Lyotropic liquid crystalline polyesters: synthesis of polyesters and copolyesters based on poly(sulfo-*p*-phenylene nitroterephthalate)

David T.B. Hannah and David C. Sherrington*

Department of Pure and Applied Chemistry, Thomas Graham Building, University of Strathclyde, 295 Cathedral Street, Glasgow, UK G1 1XL

The syntheses of the polyesters poly(sulfo-*p*-phenylene methoxyterephthalate) (**4**), poly(sulfo-*p*-phenylene 2-methoxy-5-nitroterephthalate) (**5**) and poly(sulfo-*p*-phenylene 2-bromo-5-nitroterephthalate) (**6**), and the random copolyesters poly([sulfo-*p*-phenylene nitroterephthalate]$_x$-*co*-[sulfo-*p*-phenylene terephthalate]) (**7a–c**), poly([sulfo-*p*-phenylene nitroterephthalate]$_y$-*co*-[sulfo-*p*-phenylene bromoterephthalate]) (**8a–c**) and poly([sulfo-*p*-phenylene nitroterephthalate]$_z$-*co*-[sulfo-*p*-phenylene nitroisophthalate]) (**9a–f**) are reported. It was found that, of the three new homopolyesters prepared, **5** showed lyotropic behaviour in 1 : 1 DMSO–H_2O, DMSO and DMF (DMSO = dimethyl sulfoxide; DMF = dimethylformamide). The copolymers were prepared in various monomer compositions in an effort to establish the effect of either (*a*) diluting the mesogenic character of a known liquid crystalline polyester by reducing the nitro ratio of the substituents, or (*b*) disrupting the main-chain linearity of the ester back-bone by the introduction of *meta*-arranged isophthalate units. It was found that the original polyester could incorporate up to 50% bromo- or un-substituted terephthalate units and retain the ability to form lyotropic solutions. In the case of the accommodation of nitroisophthalate units, only 9% could be tolerated. Poly(sulfo-*p*-phenylene nitroterephthalamide) (**10**) has also been synthesised and shown to form a lyotropic liquid crystalline phase in DMSO and aqueous DMSO.

The development and commercialisation of liquid crystalline (LC) polymers has recently acquired much interest in the chemical community.[1] This is in no small part due to the success of liquid crystalline products such as Kevlar, a lyotropic LC polyamide produced by Du Pont, and the series of thermotropic LC polyesters marketed by Hoescht Celanese as Vectra. The ability of such materials to form liquid crystalline phases during processing imparts superior tensile strength and high moduli in the final products. The fabrication of these, and other related, materials is restricted, though, by the conditions required for their processing. For example, Kevlar fibre is normally spun from a 98% sulfuric acid solution, whereas mouldable LC thermotropic polyesters such as Vectra are typically processed at elevated temperatures. The economic and ecological ramifications for industry are obvious. As a result, an important research aim remains the synthesis of polymer materials which have the ability to form lyotropic LC solutions in common organic solvents or even water, or thermotropic mesophases accessible at moderate temperatures.

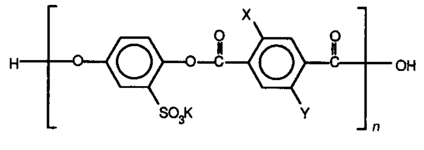
Some research groups have tackled the case of lyotropic polyamides by the introduction of solubilising groups onto the polyamide main-chain. This work has been reviewed by us and others.[2] In the case of lyotropic polyesters, we believe that success may be gained with the use of substituents which not only disrupt the main-chain regularity of the polymer, but which also offer the possibility of interactions with an appropriate solvent. Recently, we achieved some initial success in this regard with the synthesis of poly(sulfo-*p*-phenylene nitroterephthalate) **1**.[3] This polyester was shown to be the first example of a wholly aromatic polyester which forms liquid crystalline solutions in aqueous organic solvents. This polyester forms lyotropic solutions in mixtures of dimethyl sulfoxide (DMSO) or dimethylformamide (DMF) with water, and in pure water and DMF. The critical concentration for mesophase formation lies between 18 and 50% and increases with the water content of the solvent. Somewhat surprisingly, the analogous bromo- and un-substituted polyesters (**2** and **3** respectively) showed no lyotropic character.

As part of a wider research project[4] to synthesise other examples of polyesters in this class we have studied the phase behaviour of several polyesters prepared from alternative diacid units, and also copolyesters which incorporate either bromo- or un-substituted terephthaloyl units into the main chain, or which contain some degree of non-linearity by the introduction of nitroisophthaloyl units. In this way, the effect of diluting the mesogenic character of the original polyester has been monitored.

Results and Discussion

Monomer syntheses

2-Nitroterephthaloyl chloride, 2-bromoterephthaloyl chloride, 2-methoxyterephthaloyl chloride, 2-bromo-5-nitroterephthaloyl chloride and 2-methoxy-5-nitroterephthaloyl chloride were prepared by reaction of their respective diacids with thionyl chloride using DMF as a catalyst. Each was purified by distillation and fully characterised. The diacids of the latter pair were synthesised as described previously.[10,11] It was found that the diacid chlorides could also be prepared under the mild phase-transfer conditions proposed by Burdett[5] although no significant yield enhancement was found.



