

Synthesis and Characterization of Main Chain Liquid Crystalline Polyesters Containing 2,5-Bis(4-hexyloxybenzoyloxy)hydroquinone and Terephthalate Units

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ABSTRACT

The synthesis and characterization of new liquid crystalline polyesters have been described containing symmetrically di-substituted hydroquinone monomer. 2,5-Bis(4-hexyloxybenzoyloxy) hydroquinone (HQ6) and 1,6-bis(4-hydroxybenzoyloxy) hexane (H6) monomers were synthesized via multi-step routes from 2,5-dihydroxyquinone and in one step route from 4-hydroxybenzoic acid, respectively. Copolyester PHQ6-co-PH6 was synthesized through high temperature solution polymerization of HQ6 and H6 diols with terephthaloyl chloride. The homopolyesters PHQ6 and PH6 were also synthesized from respective monomers with terephthaloyl chloride by the same method. The molecular weights of polyesters containing the disubstituted hydroquinone units were not very high due to the steric hindrance of the bulky substituting groups on the hydroquinone HQ6 monomer. The homopolyester PHQ6 was soluble in common organic solvents, whereas solubility decreased for copolyester due to decreased content of end hexyloxy groups. Liquid crystalline properties were determined by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) techniques. The effect of the rigid lateral moieties on the thermal properties and liquid crystallinity was investigated on the prepared copolymer and it was compared with that of the analogous homopolyesters. Optical microscopy images showed Schlieren texture characteristic of the nematic phase for both polyester and copolyesters. The DSC experiments were also in accordance with mesophase formation. The melting points and glass transition temperature values of PHQ6 and PHQ6-co-PH6 were significantly higher than those of the PH6 homopolyester. All of the obtained compounds were characterized by conventional spectroscopic methods.

Key Words:

thermotropic polyesters;
laterally substituted polyester;
disubstituted hydroquinone;
liquid crystal texture;
DSC.

INTRODUCTION

A wide variety of thermotropic polyesters have been reported in the past 25 years due to their inherently high stiffness and strength, high use temperatures, excellent chemical resistance and low melt viscosity [1]. However,

they generally have a high melting transition temperature, which prevents melt processing before thermal degradation [2,3]. There are several synthetic strategies that reduce the melting temperatures of rigid-rod polymers and yet form

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liquid crystal phases [4].

For application purpose, it is important to control the melting temperature and other thermal transition properties, which can be accomplished by introducing flexible alkyl spacers in regular rigid main chains [5,6]. In order to lower these transition temperatures without destroying thermotropic behaviour, the approach that has been adopted is the use of substituted aromatic rings. The melting temperature can be reduced by using derivatives with bulky lateral substituents or flexible side chains on hydroquinone ring [7,8].

Alternatively, a successful approach in decreasing the T_m value of aromatic polyesters is random copolymerization. It is widely used as a versatile process to prepare tailor-made liquid crystalline polymers (LCPs), providing novel materials for fundamental and applied research [9,10]. The synthesis and characterization of methyl-, bromo-, chloro-, phenyl- and methoxy- substituted hydroquinone containing polymers were reported [7,11]. Introduction of phenyl substituents on the hydroquinone ring was found to lower the transition temperature compared to substituents such as methyl or methoxy [12]. It was also concluded that halogen, alkyl, or phenyl substituents on one or both of the aromatic rings result in the lowering of transition temperatures.

Subsequently, the effect of alkoxy substituents on the hydroquinone ring was studied and an exponential decrease in the melting temperature with the increase in the length of the substituents' chain was observed. Recently, Jin et al. have reported two series of totally aromatic thermotropic copolyesters containing 2-(α -phenylisopropyl) hydroquinone moiety polyesters [13]. Due to the rigidity of the main chain and presence of the bulky substituents on the hydroquinone units, the glass transition temperatures of the polyesters are rather high. The low melting temperatures for melt processing was reported for copolyesters.

According to Bashir et al. [7] the aromatic copolyesters of terephthalic acid with mono and symmetrically di-substituted hydroquinone form liquid crystalline melts and have isotropization temperature which is not observed for homopolyesters.

In this work, we have examined the synthesis and phase behaviour of a liquid crystalline polyester containing 2,5-bis(4-hexyloxybenzoyloxy) hydro-

quinone moieties in main chain. This homopolyester PHQ6 and its copolyester consisting of HQ6 monomer and triad aromatic ester type mesogenic unit H6 (PHQ6-co-PH6; 1:1 mol/mol) were prepared through solution polycondensation.

The purpose of this study was to investigate the effect of the rigid lateral moiety on the thermal and liquid crystalline (LC) properties of the polyesters.

EXPERIMENTAL

Materials

The purification or drying of compounds and solvents was carried out according to the common procedure. 4-Hydroxy benzoic acid, hydroquinone (1,4-dihydroxy benzene), terephthaloyl chloride, sodium hydrosulphite, *p*-chlorophenol, 2-dichlorobenzene, pentafluorophenol, bromohexane and 1,6-dibromohexane were used as received. Triethylamine hydrochloride was prepared via passing the HCl gas through the triethylamine. The monomers and polymers were synthesized according to the route outlined in Schemes I-III whose further details are given below.

