Formation of aqueous molecular nematic liquid crystal phase in poly(*p*-sulfophenylene sulfoterephthalamide)

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We report strong experimental evidence on the formation of a molecular lyotropic phase in water of a modified polyaramide, namely a fully sulfonated poly(*p*-phenylene terephthalamide) (Sulfo^{2}PPTA) that exhibits similar liquid crystalline behaviour in water to its non-sulfonated counterpart (PPTA, commercially known as Kevlar® or Twaron®) in sulfuric acid.

The liquid crystal behaviour of aromatic polyamides in solution, revealed upon dissolving these polymers in strong inorganic acids, has been intensively studied since the early seventies.[1] The interest of achieving water solubility in this kind of polymer is obvious for various commercial and environmental reasons, and several attempts have been reported in the literature.[2–4] The structural modifications of poly(*p*-phenylene terephthalamide) (PPTA) using sulfonated monomers such as sulfonated diamine and terephthalic acid chloride has been carried out by Vandenberg *et al*,[2] Kwei *et al*[3] and us[4] in order to obtain poly(*p*-sulfophenylene terephthalamide), or "sulfo PPTA". It has been shown that this polymer forms a birefringent nematic gel in water, even at very low polymer volume fractions (~1%). Further structural studies provide strong evidence that the gel formation is due to the presence of needle-like supramolecular aggregates in solution.[5,6]

In a recent publication, we reported the synthesis and the formation of a supramolecular nematic phase in a poly(*p*-phenylene sulfoterephthalamide) namely "Sulfo Invert PPTA" obtained from sulfonated terephthalic acid and *para*-phenylene diamine.[7] Surprisingly, the displacement of the sulfonic acid group, from the diamine to the acid ring, tremendously improves the solubility of the polymer resulting in a free flowing nematic solution. Nevertheless, rod-like aggregates are still formed in solution and are responsible for the formation of a supramolecular nematic liquid crystal phase. Aggregation, and therefore formation of a gel, seems to depend on the position of the sulfonic acid group in the monomer and on the nature of the counterion as well, since exchanging H^+ to Li^+ seems to favour it. The somewhat surprising impact of the position of the sulfonic acid group on the solution behaviour of these polymers led us to synthesize the fully sulfonated poly(*p*-phenylene terephthalamide), namely, "Sulfo^{2}PPTA", (Fig. 1). By reacting two sulfonated monomers, we found that the formation of supramolecular aggregates is suppressed and a true *molecular nematic liquid crystal phase* seems to be formed in water at high polymer volume fractions.

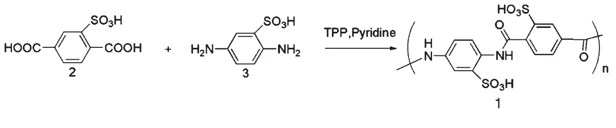

Fig. 1 Synthetic route for "Sulfo^{2}PPTA"used in this study.

For the synthesis of this fully sulfonated material, namely "Sulfo^{2}PPTA" (**1**), sulfonated terephthalic acid (sTA, **2**) and sulfonated paraphenylene diamine (sPPD, **3**) have been used. Instead of the classical low temperature polycondensation reaction developed by Kwolek[8] that requires acid chloride,[9] we used an alternative polymerization route that uses the activation of terephthalic acid by triphenylphosphite (TPP)[10,11] to make **1**.

The molecular weight (M_w) and the polydispersity index were determined using size exclusion chromatography (SEC) in sulfuric acid. Results show that the polymerization reaction typically produces samples of 15.000 g mol^{-1} with a polydispersity index of 1.8–2.3. It also contains 0.3 wt.% of Li^+ as counterions (the remainder being H^+) as determined by flame atomic absorption spectroscopy (FAAS). 3.6 wt.% of lithium corresponds to full Li^+ counterion content. Sulfo^{2}PPTA powder easily dissolved in demineralised water at room temperature and at rather high polymer concentrations (~17 wt.%), a nematic liquid crystal solution was observed. A phase diagram was obtained by optical polarization microscopy (OPM) (Fig. 2). The critical concentration for the transition from the isotropic to the nematic phase (I–N), ~17 wt.%, is relatively close to the one observed for the non-sulfonated counterpart (PPTA) in sulfuric acid when accounting for the difference in solvent density and the presence of the sulfonic acid groups that increases the mass of the repeating unit.[12] This similarity is a strong evidence for the formation of a molecular liquid crystal phase in the present case.

At room temperature, a biphasic region is observed between 13 wt.% and 17 wt.%. Such a region also exhibits a dependence on temperature, shifting the nematic phase to higher concentrations as the temperature is increased. Such temperature dependence was

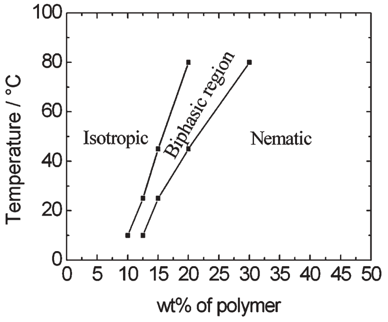

Fig. 2 Phase diagram of Sulfo^{2}PPTA in water (M_w ~ 15.000 g mol^{-1}) with 0.3 wt.% of lithium as counterions).