1 X = H, Y = NO_2

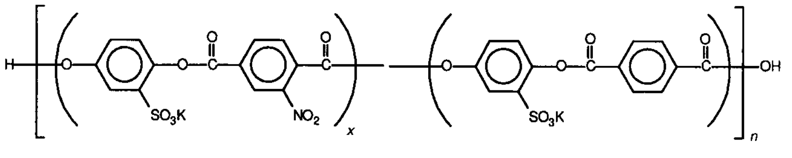
2 X = H, Y = Br

3 X = Y = H

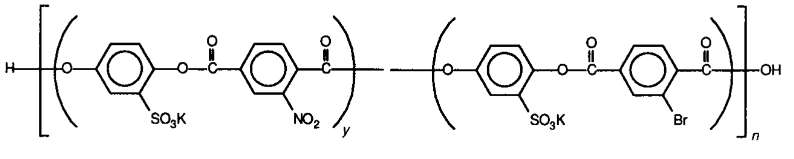
4 X = H, Y = OCH_3

5 X = NO_2, Y = OCH_3

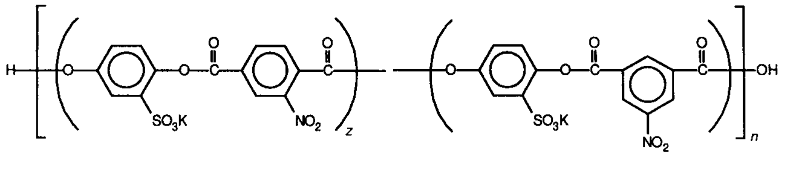
6 X = NO_2, Y = Br



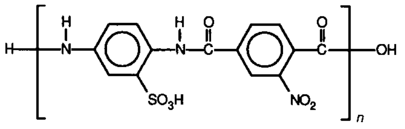
7a $x = 0.33$
b $x = 1$
c $x = 3$



8a $y = 0.33$
b $y = 1$
c $y = 3$



9a $z = 0$
b $z = 1$
c $z = 2$
d $z = 3.55$
e $z = 7$
f $z = 10$



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Polymer syntheses and physical characterisation

The polymers were synthesised using a standard interfacial procedure which was previously optimised for homopolyester synthesis.[3] The restricted solubility and ionic nature of the diol prevented the use of either single-phase solution or melt procedures.

Three novel polyesters were successfully prepared from the potassium salt of hydroquinonesulfonic acid with 2-methoxy-, 2-methoxy-5-nitro- and 2-bromo-5-nitro-terephthaloyl chlorides at room temperature (polyesters **4**, **5** and **6**) in yields of 30, 78 and 63% respectively. In each case the reaction times were comparatively short (*ca.* 1 h) and precipitates were afforded during the polycondensation. In the case of the copolyesters (**7a–c**, **8a–c** and **9a–f**), the mixture of diacid chloride monomers was added simultaneously in a single chloroform solution. In this way it was hoped that the copolymer structures were consistent with the monomer compositions and of an entirely random nature. Otherwise, their synthesis and isolation was identical to the homopolyester syntheses. The polyesters were characterised by infra-red spectroscopy, ^{1}H NMR spectroscopy, solution viscometry, differential scanning calorimetry, and elemental microanalysis. These results are summarised in Table 1.

FTIR spectra. Absorptions typical of the functional groups expected were revealed: the strong C=O stretch of the ester carbonyl near 1740 cm^{-1}; SO_3^- near 1235, 1070 and 630 cm^{-1} (S=O stretch); and the strong vibrations of the nitro function near 1540 (*anti*) and 1350 cm^{-1} (symmetric). The C—Br stretch will be below 400 cm^{-1} and is hence not observed. The C—O stretch of the methoxy group is present near 1030 cm^{-1}. In all polymers a characteristic feature is a broad absorption around 3000 cm^{-1} which can be attributed to the O—H stretch of any acidic or phenolic end-groups present or residual bound water molecules.

^{1}H NMR spectra. All of the polyesters have very similar ^{1}H NMR spectra when observed in deuterated DMSO. Briefly, two main features can be noted. Firstly, a complex set of signals is seen in the aromatic range, *ca.* 7–9 ppm, which is in turn separated into two broad sets of signals. These can be attributed to the aromatic rings of the diol and diacid units in the repeat unit. Further assignment of these peaks is difficult especially when we must take into account the random regioregularity of the substituents with respect to each other. Secondly, one (or sometimes two) peak(s) are seen at around 10–11 ppm. These are due to the acidic protons in the end-groups. Quantitative analysis of these was not attempted.