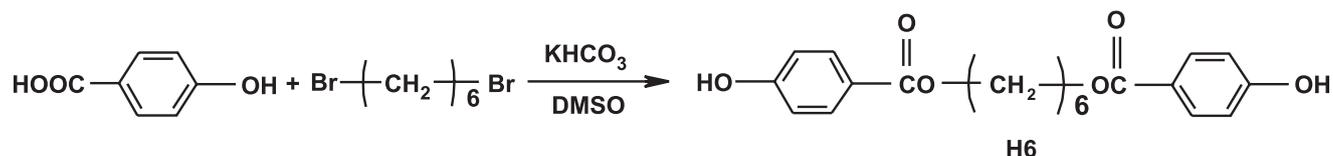
Synthetic Procedures

1,6-Bis(4-hydroxybenzoyloxy)hexane (H6)

A solution of 4.15 g (30 mmol) of 4-hydroxybenzoic acid, 3.0 g (30 mmol) of anhydrous potassium bicarbonate and 3.28 g (14 mmol) of 1,6-dibromohexane in 40 mL of dry dimethylsulphoxide was heated at 80°C (Scheme I). After 5 h, the mixture was poured into 100 mL of cold water saturated with sodium chloride and kept at 5°C overnight. Then the crude product was filtered, washed with cold water and dried. The residue was crystallized from ethanol/water (1:1; v/v) to give white crystals with 85% yield and mp: 180°C.

FTIR (KBr): $\bar{\nu}$ 3389 (OH), 2940 (CH₂), 1679, (C=O), 1591 and 1510 (aromatic), 1282 to 1120 (C-O) cm⁻¹. ¹H NMR (DMSO-d₆): δ 10.34 (s, OH), 7.80 (d, 4H aromatic, meta to OH), 6.81 (d, 4H aromatic, ortho to OH), 4.19 (t, 4H, CH₂, α to -OCOAr), 1.68 (m, 4H, CH₂, β to -OCOAr), 1.42 (m, 4H, CH₂, γ to -OCOAr) ppm.

2,5-Dihydroxy benzoquinone



Scheme I. Synthesis of 1,6-bis (4-hydroxybenzoyloxy) hexane (H6).

2,5-Dihydroxy benzoquinone (**1**) was synthesized by the method reported in the literature [14] (Scheme II). 6.88 g (62 mmol) of hydroquinone was dissolved in a 50 mL of NaOH (50% aqueous solution), and a 25 mL hydrogen peroxide (27% aqueous solution) was added dropwise under vigorous stirring. The reaction temperature was restricted at 45-50°C during the addition. The mixture was poured into a vessel containing 125 g crushed ice. The solution was then acidified with 56 mL hydrochloric acid. The precipitate was isolated, washed with water, dried and purified by crystallization from boiling dioxane. The final product was obtained as a red-orange powder with 70 % yield and mp: 213°C (with decomposition). FTIR (KBr): $\bar{\nu}$ 3300(OH), 1646(C=O)cm⁻¹. ¹H NMR (CDCl₃): δ 6.10 (s, 2H ring), 7.70 (s, 2H, OH) ppm.

4- Hexyloxybenzoic acid

4-Hexyloxybenzoic acid (**2**) was synthesized by a method reported in the literature [15] (Scheme II). A solution of 2.95 g (18 mmol) of 1-bromohexane in 30 mL of dimethylsulphoxide was added dropwise with vigorous stirring to a solution of 3 g (20 mmol) of 4-hydroxybenzoic acid in 10 mL of 5 M sodium hydroxide at 90°C. After 5 h, the reaction mixture was poured into 100 mL of water at 60°C. The solution was then acidified with hydrochloric acid. The precipitate was isolated, washed with water, dried, and purified by crystallization from ethanol/water (1:1; v/v). White crystals were obtained. Yield 92 %, FTIR (KBr): $\bar{\nu}$ 3200 to 2500 (OH, carboxylic acid), 2939 (CH₂), 1681 (C=O), 1602 and 1514 (aromatic), 1253 and 1169 (R-O-Ar) cm⁻¹. ¹H NMR (CDCl₃): δ 12.64 (br.s, OH, carboxylic acid), 8.05 (d, 2H aromatic, meta to -OR), 6.92 (d, 2H aromatic, ortho to -OR), 4.03 (t, 2H, CH₂, α to -OAr), 1.80 (m, 2H, CH₂, β to -OAr), 1.46 (m, 2H, CH₂, γ to -OAr), 1.35 (m, 4H, CH₂, δ to -OAr), and 0.90 (t, 3H, CH₃) ppm.

