Novel Wholly Aromatic Lyotropic Liquid Crystalline Polyesters. Synthesis, Characterization, and Solution Properties

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ABSTRACT: Three wholly aromatic polyesters containing sulfonate pendent groups have been synthesized by an interfacial polycondensation technique from hydroquinonesulfonic acid potassium salt and diacid chlorides. These polymers were characterized structurally using FTIR and solid-state CP/MAS ^{13}C NMR. They show varying degrees of solubility in aqueous DMSO and aqueous DMF and are most soluble in 1:1 DMSO/H_2O. Viscosity measurements of dilute solutions at concentrations less than 0.5 g/dL show a polyelectrolyte effect. The solution-phase behavior of these polyesters has been studied microscopically using aqueous DMSO, aqueous DMF, and pure DMSO, DMF, and water as solvent under crossed polarizers. Polymer 3 with a nitro group on the diacid unit shows lyotropic liquid crystal behavior in these solvent systems except in pure DMSO. The critical concentration required for formation of an anisotropic solution falls as the water content in aqueous DMSO solution increases. These polyesters decompose upon heating at high temperature and do not show thermotropic liquid crystal transitions in the solid state.

Introduction

Liquid crystalline main-chain aromatic polycondensation polymers have been the focus of much interest from industry and academe since the development and commercialization of the lyotropic liquid crystalline polyamide Kevlar (DuPont) and the thermotropic liquid crystalline polyester Vectra (Celanese).[1] Formation of a liquid crystal phase allows the fabrication of ultrahigh-strength and -modulus Kevlar fibers from concentrated solution, and the production of the high-strength engineering plastic Vectra by melt processing. The fabrication of these polymers, although feasible, nevertheless needs drastic conditions, for example, use of corrosive concentrated sulfuric acid or high boiling point amide solvents (*N*-methylpyrrolidone, hexamethylphosphoramide) to prepare polyamide solutions[1d] or a high temperature for the thermotropic liquid crystal phase of polyesters to form. Thus main-chain aromatic polycondensation polymers which form a liquid crystalline solution in common organic solvents or water or which have a lower thermotropic liquid crystal transition temperature would facilitate the fabrication, processing, and application of these polymers. As far as lyotropic liquid crystalline polymers are concerned, those polymers forming a mseomorphic phase in common organic solvents may find application in the areas of films, coatings, barrier membranes, polymer blends, and composites.[2] On the other hand, polymers with a lower thermal transition temperature might lead to easier thermal processability.

We have been attempting to synthesize polyesters and polyamides which form liquid crystals in common organic solvents or water. Some progress has been made in the case of polyamides either by modifying the amide function[3a,b,5] or by introducing appropriate substituents onto the aromatic units of the polymer backbone.[2,4,6] We have recently reviewed this progress.[7] Lyotropic aromatic polyesters are less well-known. In the early eighties, Polk et al. reported the preparation of a series of copolyesters containing cyclohexane and benzene rings.[8a–c] Some of these were shown to form mesomorphic solutions in a tetrachloroethane–*o*-chlorophenol–phenol mixture or in *o*-chlorophenol. Ogata et al. synthesized copolyesters from 4-hydroxybenzoic acid and 3,5-dimethyl-4-hydroxybenzoic acid.[9] These proved to be soluble in monochloroacetic acid or *o*-chlorophenol, and concentrated solutions of these copolymers showed liquid crystal behavior. No detailed study was described. However, most recently, Heitz et al. have synthesized a large number of substituted poly(*p*-phenylene terephthalate)s in order to achieve solubility and lyotropic liquid crystallinity in common organic solvents as well as thermotropic behavior at lower transition temperatures.[10] Hydroquinone substituted with phenylalkyl ($Ph(CH_2)_n$ ($n = 1$–3)), *tert*-butyl, and phenoxy groups was used along with terephthalic acid substituted with bromo, chloro, trifluoro, phenyl, phenylethyl, and 2-biphenyl groups. Solubility in *p*-chlorophenol, diphenyl ether, and chloroform has been achieved. The polyester with a *tert*-butyl group on the hydroquinone unit and a phenylethyl residue on the diacid unit forms a liquid crystal solution in diphenyl ether but not in chloroform or tetrahydrofuran (THF). It is believed that this is because the formation of a lyotropic liquid crystalline phase depends on the overall chain rigidity in solution and therefore on the nature of solvent.

In the search for polyesters and polyamides forming a liquid crystal phase in common solvents, we believe that the prospects will be enhanced with polymers prepared from monomers with substituents which not only disrupt the main-chain regularity of the analogous unsubstituted polymers but which also offer the possibility of strong

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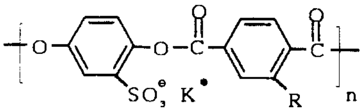
interaction with solvents. In the case of polyamides, the substituents on the monomer units should also help to decrease to some extent the strong intermolecular hydrogen bonding between the amide functions on the polymer chains.

In the present article, the synthesis and characterization of ionic wholly aromatic polyesters of the following general structure are described. These have been prepared from commercially available hydroquinonesulfonic acid potassium salt in combination with different aromatic dicarboxylic acid chlorides via an interfacial polycondensation procedure. The solution-phase behavior of these polyesters has also been studied in aqueous organic solvents of different compositions as well as in pure dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and water.