Solution viscometry. In our efforts to ascertain the molecular mass characteristics of these polyesters we considered several options. Previously,[3] aqueous phase gel permeation chromatography (GPC) of **1** was conducted; however further GPC analysis of the other polyesters was severely limited by poor solubility. Since solubility tests show that, in general, the polyesters are most soluble in 1:1 DMSO–H_2O, capillary viscosity measurements were carried out in this solvent with 0.1% LiCl added in an attempt to counteract the polyelectrolyte effect due to the ionic nature of the polymer chains. The efflux time required for the solvent (t_0) and the polymer

Table 1 Physical characterisation of polyesters

		found (%)						calculated (%)						
polyester	yield (%)	C	H	N	S	Br	Cl	C	H	N	S	Br	ν_{max}/cm^{-1}	η_{inh}/dl^{-1a}
4	30	41.9	2.9	—	9.2	—	0.5	46.4	2.3	—	8.2	—	2700–3500br (O—H), 1740s (C=O), 1200br, 1082 and 637 (S—O), 1030 (C—O)	^{b}
5	78	40.4	2.6	3.0	7.3	—	2.7	41.6	1.9	3.2	7.4	—	2700–3500br (O—H), 1760s (C=O), 1532 and 1351 (N—O), 1200br,1067 and 643 (S—O), 1020 (C—O)	^{b}
6	63	35.3	1.7	2.4	7.4	12.7	1.25	34.9	1.05	2.9	6.65	16.6	2700–3500br (O—H), 1760s (C=O), 1537 and 1362 (N—O), 1200br, 1036 and 633 (S—O)	^{b}
7a	67	42.7	2.1	0.3	8.8	—	—	45.5	1.8	1.0	8.7	—	—	0.20
7b	69	39.5	2.6	1.3	7.4	—	—	44.2	1.7	1.8	8.4	—	—	0.24
7c	69	40.6	2.4	2.2	7.3	—	—	35.2	1.6	2.7	8.2	—	2700–3600br (O—H), 1755s (C=O), 1548 and 1357 (N—O), 1243, 1088 and 633 (S—O)	0.15
8a	46	37.4	2.4	0.5	6.9	13.0	—	39.2	1.4	0.8	7.5	14.0	—	0.20
8b	54	38.1	2.2	1.5	7.2	7.3	—	40.0	1.4	1.7	7.6	9.5	—	0.20
8c	54	40.1	2.1	2.5	7.5	3.1	—	40.8	1.5	2.6	7.8	4.8	3000–3600br (O—H), 1760s (C=O), 1548 and 1362 (N—O), 1228, 1098 and 638 (S—O)	0.31
9a	92	40.35	2.7	2.9	7.4	—-	4.1	41.7	1.5	3.5	7.95	—	2700–3500 (O—H), 1741s (C=O), 1540 and 1350 (N—O), 1236, 1070 and 628 (S—O)	0.06
9b	80	39.8	2.4	2.85	8.15	—	1.5	41.7	1.5	3.5	7.95	—	2700–3500 (O—H), 1740s (C=O), 1540 and 1352 (N—O), 1236, 1070 and 630 (S—O)	0.11
9c	73	40.4	2.4	2.8	7.8	—	0.9	41.7	1.5	3.5	7.95	—	—	0.15
9d	86	40.6	2.55	3.0	7.8	—	1.3	41.7	1.5	3.5	7.95	—	—	^{b}
9e	64	40.3	2.1	2.8	7.8	—	0.7	41.7	1.5	3.5	7.95	—	—	^{b}
9f	79	41.1	2.3	2.9	7.8	—	0.8	41.7	1.5	3.5	7.95	—	—	^{b}

[a] Measured at 0.2 g dl^{-1} polymer in 1:1 DMSO–H_2O with 0.1% LiCl. [b] Not recorded.

solution (t) were measured thrice and taken as an average. The inherent viscosity was calculated as $[\ln (t/t_0)]/c$ where the concentration (c) was 0.2 g dl^{-1}. The viscosity measurements tabulated indicate a relatively low molecular mass range for these polyesters. As a comparison, for polyester **1** of $\eta_{\text{inh}} =$ 0.18 dl g^{-1}, a $\bar{M}_w$ of 4300 was obtained from statistical light scattering measurements.[3]

Differential scanning calorimetry. These measurements were performed on the polyesters over the range 25–400 °C under a nitrogen atmosphere with a heating rate of 20 °C min^{-1}. All those materials containing a nitro function exhibited a large exothermic peak with an onset tremperature of around 300 °C. This was also reported for **1**.[3] Polyester **4** showed only a small exotherm at *ca.* 270 °C and further decomposition thereafter. In no case was a thermotropic transition observed.