2,5-Bis (4-hexyloxybenzoyloxy) benzoquinone (BQ6) 2 g (9 mmol) of 4-hexyloxybenzoic acid was refluxed with thionyl chloride (13 mL) and dry dimethylformamide (DMF, 2 drops). After 5 h the excess of thionyl chloride was distilled off under reduced pressure and the residue was washed with dry hexane three times. The obtained acyl chloride was directly dissolved in the 20 mL tetrahydrofuran (THF) and 0.4 mL pyridine. This mixture was cooled to 0°C. The solution containing 0.49g (31 mmol) of 2,5-dihydroxy benzoquinone dissolved in 40 mL dry DMF was added dropwise under nitrogen atmosphere. After the addition, the reaction mixture was stirred for further 2 h at 0°C (Scheme II). A yellow solid was isolated by filtration, washing with water and drying in vacuo. Further purification was conducted by recrystallization from dioxane, and yellow needle-like crystals were obtained with 70% yield. FTIR (KBr): $\bar{\nu}$ 2937 and 2857 (CH₂), 1745 (C=O, ester), 1678 (C=O, quinone), 1604 and 1511 (aromatic), 1249 to 1132 (C-O) cm⁻¹. ¹H NMR (CDCl₃): δ 8.08 (d, 4H aromatic, meta to -OR), 6.96 (d, 4H aromatic, ortho to -OR), 6.84 (s, 2H quinone ring), 4.04 (t, 4H, CH₂, α to -OAr), 1.82 (m, 4H, CH₂, β to -OAr), 1.47 (m, 4H, CH₂, γ to -OAr), 1.35 (m, 8H, CH₂, δ to -OAr), and 0.91 (t, 6H, CH₃) ppm. Ms (m/z): 549 (10%), 205 (80%), 121 (85%).

2,5- Bis (4-hexyloxybenzoyloxy) hydroquinone (HQ6) 1.2 g (2 mmol) of 2,5-bis (4-hexyloxybenzoyloxy) benzoquinone was dissolved in a minimum amount of hot dioxane, and a 10-fold excess of Na₂S₂O₄ (10% aqueous solution) was added dropwise under vigorous stirring (Scheme II). A white product precipitated immediately. After the addition, the mixture was stirred for a further 30 min, and the product was collected by filtration, washed well with water, and then dried in vacuo. The white solid recrystallized from dioxane to give white crystals with 90% yield and mp: 187°C.

FTIR (KBr): $\bar{\nu}$ 3331(OH), 2942 and 2859 (CH₂), 1710(C=O), 1607 and 1511 (aromatic), 1263 to 1139 (C-O) cm⁻¹. ¹H NMR (DMSO-d₆): δ 9.73 (s, OH), 8.01 (d, 4H aromatic, meta to -OR), 7.06 (d, 4H aromatic, ortho to -OR), 6.57 (s, 2H, hydroquinone ring), 4.05(t, 4H, CH₂, α to -OAr), 1.71 (m, 4H, CH₂, β to -OAr), 1.40 (m, 4H, CH₂, γ to -OAr), 1.29 (m, 8H, CH₂, δ to -OAr), and 0.85 (t, 6H, CH₃) ppm. Ms (m/z): 549 (10 %), 205 (40%), 121 (85%).

Homopolyesters

The synthesis of polyester PHQ6 is described as a representative case. 0.46 g (0.8 mmol) of HQ6, 12 mg (0.009 mmol) of triethylamine hydrochloride and 10 mL of *o*-dichlorobenzene was placed in a flask. This mixture was heated to 180°C under nitrogen flow and a solution of 0.16 g (0.8 mmol) terephthaloyl dichloride in 10 mL of *o*-dichlorobenzene was added dropwise through a funnel. The mixture was stirred at 180°C until the evolution of hydrogen chloride ceased, for a period of about 5 h. The remained polymer dissolved in the hot solvent, but would be gelled if allowed to cool. The polymer was precipitated in *n*-hexane and washed with acetone (DMSO about pH6) and dried under vacuum for 48 h to give white powder with 92% yield. FTIR (KBr): $\bar{\nu}$ 2936 and 2862 (CH₂), 1746 (C=O), 1604 and 1506 (aromatic), 1251 and 1158 (C-O) cm⁻¹. ¹H NMR (CDCl₃): δ 8.08 (s, 4H terephthalate ring), 7.98 (d, 4H aromatic, meta to -OR), 7.52 (s, 2H hydroquinone ring), 6.84 (d, 4H aromatic, ortho to -OR), 3.99 (t, 4H, CH₂, α to -OAr), 1.80 (m, 4H, CH₂, β to -OAr), 1.44 (m, 4H, CH₂, γ to -OAr), 1.32 (m, 8H, CH₂, δ to -OAr), and 0.90 (t, 6H, CH₃) ppm.

For homopolymer **PH6**: Yield: 80%; FTIR (KBr): $\bar{\nu}$ 2924 and 2853 (CH₂), 1738 (C=O, terminal ester), 1715 (C=O internal ester), 1604 and 1502 (aromatic), and 1263 to 1160 (C-O) cm⁻¹.

¹H NMR (CDCl₃/C₆HOF₅): δ 8.37 (s, 4H terephthalate ring), 8.11 (d, 4H phenyl, ortho to -COOR), 7.35 (d, 4H phenyl, meta to -COOR), 4.45 (t, 4H, CH₂, α to -OCOPh), 1.90 (br, 4H, CH₂, β to -OCOPh), 1.62 (br, 4H, CH₂, γ to -OCOPh) ppm.

Copolyester (PHQ6-co-PH6)

A polymerization procedure similar to the homopolymerization was used for the synthesis of

copolyester. Copolymer with 50:50 mole ratio of HQ6:H6 (0.4 mmol) and terephthaloyl chloride (0.16 g, 0.8 mmol) was used. FTIR (KBr): $\bar{\nu}$ 2924 and 2854 (CH₂), 1741 and 1718 (C=O), 1605 and 1510 (aromatic), and 1260 to 1157 (C-O) cm⁻¹.