Polyester 1 (R=H); 2(R=Br); 3(R=NO_2)

Experimental Section

Materials. The chloroform used in the interfacial polycondensation was purified by refluxing with calcium chloride followed by fractional distillation. DMF (99%) and DMSO (99%) were purchased from Aldrich and used as received. Lithium chloride (Fisons), sodium hydroxide (Fisons), and benzyltriethylammonium chloride (99%, Aldrich) were used as received. Thionyl chloride (FSA Laboratory Supplies) was freshly distilled before use. Hydroquinonesulfonic acid potassium salt (technical grade, Aldrich) was recrystallized from water before use. Terephthaloyl chloride (99%, Aldrich) was sublimed twice before use. 2-Bromoterephthalic acid (97%, Aldrich) was used as received. Nitroterephthalic acid was obtained by hydrolysis of dimethyl nitroterephthalate (99% Aldrich) with sodium hydroxide in ethanol. It is now available from Aldrich.

Monomer Synthesis. 2-Bromoterephthaloyl Chloride (4). A mixture of 3 g (12.2 mmol) of 2-bromoterephthalic acid and 20 g (168 mmol) of thionyl chloride was heated to reflux and maintained for 15 h. The solution was then cooled, excess thionyl chloride was removed, and the residue was distilled under vacuum: yield 3.1 g (90%), bp 130 °C (0.2 mmHg); ^1H NMR ($CDCl_3$), ppm) 8.0 (1 H, dd, H_6, $J_{6-5} = 8.3$ Hz, $J_{6-3} = 0.3$ Hz), 8.2 (1 H, dd, H_5, $J_{5-6} = 8.3$ Hz, $J_{5-3} = 1.8$ Hz), 8.4 (1 H, dd, H_3, $J_{3-5} = 1.8$ Hz, $J_{3-6} = 0.3$ Hz); ^{13}C NMR ($CDCl_3$, ppm) 121.1, 129.9, 132.0, 136.7, 137.4, 141.2, 165.8, 166.4; IR (film on KCl) 1780, 1748 ($\nu_{C=O}$), 1194, 679. Anal. Calcd for $C_8H_3O_2Cl_2Br$: C, 34.1; H, 1.1; halogen as Br, 85.0. Found: C, 34.0; H, 0.9; halogen as Br, 84.0.

2-Nitroterephthaloyl Chloride (5). 2-Nitroterephthalic acid (2 g, 9.5 mmol) was refluxed with 13 g (109 mmol) of thionyl chloride for 6 h. The solution was cooled and concentrated, and the residue was distilled under vacuum: yield 2.2 g (85%), bp 180 °C (1 mmHg); ^1H NMR ($CDCl_3$, ppm) 7.9 (1 H, dd, H_6, $J_{6-3} = 0.4$ Hz, $J_{6-5} = 8.1$ Hz), 8.5 (1 H, dd, H_5, $J_{5-3} = 1.8$, $J_{5-6} = 8.1$ Hz), 8.8 (1 H, dd, H_3, $J_{3-5} = 1.8$ Hz, $J_{3-6} = 0.4$ Hz); ^{13}C NMR ($CDCl_3$, ppm) 127.1, 128.9, 136.2, 137.0, 137.3, 145.1, 165.0, 165.9; IR film on KCl) 1792, 1761 ($\nu_{C=O}$), 1544, 1350 (ν_{NO2}), 843, 765. Anal. Calcd for $C_8H_3NO_4Cl_2$: C, 38.7; H, 1.2; N, 5.6; Cl, 28.6. Found: C, 38.9; H, 1.2; N, 5.7; Cl, 28.8.

Polymer Synthesis. The interfacial polycondensations were carried out in a silanized flask equipped with a mechanical stirrer under vigorous agitation (1500 rpm). A typical polycondensation procedure is described using the preparation of polyester 3 as an example.

Poly(sulfo-*p*-phenylene nitroterephthalate) (3). Sodium hydroxide (0.53 g, 13.2 mmol), hydroquinonesulfonic acid potassium salt (1.50 g, 6.57 mmol), and 5 mL of distilled water were placed in a 100-mL three-necked silanized flask equipped with a mechanical stirrer and a nitrogen inlet. The mixture was stirred under nitrogen until a dark brown solution was obtained. To this, 1.63 g (6.59 mmol) of 2-nitroterephthaloyl chloride in 30 mL of $CHCl_3$ was added in one portion, followed by 0.30 g (1.33 mmol) of benzyltriethylammonium chloride dissolved in 1 mL of water, and the mixture was stirred vigorously. A precipitate formed immediately after addition of 2-nitroterephthaloyl chloride, and the color changed from brown to green-brown and then gray within 10 min. Vigorous stirring was maintained for another hour during which the color changed further to a lighter gray. Then the mixture was poured into 400 mL of methanol, and the solid was filtered off, washed with methanol, and dried in vacuo at 80 °C for several hours. It was then washed again with a mixture of MeOH/water (3:1) and then MeOH and finally dried again for 15 h under vacuum at 80 °C: yield 0.93 g (34%); inherent viscosity (DMSO/H_2O (1:1)/0.1% LiCl) $\eta_{inh(C=0.2\ g/dL)} = 0.45$ dL/g; IR (KCl) 1748 ($\nu_{C=O}$ ester), 1540, 1354 (NO_2), 1235, 1076 (SO_3^-), 620 (SO_3^-). Anal. Calcd for $(C_{14}H_6NSO_7K)_n$: C, 41.7; H, 1.5; N, 3.5; S, 8.0. Found: C, 41.9; H, 1.9; N, 3.4; S, 7.6; Cl, 0.8.

Large-scale synthesis 32 mmol of monomer gave 40% yield and $\eta_{inh(C=0.2\ g/dL)} = 0.22$ dL/g in duplicate preparations.

Polyesters **1** and **2** were synthesized according to the same procedure with similar monomer and phase transfer catalyst concentrations and isolated as described.