Elemental microanalysis. The microanalytical data on these materials provide some useful information. In general terms it can be seen from the chlorine content that even rigorous washing does not in some cases remove all traces of the phase-transfer catalyst and NaCl formed in the reaction. The required analytical content has been calculated ignoring the end-groups present. Nevertheless, the probable low molecular mass of the products will mean that these groups will contribute to any anomalies in the elemental data. Furthermore, for the copolyesters, we are given an indication of the copolymer composition in comparison to that expected by the feed ratios of the comonomers. It is assumed that the various diacid units will be of comparative reactivity and hence that the comonomers are most probably randomly distributed along the macromolecular chains in amounts proportional to their feed ratios. In general, the microanalytical data would tend to support this. The only significant exception is with polyester **7a** where the N content is low. An explanation for this is not immediately apparent.

Solution phase characterisation of polyesters

For homopolymers **4–6** the phase behaviour is summarised in Table 2. Firstly, it can be seen that only polyester **5** which is disubstituted on the diacid aromatic ring with a nitro and methoxy function shows any birefringence when viewed under cross-polarised light. This is apparent under shear in 1 : 1 DMSO–H_2O only above *ca.* 62 mass% polymer. In pure DMF and DMSO, alignment is seen without shear at or above concentrations of *ca.* 68 and 42 mass% respectively. The liquid crystalline texture observed in most cases was a marbled nematic type, similar to that seen previously for polyester **1** [see Fig. 4(*a*), ref. 3]. The corresponding nitro-bromo polyester **6** shows no birefringence and has relatively poor solubility, solubilising in 1 : 1 DMSO–H_2O, pure DMSO and pure DMF at concentrations no higher than *ca.* 11, 21 and 27 mass% respectively. Similarly, the methoxy polyester **4** is highly insoluble and consequently shows no lyotropicity in the test solvents. The importance of the nitro function for inducing lyotropicity is clearly demonstrated, again, when polyesters **4** and **5** are compared.

The degree and nature of the interaction between the macromolecule chains themselves and that between the chains and solvent molecules can provide a major influence on the phase behaviour of these polymers. It is for this reason that the polar nature of the nitro function appears to favour polymer–solvent interactions, thus solubilising the whole polymer chain sufficiently to allow a lyotropic mesophase. Interestingly, in thermotropic systems, steric factors have been shown to play a more significant role than polar considerations in mesophase formation.[6]

The first two series of copolymers (**7a–c** and **8a–c**) prepared were those where the introduction of diacid units, previously found to be unable to induce lyotropicity, was investigated in order to ascertain their effect on the overall liquid crystallinity of the copolymer. In both the cases where either the unsubstituted or bromo-substituted diacid was used the effect was essentially the same, *i.e.* the incorporation of these units retards the mesophase formation of the copolymer. These results are summarised in Table 3.

In both cases where the nitro content is low (*ca.* 25%) the copolymers are insoluble in the test solvent. This could be predicted from the previous results[3] where it was found that the unsubstituted polymer was not soluble in 1 : 1 DMSO–H_2O at concentrations as low as 7 mass% and the bromo polymer was insoluble at *ca.* 10 mass%. Essentially, these particular copolyesters retain the properties of the major constituent structural units. When the nitro content of the polymerisation feed was increased to *ca.* 50% and above it can be seen that the copolyesters behave in the same way as the nitro homopolyester and lyotropic solutions were obtained at 40 mass% in 1 : 1 DMSO–H_2O for monomer feed ratios where x or y equal 1 and 3. Liquid crystalline textures were as before, but copolyester **7c** exhibited regions of Schlieren and marbled textures. From this result it can be assumed that there exists a critical comonomer composition for the random copolyester of this

Table 2 Solution properties of homopolyesters

polyester	solvent	concentration[a]	observation[b]
4	H_2O	<10	insoluble
	1 : 1 DMSO–H_2O	21	insoluble
		6	reaches isotropicity
	DMSO	21	insoluble
		8	reaches isotropicity
	DMF	13	reaches isotropicity
5	H_2O	<10	insoluble
	1 : 1 DMSO–H_2O	48	isotropic gel
		55	isotropic solution
		62	nematic under shear
	DMSO	68	untextured birefringence
	DMF	42	untextured birefringence
6	H_2O	<10	insoluble
	1 : 1 DMSO–H_2O	33	insoluble
		11	reaches isotropicity
	DMSO	56	insoluble
		21	reaches isotropicity
	DMF	27	reaches isotropicity

[a]Expressed as mass% polymer in solution to nearest integer. [b]Under cross-polarised light.

Table 3 Solution properties of copolyesters with bromo- and un-substituted diacid units

copolyester	*x*	*y*	nitro diacid in feed (%)	bromo diacid in feed (%)	unsubstituted diacid in feed (%)	observation in 1:1 DMSO–H_2O[a]
7a	0.33	—	25	—	75	insoluble
7b	1	—	50	—	50	nematic solution
7c	3	—	75	—	25	nematic solution
8a	—	0.33	25	75	—	insoluble
8b	—	1	50	50	—	nematic solution
8c	—	3	75	25	—	nematic solution

[a]Under cross-polarised light.

type whereby, firstly, the copolyester will be soluble in in 1:1 DMSO–H_2O (and other related solvent systems) and, secondly, where it will form a lyotropic solution. At present it is clear that these two critical values (for they may be different) lie in the region 25–50%. Further studies are required to provide a better approximation of these values.