¹H NMR (CDCl₃/C₆HOF₅): δ 8.37 (s, H terephthalate ring), 8.28 (m, H terephthalate ring), 8.13 (dd, H phenyl, ortho to -COOR), 8.02 (t, H aromatic, meta to -OR), 7.55 (dd, H hydroquinone ring), 7.33 (dd, H phenyl, meta to -COOR), 6.90 (t, aromatic H, ortho to -OR), 4.41 (t, CH₂, α to -OCOPh), 4.05 (t, CH₂, α to -OAr), 1.89 (br, CH₂, β to -OCOPh), 1.81 (br, CH₂, β to -OAr), 1.59 (br, CH₂, γ to -OCOPh), 1.44 (br, CH₂, γ to -OAr), 1.30 (br, CH₂, δ to -OAr), and 0.87 (t, CH₃) ppm.

Methods

The following instrumentations were utilized for spectroscopic characterization: Melting points were recorded with an electrothermal 9100 apparatus. FTIR Spectra were recorded on a Bruker PS-15 spectrometer. ¹H NMR spectra were taken on a 400 MHz-Bruker SP-400 AVANC spectrometer using 50/50 pentafluorophenol-chloroform mixture as solvent with tetramethylsilane as internal standard. The inherent viscosity of the polymer solutions were measured in an Ubbelohde viscosimeter, at a concentration of 0.2 g/dL in *p*-chlorophenol at 45°C.

A Mettler 822 differential scanning calorimeter was used to determine phase transition temperatures at the heating and cooling rates of 10°C/min. The instrument was calibrated with indium regarding temperature and enthalpy. A Zeiss optical polarizing microscope equipped with long working distance objective was also used to observe phase transitions.

The samples were heated and cooled with a TMS94 hot stage and associated temperature controller. Mass spectrometry analysis was carried out using Sinnijan-MAT 8400, 70 eV apparatus.

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomers

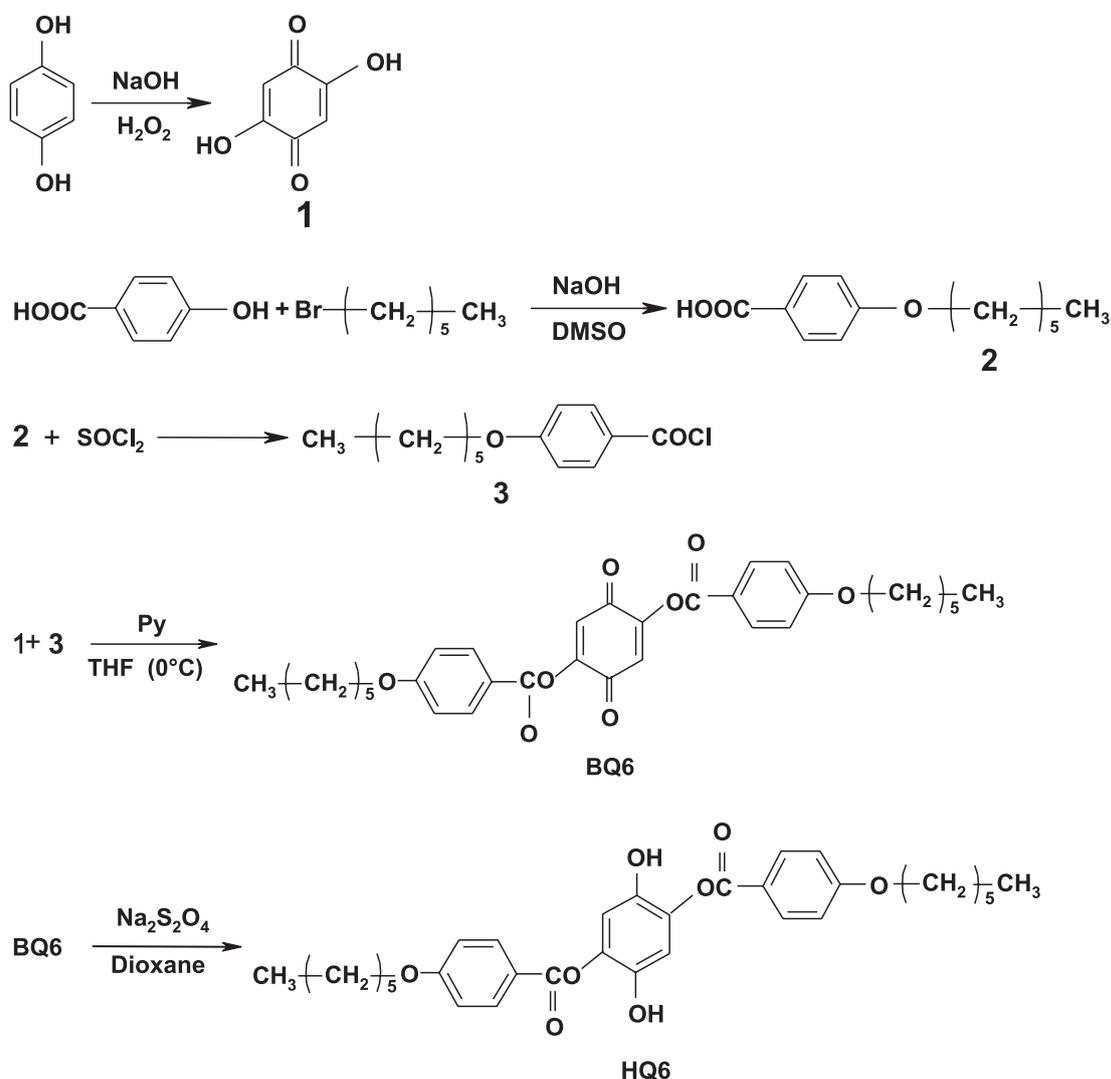
The monomer H6 was synthesized from 4-hydroxybenzoic acid and 1,6-dibromohexane in presence of KHCO₃ and DMSO solution in one step