Poly(sulfo-*p*-phenylene terephthalate) (1): yield 53%; inherent viscosity (DMSO/H_2O (1:1)/0.1% LiCl) $\eta_{inh(C=0.2\ g/dL)} = 0.48$ dL/g; IR (KCl) 1734 ($\nu_{C=O}$ ester), 1239, 1071, 629 (SO_3^-). Anal. Calcd for $(C_{14}H_7SO_7K)_n$: C, 46.9; H, 2.0; S, 9.0. Found: C, 46.8; H, 2.2; S, 9.3; N, nil; Cl, nil.

Poly(sulfo-*p*-phenylene bromoterephthalate) (2): yield 45%; inherent viscosity (DMSO/H_2O (1:1)/0.1% LiCl) $\eta_{inh(C=0.2\ g/dL)} = 0.27$ dL/g; IR (KCl) 1740 ($\nu_{C=O}$ ester), 1232, 1071, 626 (SO_3^-). Anal. Calcd for $(C_{14}H_6SBrO_7K)_n$: C, 38.4; H, 1.4; S, 7.3; halogen as Br, 18.3. Found: C, 39.8; H, 2.0; S, 6.7; halogen as Br, 17.2; N, nil.

Characterization. Inherent viscosities of polyesters were measured at 30 °C with an Ubbelohde viscometer at a concentration of 0.2 g/dL in 1:1 DMSO/H_2O in the presence of 0.1% w/v of LiCl (5 equiv of calculated $SO_3^-K^+$). Nuclear magnetic resonance (NMR) spectra of monomers were obtained in deuteriochloroform as solvent on a Bruker AMX-400 spectrometer, with carbon-13 spectra taken at 100.6 MHz. The spectra were referenced to a resonance from residual chloroform assigned a chemical shift of 7.27 ppm for ^1H NMR and 77.0 ppm for ^{13}C NMR. Cross-polarization magic angle spinning (CP/MAS) solid-state NMR was carried out on a Bruker MSL 100 at 25.2 MHz and referenced externally to tetramethylsilane (TMS). Infrared spectra were recorded from KCl disks with a Nicolet SXB Fourier transform infrared (FTIR) spectrometer. Differential scanning calorimetry (DSC) data were obtained on a DuPont 9900 thermal analyzer with the DuPont 910 differential scanning calorimeter under a nitrogen atmosphere with heating rates of 20 °C/min. Optical microscopy was performed on an Olympus polarizing microscope, and a Linkam TH600 hot stage was used in the high temperature phase behavior studies, with heating and cooling rates of 10 °C/min. Elemental microanalyses were obtained from the microanalysis service of the Department of Pure and Applied Chemistry, University of Strathclyde. Qualitative solubility tests of polyesters were conducted with polymer concentrations of approximately 1–2% (w/v) at room temperature. Solutions of polyesters for the phase studies on an optical microscope were prepared by mixing known quantity of polymer and solvent and then shaking for 2 days.

Results and Discussion

Polycondensation. Aromatic polyesters (polyarylates) are usually prepared by melt polycondensation at high temperature,[11a] solution polycondensation,[11a,b] or interfacial polycondensation methods.[11c,d] High-temperature polycondensation of a dicarboxylic acid with the diacetate of a diphenol is the most convenient and the least expensive method of synthesis.[11e] A melt polycondensation procedure developed by Kricheldorf's research group involving a silylated diphenol and a diacid chloride has also proved to be very useful.[11f] Solution polycondensation reactions involving a diphenol and a diacid chloride are commonly used. It is also possible to react a diphenol directly with

Table I
Synthesis of Polyester 1 by Interfacial Polycondensation[a]

entry	mL of H_2O/g of NaOH	polymer yield (%)	η_{inh}[b] (dL/g)	polymer microanal.[c] % C	% H	% S	Δ(% C)[d]
1	13	49	0.24	45.2	2.4	8.6	1.7
2[e]	13	64	0.26	45.0	2.6	8.3	1.9
3[f]	13	31	0.60	45.4	2.4	8.4	1.5
4	100	40	0.18	44.4	2.2	8.7	2.5

[a] Polycondensation using equal equivalents of hydroquinonesulfonic acid potassium salt and terephthalic acid chloride, 2 equiv of NaOH, 0.2 equiv of $BzEt_3N^+Cl^-$, and $CHCl_3$ as organic solvent in an untreated glass flask at room temperature. [b] Inherent viscosity measured in DMSO/water (1:1)/0.1% LiCl at 30 °C with a polymer concentration of 0.2 g/dL. [c] Calculated values (%) for polyester 1 ($(C_{14}H_7SO_7K)_n$): C, 46.9; H, 2.0; S, 9.0. [d] $\Delta(\%\ C) = \%\ C_{calcd} - \%\ C_{found}$. [e] With a mechanical stirring speed of 1500 rpm. [f] DMF (mL/mmol of monomer = 5) was added 5 min after the precipitate formed.

Table II
Synthesis of Polyesters 1–3 by Interfacial Polycondensation[a]

polyester	yield (%)	η_{inh}[b] (dL/g)	microanal.[c] % C	% H	% S	% N	% X
1	53	0.48	46.8	2.2	9.3	nil	nil[d]
			(46.9)	(2.0)	(9.0)		
2	45	0.27	39.8	2.0	6.7	nil	17.2[e]
			(38.4)	(1.4)	(7.3)		(18.3)
3	34	0.45	41.9	1.9	7.6	3.4	0.8[d]
			(41.7)	(1.5)	(8.0)	(3.5)	

[a] Polycondensation using equal equivalents of hydroquinonesulfonic acid potassium salt and diacid chloride, 2 equiv of NaOH, 0.2 equiv of $BzEt_3N^+Cl^-$, and $CHCl_3$ as organic solvent in a silanized flask with a mechanical stirring speed of 1500 rpm. [b] Inherent viscosity measured in DMSO/water (1:1)/0.1% LiCl at 30 °C with a polymer concentration of 0.2 g/dL. [c] Numbers in parentheses are calculated values. [d] Chlorine content. [e] Total halogen content as bromine.

