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A supramolecular nematic phase in sulfonated polyaramides

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A water-soluble polyaramide "sulfo-invert-PPTA" surprisingly, already at a molecular weight of 10,000 g mol^{-1}, exhibits a nematic liquid crystalline phase in water at very low polymer concentrations, around 1–2wt%, indicating that supramolecular assemblies of molecules are the building blocks of the nematic phase.

Previous work by Kwei[1] and ourselves[2] report that poly-(*p*-sulfophenylene-terephthalamide), or "sulfo PPTA", forms a birefringent nematic liquid crystalline gel in water. Further structural studies provide strong evidence for the presence of supramolecular aggregates in these gels.[3,4] Similar behaviour was recently reported for poly(*p*-benzamide) in DMAc/LiCl.[5]

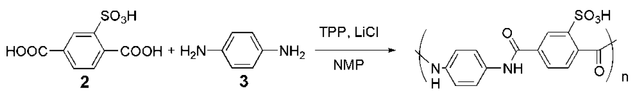
We have found that by displacing the sulfonic acid group along the polymer backbone – from the diamine to the acid ring – it is possible to avoid gel formation in water and instead a free flowing nematic phase is obtained. The synthesis and characterisation of this material "sulfo-invert-PPTA" (**1**) will be discussed. Interestingly, despite the rather low molecular weight of our samples, lyotropic nematic behaviour is observed in water at very low polymer concentration, around 1wt%. We propose that this is due to the presence of supramolecular aggregates in these lyotropic nematic solutions.

The aramid polymer PPTA is usually obtained *via p*-phenylenediamine and terephthalic acid chloride. On the introduction of the sulfonic acid group on the terephthalic acid (**TA**), the acid chloride form could not be obtained. An alternative polymerization of polyaramides was developed during the 1970's, by Yamazaki *et al.*,[6] Higashi *et al.*,[7] Preston *et al.*[8] and Russo *et al.*[9] all based on the use of terephthalic acid and triphenylphosphite (TPP) (Scheme 1). The polymerization conditions that have been used here were inspired by the work of these authors.

To perform the synthesis the required 2-sulfoterephthalic acid (**sTA, 2**) was readily obtained by oxidation of 2,5-dimethylbenzenesulfonic acid with potassium permanganate in water followed by precipitation from solution using hydrochloric acid.†

Determination of the molecular weight (Mw) and polydispersity index of our samples was achieved using Size Exclusion Chromatography (SEC) in sulfuric acid.‡ Sulfuric acid was used as the solvent in order to prevent aggregate formation. SEC shows that the polymerization reaction gives materials of approximately 10,000 g mol^{-1} with a polydispersity index of 2.

Dissolving the sulfo-invert-PPTA powder in demineralised water reveals nematic liquid crystal behavior at surprisingly low polymer concentrations. A biphasic solution is found at 1wt% where the upper 5% part is a biphasic nematic and isotropic mixture (see Fig. 1§) and the remaining lower part is fully nematic. Fully nematic solutions showing Schlieren textures are obtained for solutions with polymer concentrations between 2 and 4wt%. For higher concentrations (5 ~ 6wt%) coloured nematic textures are obtained as shown in Fig. 2. This reveals that the system has a substantial level of birefringence.



Scheme 1 Polymerization route of "sulfo-invert-PPTA" (**1**) using 2-sulfoterephthalic acid (sTA, **2**) and *p*-phenyldiamine (PPD, **3**).

The poor solubility of sulfo-PPTA has been previously discussed by Chu-Evan *et al.*,[3] whereby the sulfonic acid group interacts with the proton of the amide bond, reducing the solubility of the polymer chain in solution and leading to the observed gel formation. The enhanced solubility of sulfo-invert-PPTA as compared to sulfo-PPTA might be explained by the presence of both the carbonyl and sulfonic acid groups on the same monomer. It is expected that water will interact in a much stronger manner due to a clear separation between the sulfonic acid and the amino groups than in the case of sulfo-PPTA. This may explain why a solution of sulfo-PPTA with comparable molecular weight to those prepared here forms a birefringent gel[5b] instead of a liquid nematic phase. The hydrophobic interaction of the unsubstituted aromatic ring is suspected to contribute to the aggregation of the polymer chains.

Further characterization of the supramolecular liquid crystal phase was achieved using X-ray scattering (XRD)¶. The 2-D data for a 6wt% solution in water is displayed in Fig. 3, including the equatorial reflection in log-log scale, which reveals a -1 slope at high q values characteristic of a rod like system.