Secondly, a series of copolyesters (**9a–f**) was prepared which incorporated a varying amount of the 5-nitroisophthaloyl unit. The use of *meta*-arranged substituents in the backbone of liquid crystalline polymers has been wide in the case of thermotropic polymers. Indeed, Cai and Samulski[7] have reported thermotropic polyesters which contain up to 85% isophthalic acid units. However, these types of units have not been considered as modifying groups in the synthesis of lyotropic polymers. It was our belief that the introduction of the 5-nitroisophthloyl unit into our existing polymer chain would have a marked effect on the solubility of the overall copolymer and it was this effect which we wished to investigate. Six new copolyesters were prepared with isophthalic contents (based on comonomer feed ratios) ranging from *ca.* 9 to 100%. The phase behaviour results are summarised in Table 4.

In general terms, it was found that the incorporation of the 5-nitroisophthaloyl unit did indeed change the solubility of the overall copolymer, giving a copolymer which becomes less soluble in aqueous organic solvents as the isophthaloyl component is increased. In fact, the wholly isophthaloyl homopolymer is a highly insoluble material. This result was somewhat surprising in that one may expect the decrease in linearity of the main-chain to favour solubility, *i.e.* the tendency towards crystallisation of the polymer chain is decreased. An explanation may lie in consideration of the role that the nitro function plays in solubilising the polymer chain. Through fluorescence measurements, we have shown that the chains in the original polyester **1** adopt a roughly parallel arrangement in the lyotropic state.[8] There is close association of the sulfonate moieties, whereas the nitro groups appear to be free to interact with the solvent molecules. Therefore, it would seem that it is the nitro groups which act as solubilising groups for the polymer chain as a whole. Hence, if we reconsider our copolymer structures, we can see that a more extended polymer chain will allow the nitro groups more freedom to interact with the solvent molecules. A more compacted, *meta*-arranged chain may well find its ability to interact with solvent molecules restricted.

This solubility trend has an expected effect on the ability of the resulting copolymers to form lyotropic mesophases in 1:1 DMSO–H_2O. The fully isophthalic polyester (**9a**) was insoluble in 1:1 DMSO–H_2O at a concentration as low as 11 mass%. The 1:1 copolymer **9b** was soluble up to *ca.* 42 mass% but formed only an isotropic solution. At isophthalic contents of *ca.* 22 and 33% (**9c** and **9d** respectively) solubility could be achieved up to *ca.* 60 mass% and untextured birefringence (poorly aligned) was observed under cross-polarisation. At 12.5% isophthalic content **9e** birefringence was seen at 53 mass%, but a fully aligned, lyotropic nematic sample was only observed with a low isophthalic content of *ca.* 9% (**9f**) at a critical concentration of 56 mass%. This high concentration value is indicative of the high degree of alignment required in solution for the lyotropic mesophase to be observed. As was mentioned earlier, for the fully *para*-arranged polyester (**1**) the critical concentration in in 1:1 DMSO–H_2O is considerably less at 33 mass%.

Interestingly, therefore, this work has confirmed the importance of the nitro substituent in the diacid aromatic ring with regard to generating lyotropicity in aqueous organic solvents. Dimethyl 2-fluoroterephthalate has recently become available and so fluoroterephthalic acid is now accessible *via* hydrolysis of this diester. It would be interesting in due course to see if the powerfully electron-withdrawing fluoro group has the same influence as the nitro group.

Poly(sulfo-*p*-phenylene nitroterephthalamide) 10

In the course of synthesising the above polyesters it occurred to us to examine the same substituent pattern in an analogous aromatic polyamide. This led us to synthesise polymer **10**.

The polyamide was synthesised by the solution reaction of 2,5-diaminobenzenesulfonic acid with 2-nitroterephthalic acid

Table 4 Solution properties of copolyesters with nitroisophthaloyl units

copolyester	*z*	isophthalic content[a]	concentration in 1:1 DMSO–H_2O[b]	observation[c]
9a	0	100	11	insoluble
9b	1	50	69	insoluble
			52	insoluble
			42	isotropic solution
9c	2	33.3	49	faint birefringence under shear
			58	untextured birefringence
9d	3.55	22	36	untextured birefringence
			60	untextured birefringence
9e	7	12.5	47	nematic solution under shear
			53	nematic solution
9f	10	9.1	56	nematic solution
			62	nematic solution

[a]Expressed as a percentage of isophthaloyl diacid units with respect to all diacid units. [b]Expressed as mass% polymer to nearest integer. [c]Under cross-polarised light.

in a *N*-methylpyrrolidone (NMP)–LiCl–pyridine solution with triphenylphosphite. A DSC trace of this polyamide was very similar to that of the polyester analogue, exhibiting an exothermic peak at *ca.* 300 °C and an endothermic trough at 180 °C. The solution behaviour of this polyamide was investigated in water, DMSO and a 1 : 1 mixture of DMSO and water. The results are summarised in Table 5.