a diacid in the presence of an activating reagent which can react with the diacid to form an active intermediate diester. The latter then reacts with the diphenol. For example, Ogata et al. have used as an activating agent triphenylphosphine dichloride formed from triphenylphosphine and oxalyl chloride.[12]

In our case, the diphenol monomer chosen was hydroquinonesulfonic acid potassium salt, which does not melt but decomposes at high temperature (251 °C). This prevented us from using any high temperature melt procedure. In addition, the solubility of this monomer in the common organic solvents (chlorinated solvents, pyridine, etc.) employed in solution polycondensation reactions is very low, but it is very soluble in water. Therefore we considered using an interfacial polycondensation procedure, in which the diphenol is dissolved in water in the presence of a base such as sodium hydroxide and reacted with a diacid chloride dissolved in a chlorinated solvent, chloroform in this instance. No attempt was made to optimize the solvent, and it might be that a more polar species, e.g., 2,4-dimethyltetramethylene sulfone, might be more effective in terms of yielding higher molecular weight products (see below). A phase transfer catalyst is usually used to accelerate the rate of reaction and to minimize the secondary reactions such as hydrolysis of diacid chloride. In this polycondensation method, many factors can influence the molecular weight of the polymer.[11c,d] The most important are, for example, the concentration of the monomer in the water phase, of the monomer in the organic phase, and of the phase transfer catalyst; the chemical nature of the phase transfer catalyst; the relative volume of water and organic solvent; the stirring speed; the solubility (swellability) of the growing polymer, and the partition of monomers between the bulk phases and the interface. We were guided by the procedure used by Nayak et al. in the synthesis of poly[4,4′-thiobis(phenyl phthalate)][13] and first examined different polycondensation conditions in the preparation of polyester 1 using a flask made from untreated glass. The results of reactions using equal equivalents of diphenol and diacid chloride, 2 equiv of sodium hydroxide, and 0.2 equiv of benzyltriethylammonium chloride are summarized in Table I.

During this procedure, a precipitate is formed immediately after the mixing of the two monomers, and this tends to adhere to the glass surface rather than remaining in the organic phase or as a fine suspension. As a result, the stirring was rendered ineffective almost at once and low molecular weight polymer was obtained. For example, polyester 1 with an inherent viscosity η_{inh} = 0.24 dL/g was obtained in 50% yield using a volume of water/weight of NaOH = 13 (entry 1). The use of high-speed stirring with a mechanical stirrer did not improve the result as can be seen from entry 2, where the viscosity is only slightly higher (0.26 dL/g). In one experiment therefore (entry 3), DMF (mL/mmol of monomer = 5) was added 5 min after the precipitate formed in order to bring the latter into suspension. Polyester 1 with a much improved inherent viscosity η_{inh} = 0.60 dL/g was obtained, but with a lower yield (30%). When a much higher ratio, volume of water/weight of NaOH, was used in the preparation, a suspension of polymer did form, but this proved to be of low viscosity (0.18 dL/g) (entry 4). Possibly considerable hydrolysis occurs in this case. An alternative approach to the "postaddition" of DMF is to make the glass surface hydrophobic by silanizing it. This does yield a fine polymer suspension, and the results are shown in the Table II.

In the case of polymer 1 a good balance is obtained between the yield (53%) and the viscosity (0.48 dL/g), and likewise for polymers 2 and 3. There is also good correlation of the microanalytical data with the theoretical data with the theoretical values. From the nitrogen and chlorine contents it can be seen that the quantity of residual phase transfer catalyst in these polymers is rather low. Though we have formulated these polymers as K^+ salts, partial ion exchange may give rise to some Na^+, and indeed $PhCH_2Et_3N^+$, content. This possibility is presently being investigated further. The workup of these polymers is difficult because of their solubility in water. A mixture of MeOH/water (3:1) had to be used to try to extract the phase transfer catalyst and the sodium chloride formed in the reaction. The wet polyesters as formed proved to be even more soluble than when first dried. Therefore washing with MeOH/water (3:1) was performed after drying to minimize material loss. At this stage in our work, the yields are still unsatisfactory for large-scale preparation of these polymers, and in this respect the preparations are not fully optimized. However, the procedure is sufficiently robust to provide reproducibly sufficient material for physical characterizations. By employing silanized glassware and efficient stirring, a discrete polymer suspension can be maintained; however, the growth of macromolecular chains might still be difficult if the propagating polymer is not swollen by the organic solvent. If instead it is swollen preferentially by water, then excessive hydrolysis of the terminal acid chloride groups can result. Material loss during the workup is also a factor accounting for the low yields.

Molecular Weight and Structural Characterization. The preliminary qualitative solubility tests show that these polyesters are most soluble in 1:1 DMSO/water compared to pure DMSO, DMF, or water. Therefore

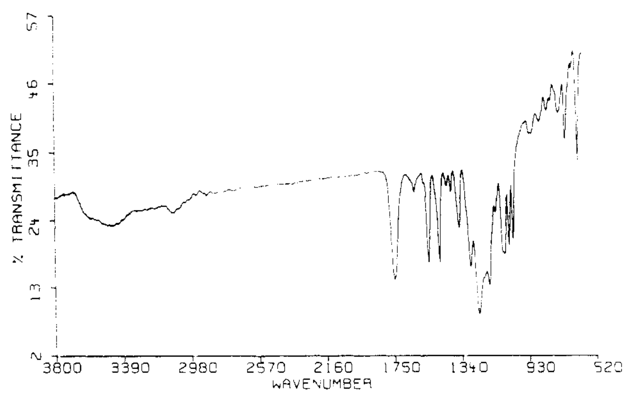


Figure 1. FTIR spectrum of polyester 3.

