologies, the ease of subsequent molding and fabrication, their high chemical and thermal stability, and their related high-performance and functional properties.^{1–7} The technological importance of liquid-crystalline structures is driven by the low melt viscosity of the mesophases, preferentially the nematic ones, which allow the production of thin-walled precision products and unique rheological properties manifested by these nanoscopically tailored materials.^{8–10}

Liquid-crystalline polymers (LCPs) derived from *p*-substituted polyesters are normally infusible unless disruptor groups are substituted onto the aromatic rings. This concept has been successfully used in main-chain LCPs to reduce the processing temperature of the rigid architecture by the introduction of

modifications with substituents on the aromatic rings and the incorporation of either comonomers of different sizes or flexible spacers.^{1–7} In general, the lowering of mesophase-transition temperature (T_m) by the introduction of substituents into the mesogenic units of the polymer depends on the size of the substituent, its local concentration, and the degree of substitution. The best documented technical melt-processable liquid-crystalline polyester is a binary copolymer of 4-hydroxy benzoic acid (HBA) and 2-hydroxy-6-naphthoic acid called Vetra.^{11–13} An increasingly large number of main-chain LCPs of *p*-hydroxy benzoic acid with different disruptors have been developed to a melt-processable range,^{14–21} but relatively few studies have been conducted with 8-(3-hydroxy phenyl) octanoic acid (HPOA), a 1,3-phenylene unit with an inbuilt aliphatic (CH₂)₇ flexible spacer. Pillai et al.²² found that the copolymer poly[1,4-oxybenzoate-co-8-(3-oxyphenyl) octanoate] exhibited T_m at 256°C. The copolymer of HBA and 4-hydroxyphenyl acetic acid also showed a mesophase transition around 220°C.²³ However, the copolyesters of HPOA had only a narrow melting range, and their thermal stability was rather low. Furthermore, substitution in the 3-position of 4-HBA by bromine enhanced this melting range, and the results are discussed in this article. The copolymer poly[3-bromo-1,4-oxybenzoate-co-8-(3-oxyphenyl) octanoate] was found to have better thermal stability and at the same time yielded a lower transition temperature

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than that of the copolyester without the bromine substitution.²⁴ These results prompted us to study the copolymers of HPOA with other substituted monomers such as 3-chloro-4-hydroxy benzoic acid (CHBA) and 3,5-dibromo-4-hydroxy benzoic acid (DBHBA). The study is focused on understanding the fundamentals of the effect of a substituent on the mesogen. These polymers contain aliphatic carbonyl groups, which will increase the hydrophilicity to impart hydrolytic degradability.^{21,22} Our previous study has shown that the copolymerization of HBA with a naturally occurring hydroxyphenylalkanoic acid such as 4-hydroxyphenylacetic acid or 3-(4-hydroxyphenyl)propionic acid yields hydrolytically degradable liquid-crystalline polyesters with improved processability.^{21,22}

EXPERIMENTAL

HBA, magnesium acetate, and acetic anhydride were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. Cardanol was obtained by double vacuum distillation of cashew nut shell liquid. The monomer HPOA was prepared by the phase-transfer-catalyzed permanganate oxidation of cardanol as reported earlier²² and purified by column chromatography with silica gel as an adsorbent and chloroform as an eluent. CHBA was prepared by the chlorination of HBA with HCl and H₂O₂²⁵ (mp = 167°C). DBHBA was prepared as follows: Methyl-4-hydroxy benzoate (7 g; prepared by the acetylation of HBA) was dissolved in a dichloromethane-methanol mixture (3 : 1 v/v). Bromine in glacial acetic acid (3 mL) was slowly added to the stirring solution at 20°C. After the addition, the temperature was raised to 40–50°C and maintained for 1 h. The product was separated by the addition of water and hydrolyzed with a 10% NaOH solution. The precipitated bromo derivative was separated, dried under vacuum, and recrystallized from methanol (three times; yield = 65%, mp = 260°C). The product was characterized by a comparison with IR and NMR data of authentic samples.

Preparation of the polymers

A mixture of CHBA (0.80 mol), HPOA (0.20 mol), and magnesium acetate (0.15%) was weighed into a three-necked, round-bottom flask. Acetic anhydride (0.08 mol) was added and refluxed at a temperature of 140°C for 3 h. Nitrogen was purged to the reaction mixture, and the temperature was raised to 160°C at a heating rate of 10°C/h. Further polymerization was conducted with the following heating program. 180°C for 1 h and 200°C for 1 h in a Dowtherm and finally between 230 and 280°C under vacuum for 2–6 h (0.1–0.01 mmHg). After cooling, the

reaction product was chipped off, washed with acetone, further purified by Soxhlet extraction with acetone/isopropanol (3.1 v/v), and dried at 80°C under vacuum (yield = 86%). Copolymers with 10, 15, 20, or 35% HPOA were prepared similarly. Copolymers of DBHBA and HPOA with molar proportions of 90 : 10, 95 : 15, 80 : 20, 70 : 30, 60 : 40, and 50 : 50 were prepared with a similar procedure.