It can be seen from the above data that this polyamide does indeed exhibit lyotropic LC phases in appropriate solvents. Although **10** is insoluble in water itself, it is very soluble in 1 : 1 DMSO–H_2O and shows a lyotropic LC phase above *ca.* 50 mass%. Similarly, in DMSO, a lyotropic LC phase is seen above a concentration of *ca.* 45 mass%. This polyamide was not found to be soluble in any other common organic solvents.

These results can be compared to the published data on the analogous poly(*p*-phenylene nitroterephthalamide).[9] This polymer is insoluble in water at room temperature and dissolves only at *ca.* 100 °C over a period of time. Aqueous polymer solutions with concentrations of 0.4–0.7 mass% are reported to be birefringent when sheared. Such a low concentration solution showing birefringence was questioned by the authors as being indicative of liquid crystallinity, and is certainly markedly different from the concentrations of *ca.* 45–50 mass% required for polyamide **10** to show anisotropic behaviour in aqueous and pure DMSO.

Conclusions

Three novel homopolyesters formed from the interfacial reaction of hydroquinonesulfonic acid and various diacid chlorides are reported. Of these, the polyester **5** bearing a nitro and methoxy function on the diacid unit exhibits lyotropicity in 1 : 1 DMSO–H_2O, DMSO and DMF. Two series of copolyesters are reported which contain increasing amounts of unsubstituted and bromo-substituted diacid units. It was found that the fully nitro polyester **1** could incorporate up to 50% of the non-mesogenic diacid and retain the ability to form lyotropic mesophases. A series of copolyesters containing increasing amounts of nitroisophthaloyl units is also reported. It was found that the overall composition of the copolymer could contain no more than *ca.* 9% of the *meta*-arranged diacid and retain the ability to form fully orientated mesophases. Furthermore, as the nitroisophthaloyl content increased the copolymer became more insoluble in aqueous organic solvents. Finally, poly(sulfo-*p*-phenylene nitroterephthalamide) **10** has been prepared and shown to form a lyotropic LC phase in DMSO and aqueous DMSO.

Experimental

Ethanol-free chloroform was prepared by elution through silica and subsequent distillation. Other solvents were used as received. Solid chemicals were supplied by Aldrich Chemical Co. and used as recieved except for hydroquinonesulfonic acid potassium salt, which was recrystallised from distilled water. ^1H NMR spectra were recorded at 250 MHz on a Bruker AMX-250 spectrometer. *J* Values are in Hz. Fourier transform infrared spectra were obtained on a Nicolet Impact 400D spectrometer. In IR data, *str* = stretch. Microanalytical data were obtained from the Microanalytical Service in the Department of Pure and Applied Chemistry of the University of Strathclyde. Optical studies were performed on an Olympus Polarising Microscope. Differential scanning calorimery studies were carried out on a Du Pont Instruments 910 DSC. Capillary viscosity measurements were made in an Ubbelohde viscometer in an equilibrated water-bath at 30 °C. Statistical light scattering measurements were performed at ICI Films, Wilton. Glassware was silanised by rinsing with a 3% silicone oil in methyl ethyl ketone solution, decanting the liquid and placing in a furnace at 400 °C for 4 h.

Table 5 Solution properties of poly(sulfo-*p*-phenylene nitroterephthalamide) (**10**)

solvent	concentration[a]	observation[b]
H_2O	< 10	insoluble
DMSO	45	nematic solution
	40	isotropic solution
1 : 1 DMSO–H_2O	50	nematic solution

[a]Expressed as mass% polymer to the nearest integer. [b]Under cross-polarised light.

Synthesis of monomers

2-Methoxy-5-nitroterephthalic acid[10] and 2-bromo-5-nitroterephthalic acid.[11] These were prepared as described in the literature. The acid chlorides were prepared by refluxing the appropriate diacid compound in thionyl chloride and purified by micro-distillation including *2-bromoterephthaloyl chloride* and *2-nitroterephthaloyl chloride* which were prepared as previously described.[3]

2-Methoxyterephthalic acid. A mixture of 2,5-dimethylanisole (3.0 g, 22.03 mmol), potassium permanganate (12.0 g, 75.93 mmol) and distilled water (300 ml) was refluxed for 5 h. The mixture was cooled to room temp. and poured into stirred cold ethanol (200 ml). This mixture was then filtered, washed thoroughly with water, reduced under vacuum, and acidified with conc. hydrochloric acid. The resulting white precipitate was collected by filtration, washed with water and dried (2.26 g, 52.3%), mp 287–288 °C (lit., 280 °C[12] or 296–297 °C[13]) [Found: C, 54.8; H, 4.0. $C_9H_8O_5$ (196.16) requires C, 55.1; H, 4.1%]; υ_{max}/cm^{-1} (KBr) 1703 (C=O *str*); δ_H ([$^2H_6$]DMSO) 3.87 (3H, s, OCH_3), 7.55 (2H, br d, $J_{5,6}$ 8, 5,6-H), 7.68 (1H, d, $J_{3,5}$ 8, 3-H), 13.15 (2H, br s, 2× CO_2H); δ_C ([$^2H_6$]DMSO) 55.82 (OCH_3), 112.51 (3-C), 121.00 (5-C), 125.72 (1-C), 130.33 (6-C), 134.52 (4-C), 157.51 (2-C), 166.60 and 167.00 (both CO_2H).