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also reported for molecular lyotropic systems such as PPTA/H_2SO_4[12] and PBLG/DMSO.[13]

Solutions with concentrations between 17 and 30 wt.% exhibit a homogenous nematic phase with typical Schlieren textures while at higher concentrations, 40 to 50 wt.%, typical coloured nematic textures are observed (Fig. 3). Sulfo^{2}PPTA water solutions were also investigated with X-ray scattering. In Fig. 4, the scattering intensity from a 50 wt.% solution of a molecule of $M_w \sim 15.000$ g mol^{-1} containing 0.3 wt.% of lithium as counterions, is displayed. The sample was subjected to a ~4 T magnetic field that makes 45 °C with the horizontal line, which is responsible for the alignment of the nematic phase. The result is the formation of two scattering spots on the 2D detector (inset). The distance associated to the scattering peak is ~20 Å, indicating a rather molecular nematic solution with little or no molecular aggregation. When only H^+ counterions are present, the scattering peak for a far smaller molecule, $M_w \sim 2.000$ g mol^{-1} at 50% and 30 °C is observed at ~18.5Å. The overall picture, including this oligomer one, is compatible with a molecular liquid crystal phase, the distance between molecules being slightly decreased in the case of smaller molecular weight (and H^+ as counterions). The peak position seems to be independent of the molecular weight of the sample in solution, a fact that is characteristic of a molecular liquid crystalline solution.

In order to estimate the level of order in the solution, azimuthal scans along the anisotropic peak were investigated (Fig. 4). The order parameters obtained were 0.69 and 0.72 for the 0% and 0.3% lithium content samples, respectively.

The effect of temperature on the order parameter has been further investigated with a 50 wt.% solution and its dependence on temperature is displayed in Fig. 5. As expected, $<P_2>$ decreases when the temperature increases and the effect of temperature seems to follow the model described by the extended Maier–Saupe theory[14] that applies to molecular uncharged PPTA solutions in sulfuric acid. This is another strong indication that the polymer chains are fully dissociated in solution. The details of the deviations from the model are probably due to electrostatic interactions that are not taken into account in the model. The standard Maier–Saupe model is also represented in Fig. 5 for completeness.

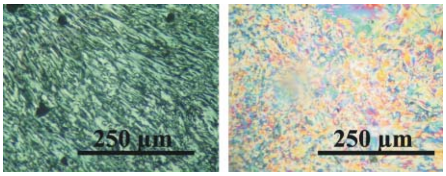

Fig. 3 (Left hand side.) Optical polarization micrograph (OPM) of a 20 wt.% Sulfo^{2}PPTA solution in water, exhibiting a Schlieren texture. (Right hand side.) OPM of a 50 wt.% Sulfo^{2}PPTA in water. ($M_w \sim$ 15.000 g mol^{-1} with 0.3 wt.% of lithium as counterions).

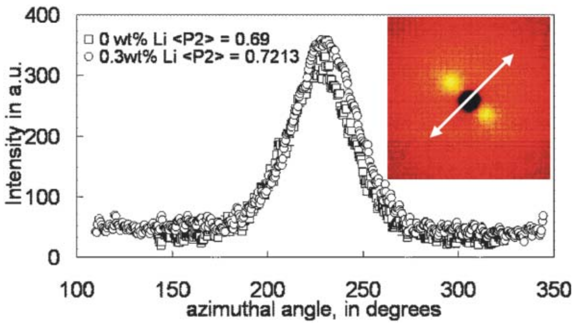

Fig. 4 Azimuthal scan of a 50 wt.% Sulfo^{2}PPTA solution at 30 °C, with 0 wt.% Li with $<P_2> = 0.69$ and with 0.3 wt.% with $<P_2> = 0.72$. Inset. 2D detector X-ray pattern of a 50 wt.% solution at 60 °C. The white arrow indicates the direction of the external magnetic field (~4 T).

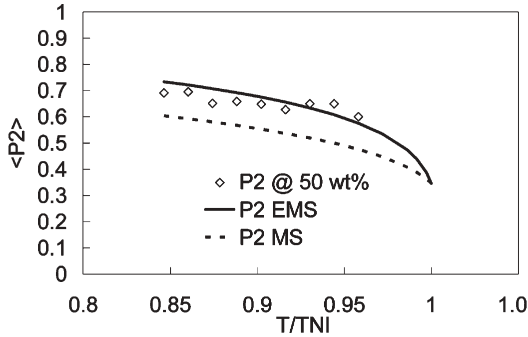

Fig. 5 Evolution of $<P_2>$ versus T/T_{NI} with T_{NI} the nematic–isotropic transition temperature, for a 50 wt.% solution ($M_w \sim$ 15.000 g mol^{-1}). Maier–Saupe and the extended Maier–Saupe models are also represented for the present case.

We reported above strong evidence for the formation of a molecular nematic phase in water for a fully sulfonated polyaramide. Using optical polarization microscopy and X-ray scattering, two different samples were investigated: a fully acid form of Sulfo2PPTA and a sample containing a fraction of lithium counterions (0.3 wt.%). The solutions exhibit (1) isotropic to nematic transition at concentrations similar to that observed for non-sulfonated PPTA in sulfuric acid; (2) a temperature concentration phase diagram typical for molecular liquid crystals and (3) a dependence of the order parameter $<P_2>$ with temperature that is observed for typical molecular non-ionic nematic liquid crystal phases such as PPTA/H_2SO_4 solutions. Contrary to the formation of supramolecular micrometre-long aggregates with nanometric cross sections observed in mono-sulfonated polyaramide solutions,[7] a small chemical modification on the sulfonated molecules, that is, the introduction of a second sulfonic group in the repeating unit, provides a drastic change in the solution structure. This offers new possibilities for the understanding of polyelectrolyte suppramolecular aggregation in solution, in the one hand, and it provides finally, a synthetic system allowing for the study of polyelectrolyte liquid crystal phases, in the other hand.

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