HPOA/CHBA

ANAL. Calcd: C, 67.65%; H, 5.64%. Found: C, 67.41%; H, 6.62%; Cl, 17.18%. Fourier transform infrared (FTIR; KBr pellet, cm⁻¹): 2981, 2853 (ν_{CH_2} , aliphatic), 1758 (C=O stretching), 1600 ($\nu_{\text{C}=\text{C}}$, Ar, s), 1240 (C–O stretching).

HPOA/DBHBA

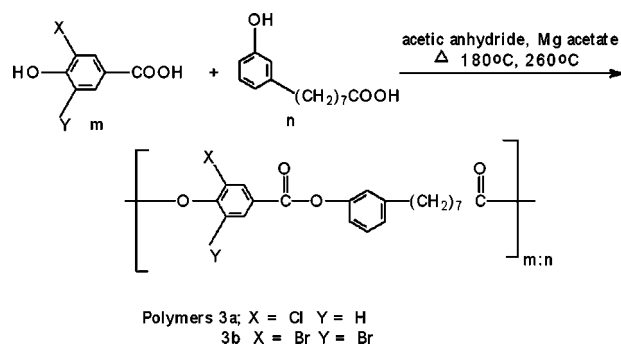
ANAL. Calcd: C, 50.90%; H, 4.20%; Br, 31.19%. Found: C, 50.81%; H, 4.11%; Br, 31.10%. FTIR (KBr pellet, cm⁻¹): 2853, 2942 (ν_{CH_2} , aliphatic), 1755 ($\nu_{\text{C}=\text{O}}$, s), 1600 ($\nu_{\text{C}=\text{C}}$, Ar, s), 1230 (C–O stretching), 671 (C–Cl stretching), 738 (C–Br stretching).

Methods

IR spectra were recorded on a Nicolet Impact 400D FTIR spectrophotometer (Waltham, MA). The inherent viscosities of the copolymers were determined with an Ubbelohde viscometer. Thermogravimetric analysis (TGA) measurements were performed on a DuPont TGA-2000 (DE) under an atmosphere of nitrogen. The differential scanning calorimetry (DSC) measurements were carried out on a DuPont 2100 Thermal Analyst differential scanning calorimeter under a nitrogen atmosphere. ¹H-NMR was recorded on. Optical microscopy observations were performed with a Nikon polarizing microscope with a hot stage. Wide-angle X-ray diffraction (WAXD) patterns were recorded with a Rigaku D_{max} powder diffractometer with Ni-filtered Cu K α radiation.

RESULTS AND DISCUSSION

A number of copolyesters of different molar proportions containing HPOA as a disruptor monomer for its thermotropic liquid-crystalline properties with CHBA and DBHBA were prepared. The preparation involved the *in situ* acetylation of the monomers followed by polycondensation in the melt in the presence of magnesium acetate as a transesterification catalyst. The polymerization was carried out in an inert atmosphere at different heating rates as described in the Experimental section. To attain a high molecular weight, the postpolymerization of the oligomers was conducted under vacuum at



Scheme 1 Preparation of copolymers of HPOA and HBA derivatives.

temperatures between 230 and 280°C. A further increase in the temperature resulted in the formation of charred products. After the reaction, the polymer that formed had to be chipped off and powdered to carry out Soxhlet extraction. The yields of the copolymers ranged from 90 to 92%. Scheme 1 depicts the reaction sequence involved in the preparation of the copolymers.

The formation of the copolyesters was followed by FTIR spectra. Successful esterification of terminal groups could be confirmed by the substantial reduction in the characteristic O—H stretching absorption frequency in the spectra. Besides, in all the spectra, the copolyesters showed the characteristic carbonyl stretching frequency of the ester groups in the ranges of 1755–1760 (C=O stretching) and 1240–1230 cm^{-1} (C—O stretching) and the expected CH stretching frequency of the aliphatic groups in the range of 2981–2942 cm^{-1} . The FTIR spectra also showed absorption frequencies at 671 (C—Cl stretching) and 738 cm^{-1} (C—Br stretching) for **P1** and **P2** polymers, respectively.