2-Methoxyterephthaloyl chloride.[14] (100%), mp 51–52 °C [Found : C, 46.2; H, 2.6; Cl, 30.6. $C_9H_6Cl_2O_3$ (233.05) requires C, 46.4; H, 2.6; Cl, 30.4%]; υ_{max}/cm^{-1} (C=O *str*); δ_H ($CDCl_3$) 4.02 (3H, s, OCH_3), 7.67 (1H, d, $J_{3,5}$ 2, 3-H), 7.81 (1H, dd, $J_{5,3}$ 2, $J_{5,6}$ 8, 5-H), 8.09 (1H, d, $J_{6,5}$ 8, 6-H); δ_C ($CDCl_3$) 56.8 (OCH_3), 114.0 (3-C), 123.1 (1-C), 128.8 (5-C), 133.5 (6-C), 138.8 (4-C), 158.7 (2-C), 164.1 and 167.7 (both *C*OCl).

2-Bromo-5-nitroterephthaloyl chloride. (95.0%), mp 53–55 °C, bp 135–140 °C at 0.02 mbar [Found: C, 29.55; H, 0.8; N, 4.0; Cl, 21.9; Br, 23.7. $C_8H_2NO_4BrCl_2$ (326.92) requires C, 29.4; H, 0.6; N, 4.3; Cl, 21.7; Br, 24.0%]; υ_{max}/cm^{-1} ($CHCl_3$) 3030s (C—H *arom str*), 1778br (C=O *str*), 1540 (N—O *anti str*), 1350 (N—O *symm str*); δ_H ($CDCl_3$) 7.99 (1H, s), 8.74 (1H, s); δ_C ($CDCl_3$) 128.15 (6-C), 128.27 (2-C), 133.97 (4-C), 135.97 (3-C), 138.57 (1-C), 143.11 (5-C), 163.64 and 164.06 (both *C*OCl).

2-Methoxy-5-nitroterephthaloyl chloride. (76.1%), bp 175–180 °C at 0.03 mbar [Found: C, 38.8; H, 1.9; N, 5.15; Cl, 25.45. $C_9H_5NO_5Cl_2$ (278.05) requires C, 38.9; H, 1.8; N, 5.0; Cl, 25.5%]; υ_{max}/cm^{-1} ($CHCl_3$) 1786br (C=O *str*); δ_H ($CDCl_3$) 4.13 (3H, s, OCH_3), 7.10 (1H, s, 3-H), 8.89 (1H, s, 6-H); δ_C ($CDCl_3$) 57.96 (OCH_3), 110.69 (3-C), 130.86 (1-C), 136.05 (4-C), 139.30 (5-C), 162.11 (2-C), 162.92 and 164.95 (both CO_2H).

5-Nitroisophthaloyl chloride. (97.2%), bp 145–150 °C at 0.06 mbar (lit.,[15] mp 67–68 °C) [Found: C, 39.3; H, 1.3; N, 5.1; Cl, 28.6. $C_8H_3NO_4Cl_2$ (248.02) requires C, 38.7; H, 1.2; N, 5.65; Cl, 28.6%]; υ_{max}/cm^{-1} ($CHCl_3$) 3095, 1761s (C=O *str*), 1632, 1363, 1260, 1157; δ_H ($CDCl_3$) 9.12 (1H, t, $J_{2,4}$ and $J_{2,6}$ 2, 2-H), 9.22 (2H, d, $J_{4,2}$ and $J_{6,2}$ 2, 4-H and 6-H); δ_C ($CDCl_3$) 131.09 (4-C), 136.19 (2-C) 137.62 (1-C and 3-C), 149.06 (5-C), 165.83 (2 × COCl).

Synthesis of polyesters 4–9

General procedure.[3] Hydroquinonesulfonic acid (6.57 mmol) was dissolved in distilled water (5 ml) containing sodium hydroxide (0.53 g, 13.2 mmol) and stirred under nitrogen in a silanised flask. To this was added a thoroughly mixed chloroform solution (30 ml) of the relevant diacid chloride(s) (to a total of 6.57 mmol) in one portion. This was followed by the addition of a phase-transfer catalyst, benzyltriethylammonium chloride (0.2 equiv), in distilled water (1 ml). Normally rapid precipitation occurred concurrent with a change in solution colour from brown through a vibrant red to a strong yellow, before typically affording a peach coloured product. The polymer product was precipitated in methanol, dried, washed with a methanol water (3:1) mixture and re-dried under vacuum. Analytical data is contained in Table 1.