viscosity measurements were conducted in this mixture. The results in the 0.2 g/dL concentration range showed a polyelectrolyte effect as a result of the potassium sulfonate groups on the polymer chains. In the measurements of the viscosity of polyester 1 of different molecular weights, the addition of 0.1% of LiCl sometimes eliminated the polyelectrolyte effect, but sometimes not. We decided therefore to use the inherent viscosity at 0.2 g/dL in the presence of 0.1% of LiCl in DMSO/water (50 vol %) as a relative measure of the polymer molecular weight to assess the success of the poycondensation. The other important criterion was the microanalysis, especially the carbon content. Aqueous phase gel permeation chromatography of one sample of polyester 1 was also conducted. An Aquagel column was employed and calibrated with poly(ethylene oxide) and poly(ethylene glycol) standard samples of molecular weight in the range 1470–50 400. For polyester 1 with an inherent viscosity $\eta_{\mathrm{inh}(C=0.2\ \mathrm{g/dL})}$ = 0.60 dL/g, a number-average molecular weight M_n = 73 600, a weight-average molecular weight M_w = 77 100, and a polydispersity of 1.05 were obtained. It seems that the hydrodynamic volume of this polyester is very high, probably due to the high solvation of the polymer in water and the strong intermolecular interaction between the ionic sulfonate groups, leading to chain aggregation. Similar water phase behavior has been observed by Reynolds et al. with poly[(*p*-phenyleneterephthalamido)propanesulfonate].[5] Attempts to use a phosphate buffer solution (pH = 7) in the presence of sodium nitrate as solvent to conduct the gel permeation chromatography measurements were not successful, because polyester 1 could not be solubilized in this medium. Vapor pressure osmometry has previously been used successfully in the measurement of the absolute number-average molecular weight of numerous polyesters using chlorinated solvents or DMF etc.[13,14] In this work difficulties have been encountered in attempting to measure M_n of polyester 1 (η_{inh} = 0.60 dL/g) in the mixture DMSO/water (50 vol %) since the solubility of the polymer is not sufficiently high.

FTIR spectra of polyesters 1–3 show absorptions typical of the functional groups expected: C=O of the ester group near 1740 cm^{-1}; SO_3^- near 1235, 1070, and 630 cm^{-1}; and NO_2 near 1540 and 1350 cm^{-1}. The spectrum of polyester 3 is shown in Figure 1.

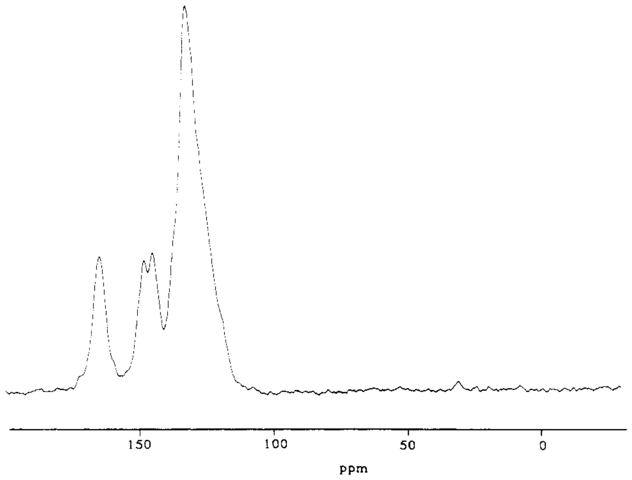


Figure 2. Solid-state CP/MAS ^{13}C NMR spectrum of polyester 1.

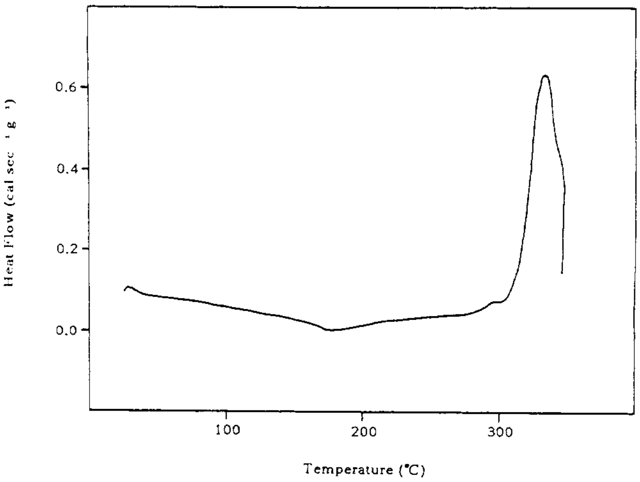


Figure 3. DSC heating curve for polyester 3.

Polyesters 1 (η_{inh} = 0.48 dL/g), 2 (η_{inh} = 0.27 dL/g), and 3 (η_{inh} = 0.45 dL/g) are soluble enough in DMSO-d_6/D_2O (50 vol %) for NMR measurements to be made at 400 MHz. However, the carbon-13 spectra showed a low signal-to-noise ratio. Hence, solid-state CP/MAS carbon-13 NMR spectra were also obtained directly from powder samples. The spectrum of polyester 1 is shown in Figure 2. The ester carbonyl carbon at 164.9 ppm, the quaternary aromatic carbons at 148.2 and 145.1 ppm, and the aromatic tertiary carbons at 132.5 ppm can be clearly identified. Interestingly, a small peak at 31.1 ppm is also present. Furthermore, in the solution ^{1}H NMR spectrum, peaks from protons attached to aliphatic carbon are also apparent. This can be attributed to residues of the phase transfer catalyst, benzyltriethylammonium chloride, the cation of which may be ion-paired with the polymer-bound SO_3^- group. The quantities however are very small as confirmed by the elemental analyses.

