polymer communications

Thermotropic liquid crystalline copolyester based on 8-(3-hydroxyphenyl) octanoic acid and *p*-hydroxybenzoic acid

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A thermotropic liquid crystalline copolyester formed by polycondensation of 8-(3-hydroxyphenyl) octanoic acid (3-HPOA) and *p*-hydroxybenzoic acid has been synthesized and characterized. 3-HPOA having both a flexible segment and a rigid kink in its structure has been synthesized by phase transfer catalysed oxidation of cardanol. The copolyester was anisotropic under crossed polarized light between 200°C and 409°C. D.s.c. showed two mesophase transitions with maxima at 256°C and 342°C, respectively.

(Keywords: cardanol; thermotropic liquid crystalline copolyester; synthesis; characterization; 3-HPOA; *p*-HBA)

Introduction

Thermotropic liquid crystalline (LC) polymers have attracted much attention in recent years because of their potential use as high performance materials[1–6]. The earlier attempts to prepare processable thermotropic LC polymers of fully aromatic polyesters were, in fact, hampered by their intractability and insolubility[7]. A number of chemical approaches have since been adopted to lower the melting points of these polymers to a processable range without destroying the mesogenic order. They include[8–16]: (1) introduction of disruptors (flexible spacers, rigid kinks, etc.) into the straight chain polymers; (2) substitution of the aromatic rings; and (3) copolymerization with other aromatic monomers. Thus, copolymerization of *p*-hydroxybenzoic acid (*p*-HBA) with other aromatic monomers such as 2,6-hydroxynaphthoic acid, terephthalic acid or *p,p'*-biphenol gives rise to melt processable LC copolyesters. Two of the first commercial polymers are Xyder and Vectra[17,18]. These copolyesters have melting points near 300°C and hence are still rather difficult to process. In principle it should be possible to lower the melting points further by copolymerization with monomers having a flexible spacer and a 'rigid kink' in its structure. We report here the synthesis and characterization of a new monomer, 8-(3-hydroxyphenyl) octanoic acid (3-HPOA), having such structural features, its homopolyester and its thermotropic LC copolyester with *p*-HBA. 3-HPOA was prepared from cardanol, an unsaturated hydrocarbon phenol[19] obtained from the plant *Anacardium occidentale* L.

Experimental

Materials. Cardanol (37330-39-5) (I) was obtained by double vacuum distillation[20] of cashew nut shell liquid (8007-24-7). Tricaprylylmethylammonium chloride (Aliquat 336), triphenylphosphine oxide (TPPO) and oxalyl chloride (OC) were obtained from Aldrich and were used as received. Potassium permanganate and other chemicals and solvents were obtained from BDH.

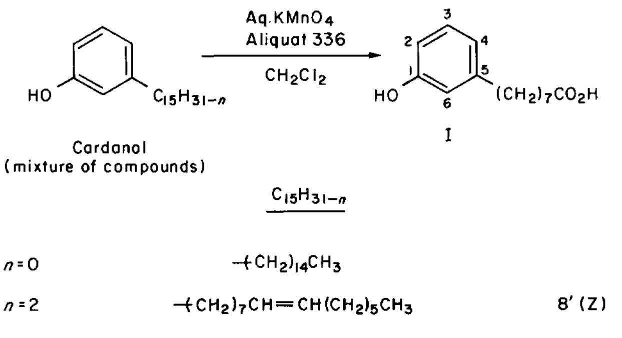
Monomer synthesis. 3-HPOA was prepared by the phase transfer catalysed permanganate oxidation[21,22] of cardanol using a patented process[23] (*Scheme 1*).

Prior to oxidation, cardanol was acetylated to stabilize the phenolic moiety against permanganate attack. Acetylation[24] was carried out conventionally using acetic anhydride and pyridine.

Elemental analysis of acetylated cardanol (AC) (%): calculated, C 80.7, H 9.9; found, C 80.3, H 10.0. I.r. (cm^{-1}, neat): 1767 (–C=O), 1205 (O–C(O)–O), 1375 (CH_3).

The oxidation was performed in the presence of a phase transfer agent such as Aliquat 336 so that the permanganate ion is transferred from the aqueous phase to the organic phase (methylene chloride) containing AC at 30 ± 1°C. The non-aqueous layer was extracted with 10% NaOH solution which was warmed to deacetylate the product. The alkaline extract was neutralized with concentrated HCl and extracted with ether which was washed with water and dried, and the ether evaporated off in a flash evaporator. The product was microdistilled under vacuum using a Krugelrohr apparatus and the fraction distilling at 200–210°C was collected and recrystallized from ether [m.p. 62°C, M_w 236.16 (mass)].