(Scheme I). With the method shown in Scheme I, good yield was obtained with high grade purity compared with the method in the literature yielded in three steps [16].

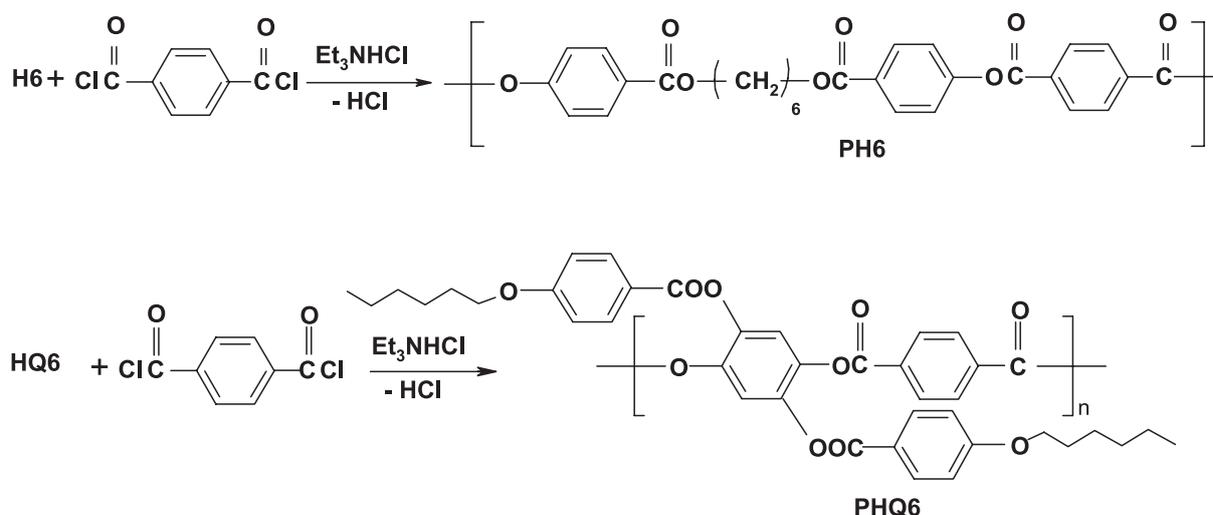
2,5-Bis(4-hexyloxybenzoyloxy) hydroquinone (HQ6) monomer was synthesized via multi-step routes from 2,5-dihydroxyquinone and 2,5-bis(hexyloxybenzoyloxy)benzoquinone by a method (Scheme II) described by Cao et al. [17]. 2,5-dihydroxyquinone was obtained by the hydrogen peroxide oxidation of hydroquinone in good yield [14]. In synthesizing compound BQ6, the purity of acyl chloride (compound 3) is important since, trace amounts of SOCl_2 may react with

2,5-dihydroxybenzoquinone resulting in black oily by-products or even a complete failure.

All of the monomers and their intermediates were proved via their structures by using FTIR, ^1H NMR, mass spectrometry (MS), etc. An optional polarizing microscope with a heating stage and DSC were used for measuring the melting temperature (T_m) and isotropization temperature (T_i) of the compounds. The low molecular compounds 4-hexyloxybenzoic acid (compound 2) and benzoquinone derivative (BQ6) showed mesogenic properties through DSC and observation by POM method. Upon heating and cooling, compound 2 and BQ6 were melted at 119°C and 106°C into a liquid crystal phase, respectively.



Scheme II. Synthesis of 2,5-bis(4-hexyloxybenzoyloxy) hydroquinone (HQ6).



Scheme III. Synthesis of homopolymers PHQ6 and PH6.

The Schlieren textures which were typically the features of the nematic liquid crystallines were observed. The isotropization was observed at 180 and 152°C, respectively (Table 2).