Differential scanning calorimetry measurements were performed on the three polyesters over the temperature range 30–400 °C under nitrogen. Polyester 3 with nitro substituents showed a large exothermic peak with an onset temperature of 315 °C (Figure 3).

Similar thermal behavior of a nitro-substituted polymer has been observed by Chaudhuri et al. with their aromatic polyamides made from 2-nitro-*p*-phenylenediamine.[15] In their work, this exothermic peak was correlated with the weight loss in the same temperature range, and it was suggested that the effect was associated with some chemical reaction and not attributed to crystallization. In our case, this transition appeared at lower temperature. For polyesters 1 and 2, a large endothermic transition was observed around 125 °C extending to ca. 230 °C; then further decomposition occurred from 370° and 270 °C for polyesters 1 and 2, respectively. None of the polyesters showed thermal transitions in the DSC which could be attributed to thermotropic liquid crystal behavior.

Phase Behavior. The formation of liquid crystalline solutions of aromatic polycondensation polymers is complex and determined by several key factors.[1h,16] The polymers generally should have a rodlike structure with an extended rigid chain character to facilitate the alignment of the macromolecular chain along a particular direction. The solubility needs to be sufficiently high to exceed the critical concentration at which the formation of a biphasic solution (i.e., a liquid crystal coexisting with an isotropic phase) occurs. The degree and nature of the interaction between the macromolecular chains themselves and that between the chains and solvent molecules can also provide a major influence on the phase behavior of the polymers. The solubility and chain stiffness of a polymer are themselves affected by the polymer microstructure, molecular weight, polymer–polymer and polymer–solvent interactions, and temperature. Therefore it seems that the introduction of highly polar groups onto a polymer chain might increase polymer–solvent interaction and also polymer–polymer interaction, hence increasing the solubility and the prospect of the formation of liquid crystalline solutions in common polar solvents and/or water. In the present work, we aimed to synthesize ionic polyesters **1**–**3** using sulfonated hydroquinone as one of the monomers in order to encourage interaction with water, while using a substituent on the diacid unit to create irregularity along the macromolecular chain and hence a less compact and less symmetrical chain structure. These features might also be expected to facilitate the penetration of solvent (water) molecules into the polymer. Polar substituents might also introduce additional dipolar interactions between the macromolecular chains and hence favor the long-range cooperative alignment of the polymer chain.

In the initial stages of this work, we have used three readily available diacid chlorides, terephthaloyl chloride, 2-bromoterephthaloyl chloride, and 2-nitroterephthaloyl chloride. We observed that with polyester **1** (η_{inh} = 0.48 dL/g), an isotropic solution is obtained at 2 wt % polymer content in DMSO/H_2O (50 vol %), and a biphasic mixture of isotropic solution and solid particles at 7 wt %. The solubility of polyester **2** (η_{inh} = 0.27 dL/g) in DMSO/H_2O (50 vol %) is also low; a biphasic mixture of isotropic solution and solid particles is obtained at 10 wt % polymer content. In contrast, the phase behavior of polyester **3** (η_{inh} = 0.22 dL/g) is remarkably different, and the results are summarized in Table III.

In DMSO/H_2O (50 vol %), this polymer forms an isotropic solution at 12 wt % concentration, but at 18 wt % a biphasic mixture of anisotropic and isotropic solutions is observed under crossed polarizers on the optical microscope. An aligned birefringent texture results upon shearing the sample. In the 33–50 wt % concentration range, the whole liquid phase appears to be anisotropic. Application of pressure or shear causes the spherulitic entities to deform, break up, and coalesce into new ones revealing the fluid nature of the observed birefringent structures. From 50 to 70 wt %, a more viscous but shearable gel results (Figure 4a,b). Upon application of shear, elongated domains form (Figure 4a). Only a few solid particles are present even at 70 wt %. This is, to the best of our knowledge, the first report of a polyester forming a liquid crystalline phase in an aqueous organic solvent.[17] These first findings have encouraged us to study the phase behavior in other solvent systems.

In a mixture of DMSO/water (70 vol %), only at 55 wt % polymer can a liquid crystal solution with strong birefringence be observed as can be seen in Figure 4c. The critical concentration for the formation of an anisotropic phase in DMSO/H_2O (70 vol %) is therefore higher than in DMSO/H_2O (50 vol %). When pure DMSO was employed, an isotropic gel was obtained even at a polymer content of 58 wt %, and at 66 wt % a mixture of isotropic gel and insoluble solid was obtained. On reducing the DMSO content of the solvent to 30 vol %, very interesting phase separations are observed (Figure 5). At 25 wt % polymer, an anisotropic phase with isotropic inclusions develops (Figure 5a). When it is sheared and then left to stand for several minutes, a much more organized anisotropic phase forms and the quantity of anisotropic phase increases at the same time (Figure 5b). Similar structures have been reported in the literature by Aharoni et al. with lyotropic poly(hexyl isocyanates) in tetrachloroethane.[18] This is indeed a phenomenon of phase separation, formation of an anisotropic phase with isotropic inclusions which do not tend to form circular droplets but which maintain a substantial degree of angularity, in the present case, mostly tetragonal. There appears to be a state of equilibrium, because when sheared and then left to stand, the original phase-separated structure forms again within a few minutes. According to Chandrasekhar,[19] the tetragonal appearance and angularity of these inclusions are a consequence of the orientational and translational order associated with the inclusions. Aharoni has argued that the birefringent anisotropic phase in between the inclusions results from the parallel alignment of polymer chains to the edges of the isotropic inclusions during growth of the latter; this alignment is a measure of the lateral, translational order. The orientation of polymer chains in the ordered phase also changes to follow the contour of the isotropic inclusions.