Elemental analysis (%): calculated, C 71.2, H 8.5; found C 71.0; H 8.2. *FT*i.r. (cm^{-1}, KBr): 1696 (C=O),



Scheme 1 Synthesis of 3-HOPA (I) from cardanol

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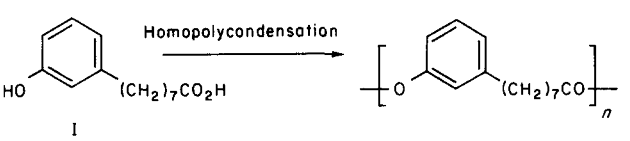
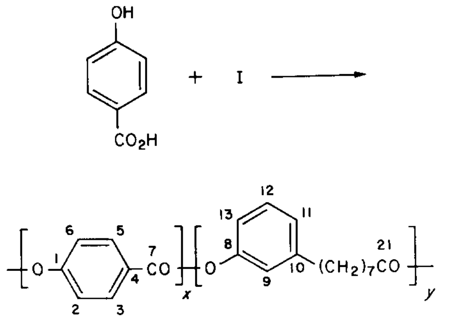


Scheme 2 Homopolycondensation of 3-HPOA



Scheme 3 Synthesis of the copolyester poly(1,4-oxybenzoate-*co*-1,3-phenyloctanoate)

1591 (aromatic), 2929, 2852 ($-CH_2-$), 3345 (b. OH str.). ^{1}H n.m.r. (δ): 6.6–7.2 (m, 4 H, aromatic), 2.5 (t, 2 H, CH_2Ar), 2.3 (t 2 H, CH_2CO_2H), 1.5 (m, 10 H, $(CH_2)_5$). ^{13}C n.m.r. (H decoupled, $CDCl_3$, ppm): 180.4 (C=O), 155.7 (C_1), 144.9, (C_3) 129.5 (C_5), 120.9 (C_4), 115.6 (C_2), 112.8 (C_6), 24.4–38.8 (seven peaks, aliphatic carbons).

Homopolyester synthesis. The homopolyester of 3-HPOA was synthesized by a melt condensation process (*Scheme 2*).

3-HPOA (1 g) was heated at 200°C for 2 h in a stream of dry nitrogen in the presence of 0.05 wt% magnesium acetate in a thick-walled polymerization tube. The temperature was then raised to 250°C and the reaction continued for 1 h under vacuum. The tube was opened and the product was washed with methanol and dried under vacuum at 55°C.

Elemental analysis (%): calculated, C 77.0, H 8.3; found, C 77.0, H 8.2. *FT*i.r. (cm^{-1}, KBr): 1738 (–C=O), 1600 (aromatic), 2927, 2853 ($-CH_2$).

Copolyester synthesis. The copolyester was synthesized (*Scheme 3*) using the method of Ogatha[25].

A 100 ml four-necked flask equipped with a mechanical stirrer, a dropping funnel, a reflux condenser and a gas inlet was flushed with dry nitrogen and then charged with chlorobenzene (20 ml), TPPO (5.58 g, 0.02 mol), and OC (2.5 g, 0.02 mol) in chlorobenzene (7.5 ml). The mixture was stirred over a period of 10 min. When the evolution of gas was over, the solvent was distilled off and a mixture of *p*-HBA (1.38 g, 0.01 mol) and 3-HPOA (2.36 g, 0.01 mol) was added and heated with stirring to 150°C for 30 min. The mixture was then cooled to room temperature and chlorobenzene (20 ml) was again added followed by a solution of triethylamine (4.05 g, 0.04 mol) in pyridine (5 ml) and heated to reflux for 1 h. The product was transferred into a 1 litre beaker containing methanol (1000 ml), agitated for 10 min and filtered. The filtrate was washed with hot methanol several times and dried at 55°C *in vacuo*.

Elemental analysis (%): calculated, C 74.6, H 6.5; found, C 74.1, H 6.2. *FT*i.r. (cm^{-1}, KBr): 2927, 2853 (CH_2), 1738 (C=O), 1600, 1561, 1558, 1508 (aromatic), 1264.4 (C_1–C_7–O), 1201 (C_{20}–C_{21}–O).