Attempts to characterize the molecular weights of the polyesters were unsuccessful because of the insolubility in solvents commonly used for thermotropic LCs. Mixed solvents such as *p*-cresol/trifluoroacetic acid and *p*-chlorophenol/trifluoroacetic acid showed slight solubility for **P1** polymers, whereas **P2** polymers were much less soluble (Table I). Their insolubility in these solvents clearly demonstrated that the solubility was a complicated result of crystallinity and main-chain solvation.

The viscosity of the polymers was determined with a very dilute concentration (0.01%) of a *p*-chlorophenol/trifluoroacetic acid (3.1 v/v) mixture. The inherent viscosities of the soluble portion of the polyesters were found to be in the range of 0.76–1.2 dL/g for **P1** polymers and in the range of 0.8–1.6 dL/g for **P2** polymers (Table I). From the obtained values, it could be inferred that the molecular weights of the polymers were sufficiently high. Han and Bhowmik²⁶ recently reported that the effect of the molecular weight on the thermal properties and optical texture of copolyesters is negligible for polymers with inherent viscosity values in this range.

The thermal properties of the polymers were studied with DSC and TGA. Studies revealed that the amount of HPOA content incorporated into the backbone of the substituted HBA monomers had a detrimental effect on the liquid-crystalline behavior. As expected, T_m was lower than the T_m values of a corresponding unsubstituted copolymer.¹⁹ In this study, copolymers with 20% HPOA content were selected for a detailed study.

In the DSC thermogram (Fig. 1) of the copolyester of CHBA/HPOA (80 : 20) during the first heating cycle at a rate of 20°C/min in nitrogen, endotherms at 227 and 297°C corresponding to the mesophase transition and isotropization temperatures, respectively, were observed. The glass-transition temperature (T_g) observed at 54°C indicated the amorphous nature. On cooling at 20°C/min, the respective exotherms were observed to be very small, and this could be due to the prevention of good alignment to the liquid-crystalline domain at this cooling rate.

The identification of an optical texture typical of liquid-crystalline phases was conducted with a polarized light microscope. The copolymers containing more than 50% HPOA did not show a well-defined textural pattern. Small birefringent regions were observed on the polymer under the polarized light microscope, and as the temperature was increased, the domains began to appear at 199°C, increased gradually with temperature, and finally became isotropic at 297°C. The observed mesophase texture was nematic schlieren. On shearing between glass plates at about 300°C and on cooling also, well-defined optical textures were observed. The preservation of a nematic texture at room temperature

TABLE I
Solubility and Inherent Viscosity of the Copolymers

Polymer	<i>p</i> -Cresol/ trifluoroacetic acid	<i>p</i> -Chlorophenol/ trifluoroacetic acid	THF	Inherent viscosity (dL/g)
P1	+-	+-	-	1.02
P2	+-	+-	-	1.20

- = insoluble; +- = partially soluble.

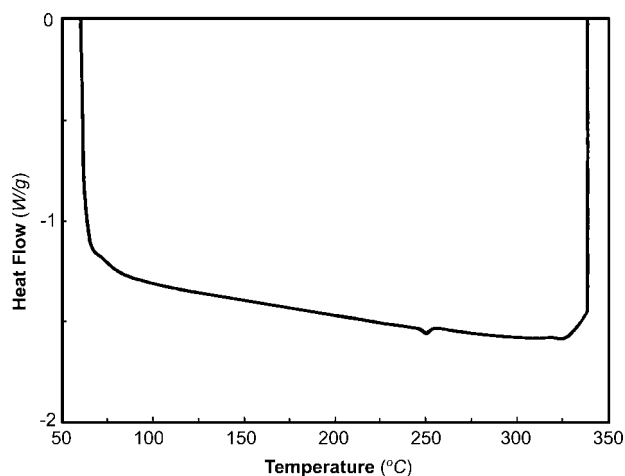


Figure 1 DSC thermogram of a copolyester of CHBA/HPOA (80 : 20) during the first heating cycle at a rate of 20°C/min in nitrogen.

revealed the possibility of producing a highly oriented structure by extrusion.