Table III
Solution Properties of Polyester 3 (η_{inh} = 0.22 dL/g) at Room Temperature

solvent	polymer concn (wt %)	soln properties[a]
H_2O	5	isotropic solution
	18	biphasic solution[b]
	30	birefringent gel
DMSO/H_2O (15 vol %)	16	biphasic solution[b]
	25	lyotropic solution
	40	birefringent gel
DMSO/H_2O (30 vol %)	20	isotropic solution
	25	biphasic solution[b]
	30	lyotropic solution
	50	birefringent gel
DMSO/H_2O (50 vol %)	12	isotropic solution
	18	biphasic solution[b]
	33	lyotropic solution
	50	birefringent gel
	70	highly viscous birefringent gel
DMSO/H_2O (70 vol %)	50	isotropic solution
	55	lyotropic solution
	60	birefringent gel and solid
DMSO	58	isotropic gel
	66	isotropic gel and solid
DMF/H_2O (50 vol %)	40	isotropic solution
	52	lyotropic solution[c]
	60	lyotropic solution[d]
	70	birefringent gel
DMF	56	biphasic gel[e]
	70	highly viscous birefringent gel

[a] Observation on an optical microscope between crossed polarizers at room temperature. [b] Lyotropic phase coexisting with isotropic solution. [c] Weak shear birefringence. [d] Strong shear birefringence. [e] Liquid crystal spherulites coexisting with isotropic gel.

When the concentration of polyester **3** is increased to 30 wt % in DMSO/H_2O (30 vol %), the whole sample becomes anisotropic with strong birefringence, and upon heating to 100 °C and then cooling, a fine birefringent

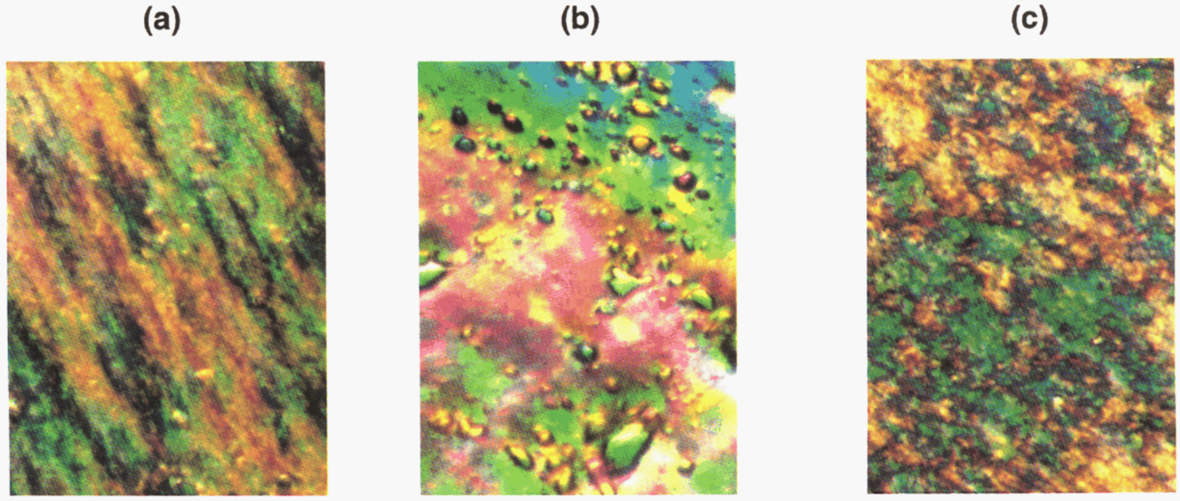


Figure 4. Optical micrographs of a solution of polyester **3** (η_{inh} = 0.22 dL/g) at room temperature between crossed polarizers (magnification ×200): (a) lyotropic solution at 50 wt % polymer content in DMSO/H_2O (50 vol %); (b) birefringent gel at 70 wt % polymer in DMSO/H_2O (50 vol %); (c) lyotropic solution at 55 wt % polymer in DMSO/H_2O (70 vol %).

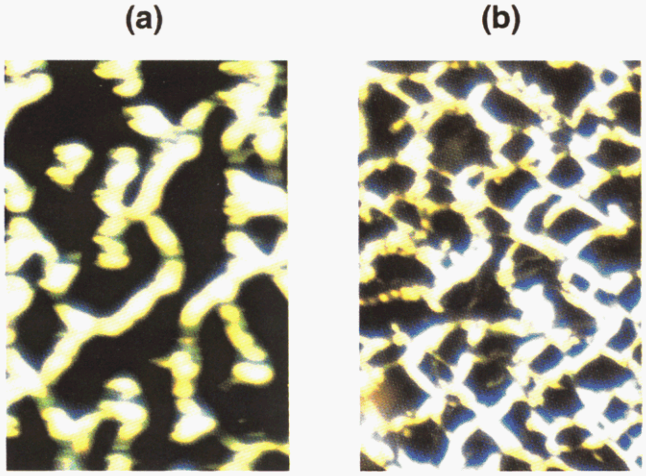


Figure 5. Optical micrographs of a solution of 25 wt % polyester **3** (η_{inh} = 0.22 dL/g) in DMSO/H_2O (30 vol %) at room temperature between crossed polarizers (magnification ×100): (a) biphasic solution; (b) sheared and left to stand for several minutes.