Synthesis of poly(sulfo-*p*-phenylene nitroterephthalamide) 10. 2-Nitroterephthalic acid (1.58 g, 7.48 mmol), 2,5-diaminobenzenesulfonic acid (1.41 g, 7.48 mmol) and anhydrous lithium chloride (0.79 g, 18.64 mmol) were dissolved in a mixture of *N*-methylpyrrolidone (15 ml), pyridine (3.75 ml) and triphenyl phosphite (3.94 ml). On addition of the latter, the solution developed a green colour. This solution was stirred by means of a mechanical overhead stirrer at 120 °C for 4 h. The solution was then cooled to room temp. and poured into cold, rapidly-stirred methanol (200 ml). The resulting yellow solid was collected by filtration, washed thoroughly with hot methanol, and dried to give a pale-green solid powder (**10**, 1.86 g, 71%) [Found: C, 46.5; H, 3.3; N, 11.4; S, 6.85; Cl, 0.4. $[C_{14}H_9N_3O_7S]_n$ $(363.30)_n$ requires C, 46.3; H, 2.5; N, 11.6; S, 8.8%]; υ_{max}/cm^{-1} (KBr) 1800–3600br (O—H *str*), 1687br (C=O *str*), 1610br, 1527 (N=O *anti str*), 1500, 1398, 1357 (N—O *symm str*), 1315, 1243 (S—O *str*), 1181, 1082 (S—O *str*), 1031, 896, 829, 762, 864, 637 (S-O *str*).

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References

1 (*a*) *Liquid Crystallinity in Polymers*, ed. A. Ciuferri, VCH, Weinheim, Germany, 1997; (*b*) A. M. Donald and A. H. Windle, *Liquid Crystalline Polymers*, Cambridge University Press, Cambridge, 1992; (*c*) C. B. McArdle, *Side-Chain Liquid Crystal Polymers*, Blackie, Glasgow, 1987.

2 (*a*) J. Lin and D. C. Sherrington, *Adv. Polym. Sci.*, 1994, **111**, 177; (*b*) M. Takayamgi and T. Katayose, *J. Appl. Polym. Sci.*, 1984, **29**, 141; (*c*) M. B. Gielselman and J. R. Reynolds, *Macromolecules*, 1990, **23**, 3118; (*d*) J. Y. Yadhav, W. R. Krigbaum and J. Preston, *Macromolecules*, 1988, **21**, 538; (*e*) E. J. Vandenberg, W. R. Dively, L. J. Filar, S. R. Patel and H. G. Barth, *Polym. Mater. Sci. Eng.*, 1987, **57**, 139; (*f*) E. J. Vandenberg, W. R. Dively, L. J. Filar, S. R. Patel and H. G. Barth, *J. Polym. Sci. Polym. Chem.*, 1989, **27**, 1387.

3 J. Lin, D. C. Sherrington, R. W. Richards, E. Nield and W. A. MacDonald, *Macromolecules*, 1992, **26**, 7107.

4 This work is derived from the PhD Thesis of D. T. B. Hannah, University of Strathclyde, 1996.

5 K. A. Burdett, *Synthesis*, 1991, 441.

6 Q.-F. Zhou, R. W. Lenz and J.-I. Jin, in *Polymeric Liquid Crystals*, ed. A. Blumstein, *Polym. Sci. Tech.*, Plenum Press, New York, 1985, p. 257.

7 F. R. Cai and E. T. Samulski, *Macromolecules*, 1994, **27**, 35.

8 H. Takahashi, K. Horie, T. Yamashita, S. Machida, D. T. B. Hannah and D. C. Sherrington, *Macromol. Chem. Phys.*, 1996, **197**, 2703.

9 E. J. Vandenberg, W. R. Dively, L. J. Filar, S. R. Patel and H. G. Barth, *J. Polym. Sci. Polym. Chem.*, 1989, **27**, 3745.

10 J.-I. Jin, Y.-H. Lee and H.-K. Shim, *Macromolecules*, 1993, **26**, 1805.

11 C. A. Panetta, Z. Fang and N. E. Heimer, *J. Org. Chem.*, 1993, **58**, 6146.

12 F. Wessely and M. Grossa, *Monatsch. Chem.*, 1966, **97**, 570.

13 N. K. Kochetkov, L. I. Kudryashov and A. N. Nesmeyanov, *Bull. Acad. Sci. USSR*, 1955, 729.

14 I. Goodman, J. E. McIntyre and D. H. Aldred, ICI Patent 993,272 1965; *Chem. Abstr.*, 1965, **63**, 8521e.

15 E.-S. M. E. Mensour, S. H. Kandid, M. E. M. Soliman and M. Ibrahim, *Polym. Int.*, 1992, **29**, 61.

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