In analogy, in the DSC thermogram (Fig. 2) of a **P2** polymer (with a molar ratio of 80 : 20 DBHBA/HPOA) in the first heating cycle, T_g at 51°C and an exotherm at 133°C due to cold crystallization were observed, but the peaks corresponding to T_m and the isotropization temperature were ill-defined. However, after annealing and on subsequent runs, the exotherm at 133°C vanished, whereas at 249°C, an endotherm corresponding to T_m was observed. Such sequence reorganization is believed to involve the formation of blocky structures in a random copolyester and is called a crystallization-induced reaction. Under the polarized light microscope, the mesophase transition occurred between 210 and 250°C, as evidenced by the formation of domains of a nematic texture. Upon heating to 300°C and on

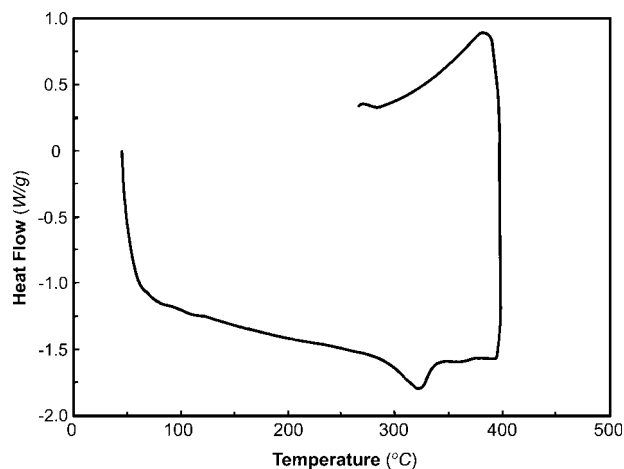


Figure 2 DSC thermogram of a **P2** polymer with a molar ratio of 80 : 20 DBHBA/HPOA in the first heating cycle at a rate of 20°C/min in nitrogen.

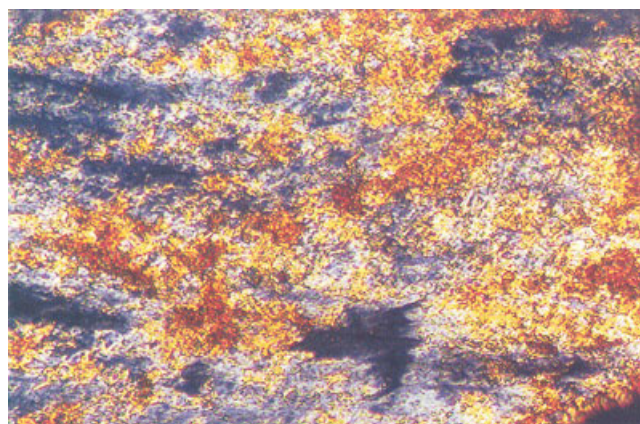


Figure 3 Polarized light micrograph of a **P2** polymer with a molar ratio of 80 : 20 DBHBA/HPOA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

shearing, the copolymers showed a threaded nematic texture (Fig. 3) with parallel bands characteristic of extended chains.

TGA scans (Fig. 4) indicate that the onset of thermal degradation occurred as the temperature decreased with increasing HPOA (the kinked monomer content). A single-stage decomposition characteristic was observed. The temperature range in which the polymers showed a 10% weight loss was 329–345°C for **P1** polymers and 311–370°C for **P2** polymers. The amount of residual char obtained at an elevated temperature was less dependent on the HPOA content. The details regarding thermal behavior are given in Table II. Investigations of WAXD powder patterns of the **P1** and **P2** copolymers (Figs. 5 and 6) with 20% HPOA content showed peaks centered around $2\theta = 20$ –25, indicating that some semicrystalline region was embedded in the matrix of the amorphous structure. The peaks became broad, corresponding to interchain spacing characteristic of

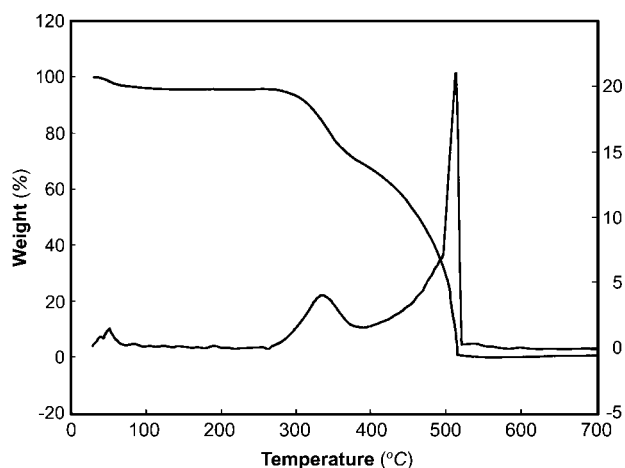


Figure 4 Typical TGA scan of copolyesters of HPOA.