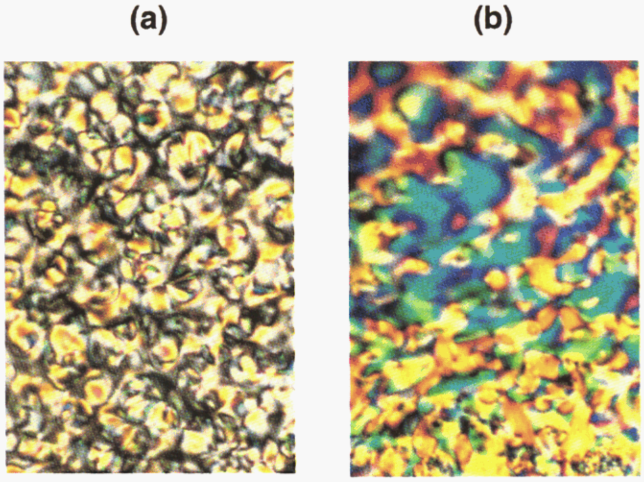


Figure 6. Optical micrographs of a solution of polyester **3** (η_{inh} = 0.22 dL/g) between crossed polarizers: (a) lyotropic solution at 30 wt % polymer in DMSO/H_2O (30 vol %) at 50 °C (magnification ×200); (b) lyotropic solution at 25 wt % polymer in DMSO/H_2O (15 vol %) at 45 °C (magnification ×100).

liquid crystalline structure is observed (Figure 6a). Finally, at 50 wt %, a viscous birefringent gel is obtained.

On reducing the DMSO content further to 15 vol %, liquid crystal solutions are obtained at 16 and 25 wt % polymer, and at 40 wt % a birefringent gel is obtained. When the 25 wt % solution is heated on a hot stage to 80 °C, the anisotropic phase generates isotropic inclusions, probably as a result of the increased quantity of isotropic phase. Upon cooling, a strong birefringent solution appears again (Figure 6b).

It does seem therefore that increasing the water content from 30 to 85 vol % in the DMSO/H_2O mixture facilitates formation of a liquid crystal phase and also decreases the concentration at which gel forms. This result comes a little as a surprise to us and prompted us to think about possible effects in pure water. Indeed at ca. 18 wt % polymer in water, liquid crystal spherulites start to form. As the concentration is raised to 25 wt %, essentially the whole liquid phase is anisotropic, and then at 30 wt % polymer, a more viscous birefringent gel is observed in the optical microscope.

It can be seen from these studies that liquid crystal solutions are readily obtained a polymer concentrations above 15–20 wt % in DMSO/H_2O mixtures with a water content ranging from 50 to 85 vol % and in pure water. The widest concentration range (18–50 wt %) for liquid crystal formation is found with DMSO/H_2O (50 vol %). This solvent composition may well offer some optimum balance of interactions with the hydrophilic part of the polyester ($SO_3^-K^+$) and the organic hydrophobic part, i.e., main-chain backbone substituted with nitro groups.

It was also of interest to see if this polyester forms liquid crystal solutions in DMF/H_2O (50 vol%). At 52 wt % polymer, an anisotropic solution is indeed formed, with strong birefringence under shearing. At 70 wt %, a shearable birefringent gel is obtained. When the 60 wt % solution is heated to 100 °C on a hot stage, an isotropic state is generated, and on cooling to room temperature, a liquid crystal solution forms again. When pure DMF is employed as solvent, liquid crystal spherulites start to form only at polymer concentration above 56 wt %, and at 70 wt % a highly viscous birefringent gel is obtained.

At the present time, the mechanism of formation of liquid crystals of polyester **3** in aqueous organic solvents is still not understood. Polymer–polymer intermolecular interactions as well as the high polymer–solvent interactions associated with the sulfonate groups seem to make an important contribution. The nitro group seems to aid the creation of random irregularities along the polymer chain and might also contribute to the intermolecular interactions. This type of novel lyotropic liquid crystalline polymer might lead to other interesting properties. Solid–liquid crystalline polymers are characterized by their high strength and high stiffness in the direction of orientation, whereas transverse properties tend to be rather poor. The interfacial adhesion is weak in blends with other polymers, which limits the application of self-reinforcing polymer blends. Ionic sulfonate and polar nitro groups as in polyester **3** might offer the prospect of improving the transverse properties. During the preparation of the present paper, the work of Weiss' research group on liquid crystalline ionomers was published.[20] They have synthesized a series of aliphatic–aromatic copolyesters from 4,4′-dihydroxy-α,α'-dimethylbenzalzine, brilliant yellow, in combination with sebacoyl and dodecanedioyl dichloride also using an interfacial polycondensation procedure. The objective was to introduce specific functional groups into the polymer that promote interchain interactions and thus to obtain liquid crystalline polymers with improved transverse properties. The copolyesters obtained in their work are thermotropic liquid crystalline species.

Conclusions

In this work, we have reported, for the first time, the synthesis by an interfacial polycondensation procedure and the characterization of aqueous/organic solvent soluble wholly aromatic ionic polyesters, substituted poly(sulfo-*p*-phenylene terephthalate). These are composed of sulfonate-substituted phenylene units with terephthalic acid or bromo- or nitro-substituted terephthalic acid units. The nitro-substituted polyester **3** forms lyotropic liquid crsytalline solutions in a wide range of DMSO/water solvent mixtures (15, 30, 50, and 70 vol %), in DMF/water (50 vol %), and in pure water and DMF. The critical concentration for the formation of an anistropic solution is around 15–20 wt % polymer in DMSO/water mixtures (15, 30, and 50 vol %) and in pure water and ca. 55 wt % in DMF/water (50 vol %) and DMSO/water (70 vol %) mixtures. Currently we are building on the approach described in this paper.

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Registry No. **1** (copolymer), 144375-63-3; **1** (SRU), 144466-17-1; **2** (copolymer), 144375-64-4; **2** (SRU), 144466-15-9; **3** (copolymer), 144375-65-5; **3** (SRU), 144466-16-0; **4**, 13815-89-9; **5**, 17178-92-6; DMSO, 67-68-5; DMF, 68-12-2; H_2O, 7732-18-5; 2-bromoterephthalic acid, 586-35-6; 2-nitroterephthalic acid, 610-29-7.