*Methods. FT*i.r. spectra were recorded using a Nicolet 20 SXB spectrophotometer. ^{1}H n.m.r. spectra in $CDCl_3$ with tetramethylsilane as internal standard were recorded using a Bruker instrument (250 MHz). Proton decoupled ^{13}C n.m.r. spectra in $CDCl_3$ were also recorded using the same instrument. ^{13}C CP/MAS solid state n.m.r. spectra were recorded using a Bruker model MSL 100. D.s.c. was carried out using a Du Pont instrument (model DSC V 2.2 A 9900). Optical micrographs were recorded using an Olympus microscope fitted with a Linkam heating unit (model PR 600/TH 600). Viscosity measurements were made using an Ubbelhode viscometer at a temperature of 50°C with *p*-chlorophenol as solvent.

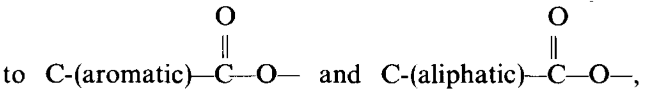
Results and discussion

Monomer synthesis. Direct oxidation of cardanol with aqueous permanganate in the presence of a phase transfer agent such as Aliquat 336 in methylene chloride always resulted in the cleavage of the phenolic moiety. This necessitated protection of the hydroxyl of cardanol to stabilize it against attack by the permanganate ion. Acetylation was found to be satisfactory even up to a pH of 3–4. Deacetylation was found to be comparatively easy and was carried out by warming the alkali extract containing the product. 3-HPOA was contaminated with a co-oxidation product (an aliphatic carboxylic acid) which was separated by Krugelrohr microdistillation.

Homopolymerization. 3-HPOA underwent polycondensation on direct heating to 250°C, but polymerization was complete only when carried out in the presence of catalysts such as lead acetate or magnesium acetate. Only low molecular weight species were obtained when the polymerization was carried out using the method of Ogatha[25].

Copolyester formation. The copolyester (1:1.5) of 3-HPOA with *p*-HBA was obtained in almost quantitative yield (96%) by using the method of Ogatha[25]. However, a minor modification of the method was found to be essential for avoiding formation of low molecular weight products. This was achieved by distilling off the solvent after the *in situ* formation of triphenylphosphine dichloride. It was found that polyester formation was initiated in the melt at 150°C, and solvent was added again after cooling the system. The copolyester was insoluble in most of the common solvents, but was sparingly soluble in *o*-chlorophenol and *m*-cresol. It was just sufficiently soluble in *p*-chlorophenol at 50°C for viscosity measurements at a concentration of 0.1 g in 10 ml. The specific viscosity ($\eta_{sp/c}$) was 1.31 dl g^{-1}).

The formation of the copolyester was established by elemental analysis, *FT*i.r. and ^{13}C CP/MAS solid state n.m.r. spectroscopy. The *FT*i.r. spectrum of the copolyester showed the characteristic carbonyl stretching frequency of the ester group C=O at 1738.3 cm^{-1}. The –CH stretching vibration of the aliphatic CH_2 segments were observed at 2926.7 and 2852.9 cm^{-1}. The four characteristic aromatic C=O stretching vibrations occurred at 1600, 1561, 1558 and 1508 cm^{-1}. The vibrations at 1264 and 1201 cm^{-1} were assigned



to $\text{C-(aromatic)}-\overset{\overset{\displaystyle O}{\|}}{C}-O-$ and $\text{C-(aliphatic)}-\overset{\overset{\displaystyle O}{\|}}{C}-O-$, respectively.

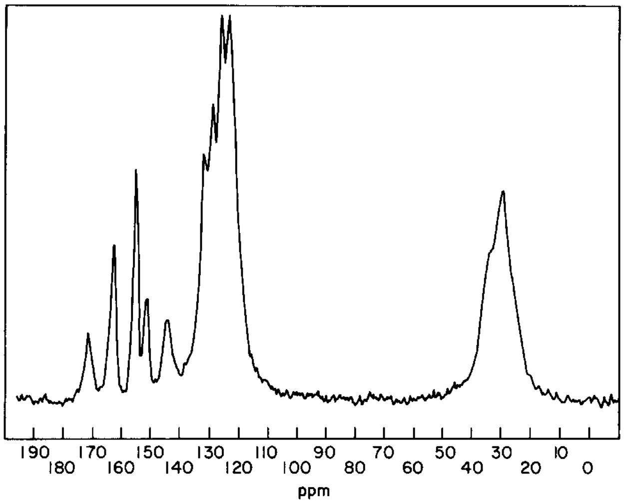


Figure 1 ^{13}CP/MAS n.m.r. spectrum of the copolyester poly(1,4-oxybenzoate-*co*-1,3-phenyloctanoate)