Synthesis and Characterization of Polymers

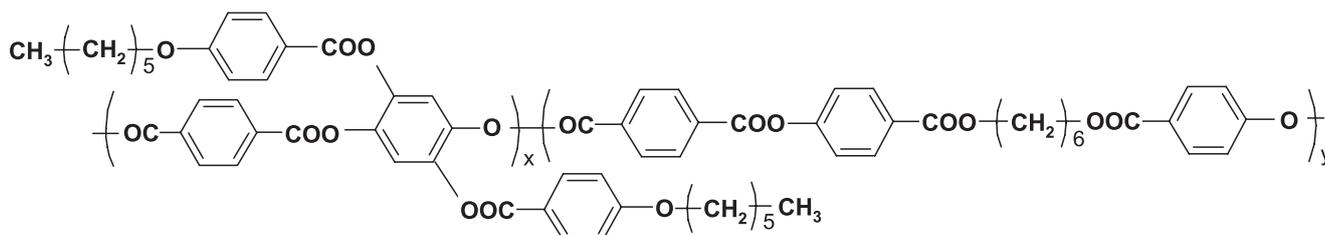
The homopolymers were synthesized according to the route outlined in Scheme III. A similar polymerization procedure to the homopolymers was used for the synthesis of copolyester. The chemical structure of copolymer is shown in Scheme IV.

The polyesters based on an alternating sequence containing a mesogenic triad unit with three aromatic rings and polymethylene flexible spacers have been described [18,19]. However, the molecular weights of these polymers were relatively low when was used the method of synthesis described by Lenz et al. [16].

In this work, high temperature solution polymerization of H6 monomer with terephthaloyl

chloride in the presence of triethylammonium hydrochloride (Et_3NHCl) catalyst was used [20]. The final product was white powder with good yield and high molecular weight which was determined from its inherent viscosity value. Polyesters containing the di-substituted hydroquinone were prepared by the same method. The molecular weight of polymers was estimated from the end group analysis by ^1H NMR [20]. For example, the intensity of the four aromatic protons peak of oxybenzoate unit at 7.98 ppm (ortho to $-\text{OR}$) and terephthaloyl unit at 8.08 ppm was used for the M_n estimation (Figure 1a).

The inherent viscosities of polymers were determined by an Ubbelohde viscosimeter at 45°C in *p*-chlorophenol. The molecular weights, average degree of polymerization (DP) and the solution viscosity value of polymers are listed in Table 1. These amounts show that the prepared polyesters containing the disubstituted hydroquinone are low



Scheme IV. Structure of synthesized copolyester PHQ6-co-PH6 ($x=0.5$ and $y=0.5$).

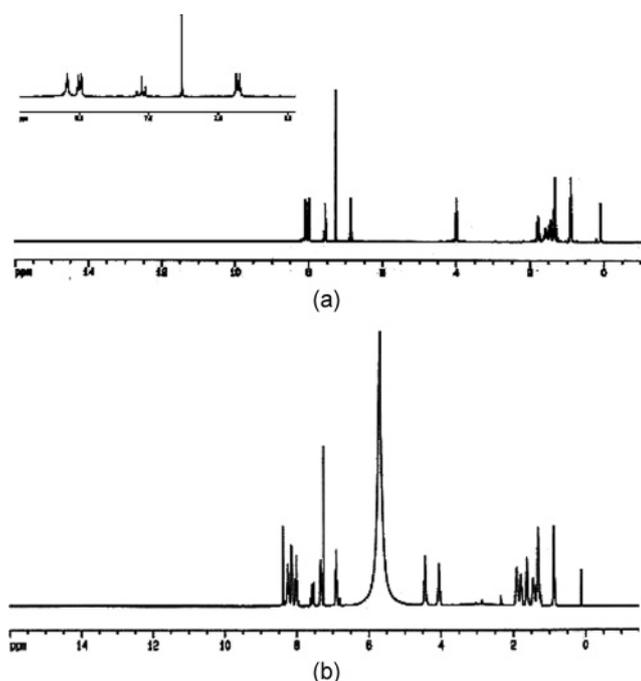


Figure1. ^1H NMR spectra of (a) PHQ6 in CDCl_3 and (b) PHQ6-co-PH6 in $\text{CDCl}_3/\text{C}_6\text{HOF}_5$.

molecular weight polymers. This can be explained by the steric hindrance of the bulky substituting groups on the hydroquinone ring near the hydroxyl groups in HQ6 monomer.

Composition of copolymer was also obtained from ^1H NMR spectrum as PHQ6-co-PH6 ($x:y=0.45:0.55$). The intensity of the peaks of copolymer at 4.05 and 4.41 ppm are due to the methylene protons of alkoxy end groups (α to $-\text{OAr}$) and backbone of the polymer (α to $-\text{OCOAr}$), respectively (Figure 1b). The PH6 polyester was insoluble in common organic solvents whereas the PHQ6-co-PH6 copolymer had

Table1. Molecular weight and inherent viscosity of polyesters.

Polyesters	η_{inh} (dl/g) ^a	M_n (g/mol)	DP ^b	Yield (%)
PH6	0.67	-	-	80
PH6 ^c	0.276	-	-	75
PHQ6	0.42	4800	6	92
PHQ6-co-PH6	0.40	3000	4	85

(^a) inherent viscosity of polymers measured in Ubbelohde viscosimeter, at a concentration of 0.2 g/dL in *p*-chlorophenol at 45°C. (^b) Estimated from end group analysis by ^1H NMR. (^c) Ref. [16].