The scattering of the sample at low angles reveals that sulfo-invert-PPTA has a substantial level of order in solution, confirmed by the azimuthal scan (Fig. 3c) through the peak in the anisotropic pattern: the calculated order parameter is 0.92. This value is unusually high for such a low polymer concentration. By comparison, a normal PPTA solution with molecular weight around 30,000 to 40,000 g mol^{-1} forms a nematic phase at 8–10 wt%, and at this point the order parameter only reaches a value of about 0.4.

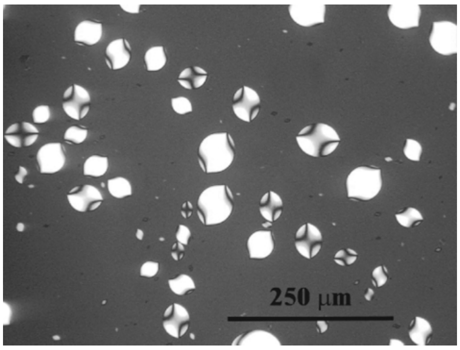


Fig. 1 Optical polarization micrograph of the upper part of a 1wt% "sulfo-invert-PPTA" solution in water: nematic droplets suspended in isotropic solvent are observed.

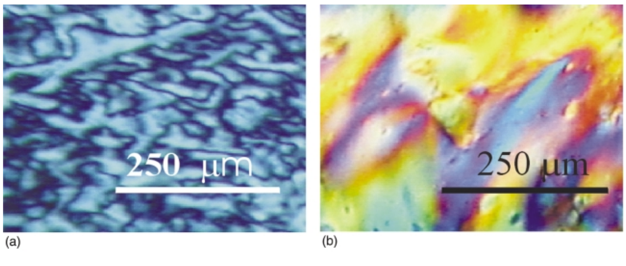


Fig. 2 Optical polarization micrograph of (a): 4wt% of "sulfo-invert-PPTA" in water, showing a nematic Schlieren texture, and (b): 6wt% "sulfo-invert-PPTA" water solution.

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Assuming that $q_{\max}$ (Fig. 3b) is associated with the distance between aggregates ~ 97 Å we can estimate the diameter of the rods using a hexagonal lattice. This gives a width of 22 Å. Using a cubic lattice does not significantly change the estimated value. Applying the Onsager[10] relation $\Phi^* = 4d/L$ for the critical I–N concentration for polydisperse rods, the length of the aggregates is estimated to be about 8700 Å. Here we take the critical concentration Φ^*, to be about 0.01. The contour length for an average sulfo-Invert PPTA chain is only 700 Å with a diameter of 5.4 Å. Consequently this would imply that there are over 2000 polymer molecules in the supramolecular rod-like aggregates

Since the polymer prepared here is a lyotropic system, it is of interest to examine the effect of shear flow on the liquid crystalline texture. Nematic solutions are well known to give rise to a variety of interesting flow phenomena, such as flow-alignment, various tumbling regimes and band texture formation. As a first result it is worth noting that upon cessation of simple shear flow,[11–12] applied manually to the sample, a clear band-texture is formed as displayed in Fig. 4.

Our results indicate the existence of a supramolecular nematic phase in sulfo-invert-PPTA in water, probably containing a microstructure of self-organized rod-like aggregates. Initial characterisation of the nematic phase was performed using optical polarization microscopy and X-ray scattering. Cessation of shear flow reveals band-texture formation. These results indicate that we have found a novel self-assembled liquid crystal polyelectrolyte. Systematic variation of the solution parameters, like concentration, thermal history, salt concentration *etc*. may provide additional information for understanding this result. This will be developed further in a forthcoming publication.

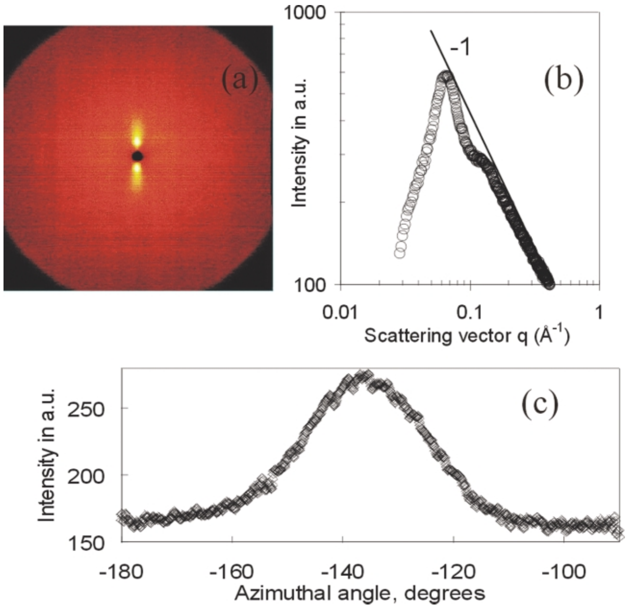

Fig. 3 (a) XRD of a 6wt% solution at 60 °C and subjected to a magnetic field along the horizontal direction, (b) 2-theta scan and (c) azimuthal scan along the peak.