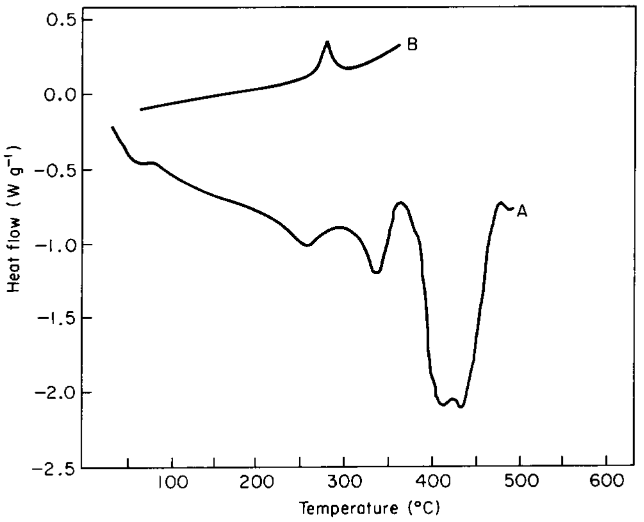


Figure 2 D.s.c. scans of the copolyester: (A) heating cycle; (B) cooling curve from 350°C

The ^{13}C CP/MAS n.m.r. spectrum of the copolyester is shown in *Figure 1*. All the quaternary carbon atoms (171.3 C_{21}, 163.0 C_7, 155.5 C_1, 151.7 C_8, 144.8 C_4 and 126.1 C_{10}) were identified through a non-quaternary suppression method[26]. All aliphatic carbons appeared merged together at 29.9 ppm and other peaks were tentatively assigned as 133.0 (C_3 and C_5), 129.4 (C_2, C_6, C_9 and C_{13}) and 124.1 ppm (C_{11} and C_{12}).

Figure 2 shows the d.s.c. trace of the copolyester measured at a heating rate of 25°C min^{-1} under nitrogen atmosphere. An inflection point at around 73–78°C might be the glass transition. A similar glass transition has been reported for the copolyester of *p*-HBA with *p*-hydroxyphenyl propionic acid[27]. The d.s.c. scan shows two endothermic transitions with maxima at 256 and 342°C, respectively, prior to becoming isotropic at 409°C. When viewed under crossed polarized light, the copolyester was anisotropic between 230°C and 409°C. However, decomposition was observed above 395°C as could be inferred from the formation of gas bubbles. On cooling from 400°C no exothermic transition to a mesophase was observed possibly due to decomposition. However, when the polyester was heated to 350°C and cooled, a single transition was observed at 275°C. *Figure 3* is an optical micrograph of the mesophase observed at 390°C. Studies to identify the mesophases and to further characterize the copolyester are under way.

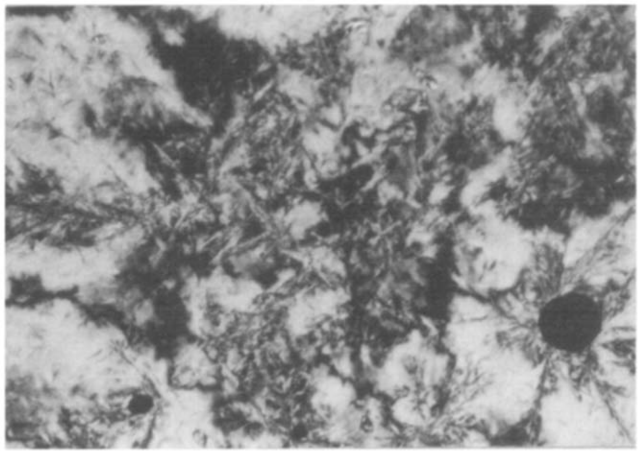


Figure 3 Optical micrograph of the copolyester taken under crossed polarized light at 290°C

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