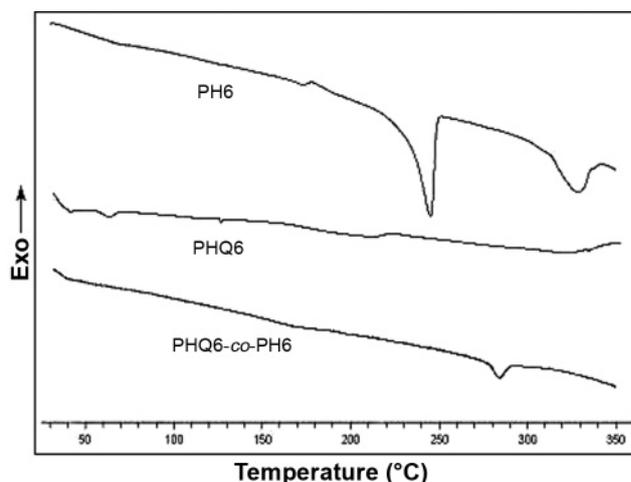


Figure2. DSC thermograms for polyesters PH6, PHQ6 and copolyester PHQ6-co-PH6.

good solubility in DMSO as well as in hot chloroform. PHQ6 Was soluble in chloroform at room temperature. It can be concluded that the polymers become more soluble with the increased content of end substituted hexyloxy groups on the lateral rods [17].

Liquid Crystalline Properties

In order to study the lateral substitution effect on liquid crystallinity, we examined thermal properties and mesomorphic behaviour in polyesters by DSC measurement and optical microscopy with a heating rate 10°C/min. The DSC thermograms of representative polymers are given in Figure 2. Their phase transition temperatures of first heating scan are listed in Table 2. The DSC thermograms of the PH6 show two endothermic peaks corresponding to T_m and T_i transitions, respectively. As shown in the Table 2, the PH6 that we prepared has higher molecular weight in comparison with the sample prepared by Lenz et al. [16]. Increasing the molecular weight leads to a shift of the melting and isotropization temperatures to the higher values.

The polyester of PH6 may be modified by the introduction of a rigid lateral group on hydroquinone ring in the suitable proportion. Therefore, we have investigated how the HQ6 unit in PHQ6-co-PH6 ($x=0.5$) can be tolerated in liquid crystalline polyester. First, we consider the PHQ6 homopolyester without rigid rod moiety along the backbone of the polymer. The DSC thermograms of the PHQ6 show an initial

Table 2. Phase transition temperatures of the polyesters determined by DSC at scan rate 10°C/min on the first heating scan and microscopy observation.

Material	Thermal transition from DSC (°C, J/g)							Thermal transition from optical Microscopy (°C)			
	T _g	T ₁	T ₂	T ₃	ΔH ₁	ΔH ₂	ΔH ₃	K→K	K→LC	LC→LC ^a	^d LC→I
PH6	52	248	330	-	24.45	11	-	-	250	-	340
PH6 ^b	-	227	290	-	-	0.54	-	-	227	-	290
II	-	60.5	106	152	21.7	57.8	13.8	61	112	-	155
BQ6	-	98	119	180	16	60	58	112	123	-	185
PHQ6	100	200	324	-	2.74	14.55	-	-	210	330	Dec. ^d
PHQ6-co-PH6	85	160	284	-	n.s. ^c	2.16	-	-	150	300	Dec. ^d

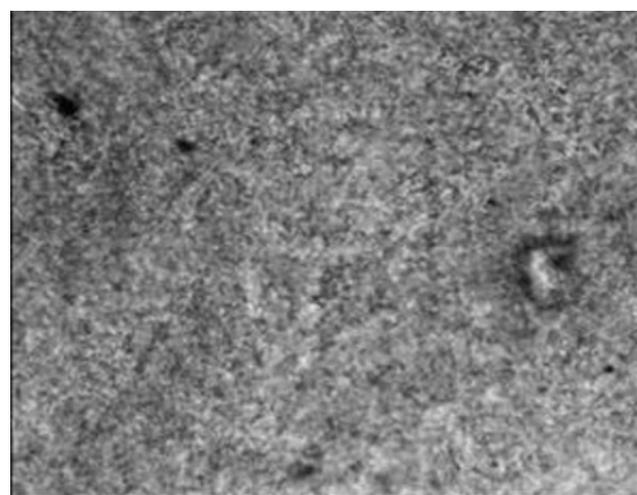
(^a) LC texture changes from dense nematic thread to highly birefringent Schliere pattern. (^b) Ref. [16]. (^c) Negligibly small. (^d) Decomposition.

base line shift along with two endothermic peaks corresponding to T_g and T_m transitions. The PHQ6 homopolymer has higher T_g than PH6 homopolymer.