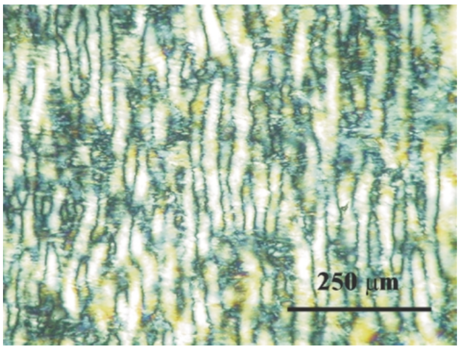

Fig. 4 Band-texture formed after cessation of simple shear flow on a 6wt% "sulfo-invert-PPTA" solution in water.

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Notes and references

† *2-Sulfoterephthalic acid* (**2**). In a 1 L reactor vessel equipped with a mechanical stirrer and a cooler, 20.84 g (0.111 mol) of 2,5 dimethylbenzenesulfonic acid were dissolved in 500 ml of water, and then 82.36 g (0.52 mol) of $KMnO_4$ were added stepwise during 5 hours. The reaction mixture was heated at reflux during 48 hours, and then filtered to remove MnO_2. HCl was added to the filtrate and immediate precipitation of **2** occurred. The yield was 15 g (54.5%). ^{1}H-NMR (DMSO-d6) δ 8.33 (s, 1H), 8 (dd, 1H, J = 1.8 Hz, J = 8.1 Hz), 7.69 (d, 1H, J = 7.8 Hz). ^{13}C-NMR (DMSO-d6) δ 169, 167 (COOH), 145, 136.1, 132.62, 130.67, 130.34, 128.656.

Polymerization. In a 500 ml 3 necked flask, 10 g (40 mmol) of **2**, 27.5 g (88.7 mmol) of TPP, 20 g of LiCl and 50 ml of pyridine were dissolved in 200 ml of NMP. The solution was heated 40 °C for 15 min and then 4.35 mg (40 mmol) of **3** added. The reaction mixture was then heated at 115 °C for 3 hours. The yellow viscous solution was precipitated in 1 L of methanol. A yellow precipitate was obtained, filtrated and washed with methanol (500 ml) and diethyl ether (500 ml) The goldish powder was dried under vacuum at 80 °C overnight, yielding 2.3 g (77%).Mw = 10,000 g mol^{-1}, PDI = 2.^{1}H-NMR (DMSO-d6) δ 11.32ppm (1H, s, NHCO), 10.5ppm (1H, s, NHCO), 8.85ppm (1H, s), 8.48ppm (s, 1H), 7.5ppm (q, 4H), 7.34 ppm (1H,s) ^{13}C NMR (DMSO-d6): 165.26 ppm, 164.37 ppm C=O, δ 144.44, 143.62, 130.69, 129.36, 128.33, 126.54, 125.89, 125.76, 120.9, 120.74, 120.03, 119.89.

‡ *Size exclusion chromatography* (SEC) has been performed by dissolving the sample in concentrated sulfuric acid (1 mg ml^{-1}) and separating it using a modified Zorbax column (250 × 6.2 mm), and concentrated sulfuric acid as the mobile phase (0.1 ml min^{-1}). A UV detector operating at 340 nm was used for detection. From the chromatograms, the Mw values were calculated using Cirrus version 1.1 GPC software (Polymer Labs). As references in the SEC analysis, a Twaron (PpPTA) yarn, type 1010 and an aramid trimer were used.

§ *Optical polarization microscopy*. The polymer samples were dissolved in hot water and ultrasonic mixing at 60 °C for 2 hours and cooled down at room temperature before further observation. A Jenapol microscope (300× magnification) has been used to study the solutions between crossed polarizer's.

¶ *X-ray scattering*. Bruker-Nonius D8-Discover set-up with a 2D detector has been used to perform the experiment. The sample was at 60 °C and the sample to detector distance set at 29cm, and the incident beam wavelength is 1.54 Å. In order to enhance the alignment of the liquid crystalline solution, the sample was subjected to a magnetic field of approximately 4T in the horizontal direction.

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