TABLE II
Thermal Data for the Copolymers

Polymer	T_g ($^{\circ}\text{C}$)	T_{10} ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)
P1	54	345	K 227 N 297
P2	51	370	K 249 N _{dec} > 370

A *p*-chlorophenol/trifluoroacetic acid ratio of 3 : 1 (v/v) and a temperature of 30 $^{\circ}\text{C}$ were used. For **P1**, 80 : 20 CHBA/HPOA was used; for **P2**, 80 : 20 DBHBA/HPOA was used. T_{10} is the 10% decomposition temperature.

K, crystal; N, nematic; N_{dec}, nematic-decomposing.

amorphous polymers in the case of the WAXD patterns of copolymers with higher amounts of HPOA.

To evaluate the effect of the composition of the monomers on the mesophase transition, copolymers with different compositions of the monomers were prepared. In the case of the **P1** series, copolymers with 10, 15, 20, or 35% HPOA exhibited well-defined optical textures, whereas for copolymers with a higher percentage of HPOA incorporated, only in some regions could a mesophase texture be found under polarized light microscopy. The mesophase temperature range was 220–235 $^{\circ}\text{C}$ (Table II). In the **P2** series, T_m was found to increase up to 20% HPOA, but with a further increase in the HPOA content, the mesophase transition range decreased gradually, and above 50% HPOA, no T_m was observed. Thus, for the **P2** polymers with 20, 15, or 10% HPOA, T_m was observed at 249, 243, and 241 $^{\circ}\text{C}$, respectively.

From these observations, it could be inferred that the stability of the liquid-crystalline phase depends very much on the method of preparation and the nature of the substituents as in other reported cases that in turn parallel the degree and perfection of crystallites.^{27–29} Kricheldorf and coworkers^{15,18} reported extensively on a polyester built of substituted HBAs. The homopolymers of the monomers in this study did not exhibit T_m .^{18,30} This study revealed that copolymers with less than 50% disruptor on the polymer backbone were capable of preserving the liquid crystallinity. This indicates that the random distribution of both unsymmetrical and symmetrical units of different sizes can reduce the mesophase-forming ability as well as thermal transi-

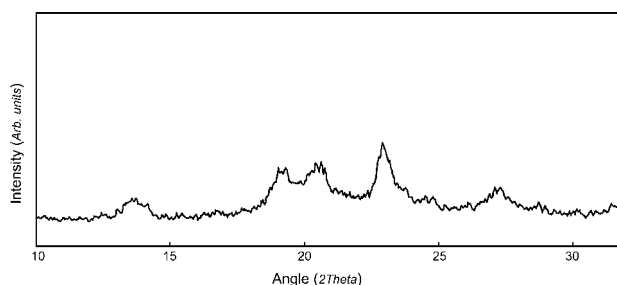


Figure 5 WAXD powder patterns of **P1** copolymers with 20% HPOA content.

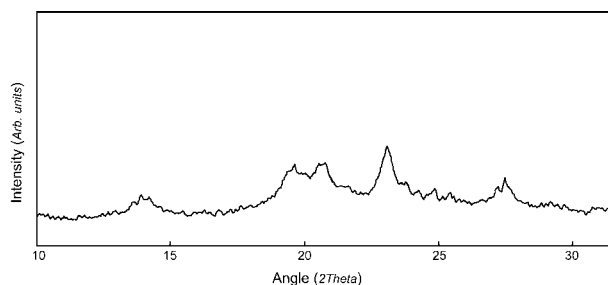


Figure 6 WAXD powder patterns of **P2** copolymers with 20% HPOA content.

tions due to the repulsive forces that disrupt close chain packing. The HPOA disruptor can disturb the lateral distance of a neighboring chain and a perfect array of van der Waals and dipole forces along an individual chain and also reduce the persistent length. The observation that the 3-chloro series is more efficient in reducing T_m over the 3,5-dibromo series is due to the positional isomerism along the polymer chain.

Although in the **P2** series the presence of the DBHBA monomer can exert some lateral attractive force because of high polarizability in the lateral direction, the reduction of T_m and the broad melting range obtained for these polymers together with good thermal stability offer the possibility of melt processing in their nematic liquid-crystalline phase.

CONCLUSIONS

Two series of semiflexible random copolymers containing HPOA as a disruptor with either CHBA or DBHBA were prepared and characterized. The copolymers were insoluble in common solvents and thermotropic LCPs. The viscosities were in the range of 0.76–1.6 dL/g. Studies revealed that the amount of disruptor incorporated into the backbone of the substituted HBAs had a detrimental effect on the liquid-crystalline behavior. T_m , obtained between 210 and 250 $^{\circ}\text{C}$, indicated the possibility of melt processing. The polymers exhibited good thermal stabilities. The WAXD studies revealed the existence of a small semicrystalline region embedded in the matrix of the amorphous structure.

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