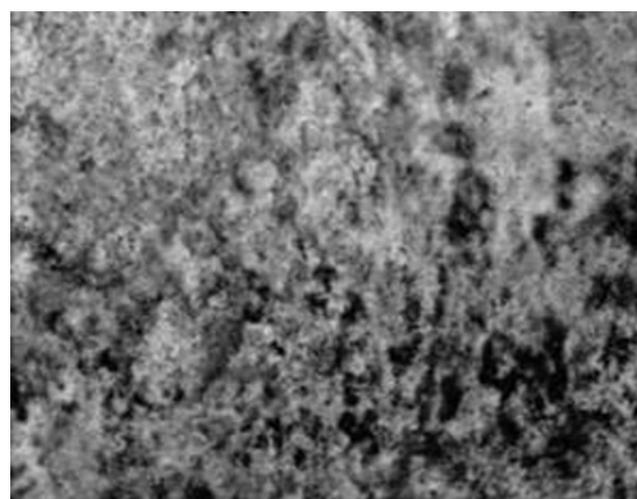
The rigidity of the backbone together with the presence of the rigid aromatic substituent results in high T_g values for PHQ6 homopolymer. In the thermogram of PHQ6 polyester is seen an extremely broad endotherm peak at 324°C, which is followed by another broad endotherm peak at about 200°C. These endothermic transitions were identified by OPM observation. The first transition corresponds to a crystal-nematic transition of the LC polyester. The second endotherm is a transition from one LC phase to another LC phase which is characterized by a change from dense threaded nematic texture (Figure 3a) to a highly birefringent Schliere texture (Figure 3b). This transition is accompanied by a decrease in the melt viscosity and subsequently easier flow of the polymer. The DSC thermograms did not show the endothermic peak for isotropization up to decomposition degradation temperature of 400°C. This drop in viscosity observed for polyester PHQ6 and copolymer is characteristic of the nematic transition and was also reported in the other polyesters [21].

In the thermogram of copolymer containing both rigid lateral and rigid rod like moiety along the backbone of the polymer, PHQ6-co-PH6, the very broad endotherm peak has apparently shifted to lower temperature of about 160°C. A higher temperature well defined endotherm peak is appeared at 284°C.

On the OPM analysis the onset of flow occurred at 150°C and the birefringence intensity increased

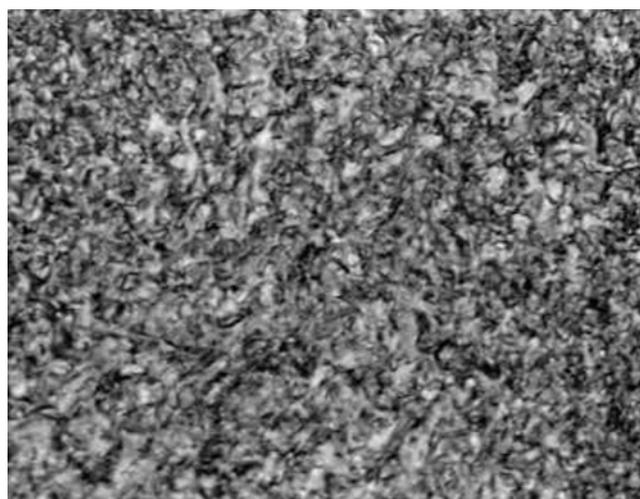


(a)

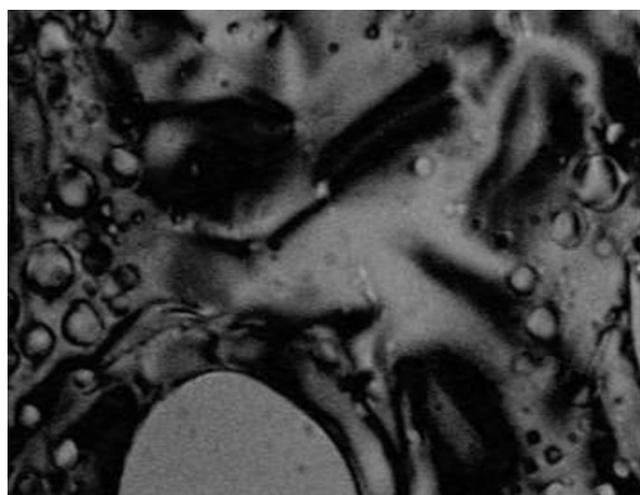


(b)

Figure 3. Optical polarized micrographs for PHQ6 (magnification 200x) (a) 250°C; (b) 330°C.



(a)



(b)

Figure 4. Optical polarized micrographs of PHQ6-co-PH6 at (a) 180°C and (b) 300°C (magnification 200x).

about 300°C. The melting temperature of copolymer was almost 88°C and 40°C lower than that of each of PH6 and PHQ6 homopolymers, respectively. Another point worthy of notice from Table 2 is that the T_g value of copolymer is almost between those of PHQ6 and PH6, which is a distinct feature of random copolymers.

Figure 4 shows the changes which occurred in the appearance of PHQ6-co-PH6 on the OPM observations with increasing temperature. In Figure 4 it can be seen the change in appearance of polymers from the highly threaded texture (Figure 4a) to the Schliere texture (Figure 4b).

CONCLUSIONS

Two new thermotropic polyester and copolyester containing the 2,5-bis(4-hexyloxybenzoyloxy) hydroquinone moieties were synthesized by high temperature solution polymerization. The polyesters showed a nematic texture under crossed polar and a transition from a dense threaded nematic texture to a highly birefringent Schliere pattern at high temperatures. Due to the rigidity of the main chain and the presence of the rigid substituents on the hydroquinone unit, the glass transition temperature of polyesters was rather high. The melting point of copolyester was lower than that of the homopolyester. The isotropization temperatures, was not found with the polymers.

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