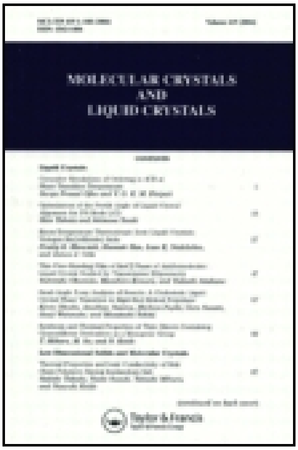

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A Direct Observation by XRD of Reorientation in a Supramolecular Liquid Crystal Polymer Induced by Magnetic Field

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A Direct Observation by XRD of Reorientation in a Supramolecular Liquid Crystal Polymer Induced by Magnetic Field

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Sulfonated polyaramide poly(p-phenylene-sulfo-terephthalamide), or "Sulfo Invert PPTA", self-assembles in water to form rod-shaped supramolecular aggregates that exhibit nematic liquid crystalline behaviour at remarkably low polymer concentration. The phase diagram is found to be rather athermal, which is an indication that the nematic phase stability is dominated by entropic excluded volume interactions. We describe the transient reorientation of this supramolecular nematic liquid crystal when an aligned sample is subjected to a magnetic field perpendicular *to the original orientation of the director. It is directly visible from time-resolved X-ray diffraction that the director alignment changes to the direction of the external field via two different pathways. These pathways consist of regions of the director field turning either clockwise or counter-clockwise leading to the doubling of the diffraction peak during the transient reorientation process. Analysing this process in more detail may provide means to determine the viscous and elastic coefficients of our supramolecular nematic liquid crystal polymer.*

Keywords: magnetic field; nematic phase; self-assembly; X-ray diffraction

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INTRODUCTION

It is well know that when a uniformly oriented nematic liquid crystal sample with a positive anisotropy is subjected to a magnetic or electric field, the alignment of the director will change towards the direction of the applied external field [1]. Due to the fast time response of typical low molar mass nematic liquid crystal systems, generally in the order of a second or less, techniques such as nuclear magnetic resonance (NMR) have been used to investigate the transient reorientation process [2,3]. Of course, in low molar mass nematic liquid crystal systems the time response in an applied electric field is an important technological issue especially for LC display devices.

Physically, two reorientation cases are possible depending on the value of the angle θ between the applied field and the original orientation of the director. When $\theta < \pi/4$, simple monolithic rotation of the director occurs, and the director aligns towards the field along the shortest pathway. However, when $\theta \approx \pi/2$ the nematic phase may in principle rotate through two different pathways as schematically shown in Figure 1. In this case, both clockwise and counter-clockwise alignment towards the applied field will occur.

In such an experiment a spatial instability occurs – where the original uniform director alignment is disrupted and the reorientation process proceeds via a transient distortion of the director field. Only a few studies on lyotropic polymers [4–6] have been carried out to investigate this field-induced transient reorientation. Here we report such experiments on a supramolecular nematic liquid crystal polymer in aqueous solution. In order to detect the director alignment we use X-ray scattering, which provides a *direct observation* of the transient instability. The system we investigate here has been described in [7] where it was shown that our sulfonated aramid polymer self

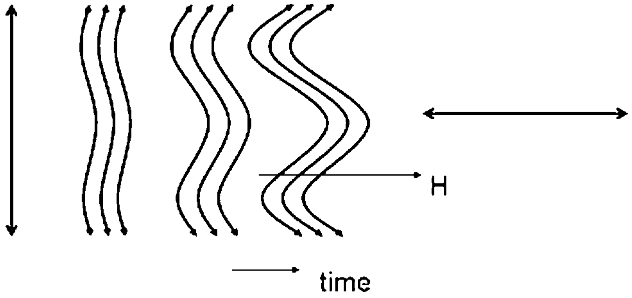

FIGURE 1 Schematic representation of reorientation in the case of $\theta = \pi/2$.

assembles into long supramolecular aggregates with a cross-section of a few nanometers. This system exhibits a nematic phase at very low polymer concentration. Moreover the phase behaviour is athermal i.e., it hardly depends on temperature. This is a clear indication that steric (excluded volume) effects dominate the stability of the nematic phase giving rise to an entropy term governing the phase diagram.

EXPERIMENTAL

The polymer poly-(p-phenylene-sulfo-terephthalamide), or Sulfo Invert PPTA, has been synthesized as previously described [7], see Figure 2. Polymers in the acid form have been used. The samples have molecular weight, M_w, of 15.000 g·mol^{-1} and a polydispersity index of 2, as determined by Size Exclusion Chromatography (SEC) in sulfuric acid.

The polymer powders were dissolved in distilled and de-ionized water. The samples were heated to 100°C during 5 minutes in sealed tubes and then ultrasonically mixed for at least 2 hours at 60°C. The samples were then put into open-ended X-ray capillaries by using suction. The suction process was also performed at 60°C. The capillary was sealed with rapid epoxy glue. This operation takes 90 seconds and usually, in a few (3 to 5) minutes the measurement of the first X-ray spectrum starts. During the experiments the capillary was placed inside a graphite tube containing a transverse hole, which allows the incident and scattered X-rays to pass through. The temperature of the graphite tube can be raised by passing a DC current through it, which causes Ohmic heating. The temperature of the graphite tube is measured using a thermo-couple. Using a PID temperature controller and a power supply allows this graphite sample holder to be regulated very accurately (approx. 10 mK fluctuations). In addition, high heating and cooling rates around 300 K/minute can be applied. The temperature of the X-ray capillary itself is determined via a calibration curve obtained from samples with known transition temperatures. The X-ray measurements were carried out on a

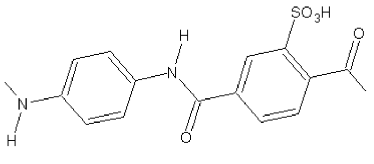

FIGURE 2 Structure of Poly-(p-sulfophenylene-terephthalamide) or Sulfo Invert PPTA, used in this study.

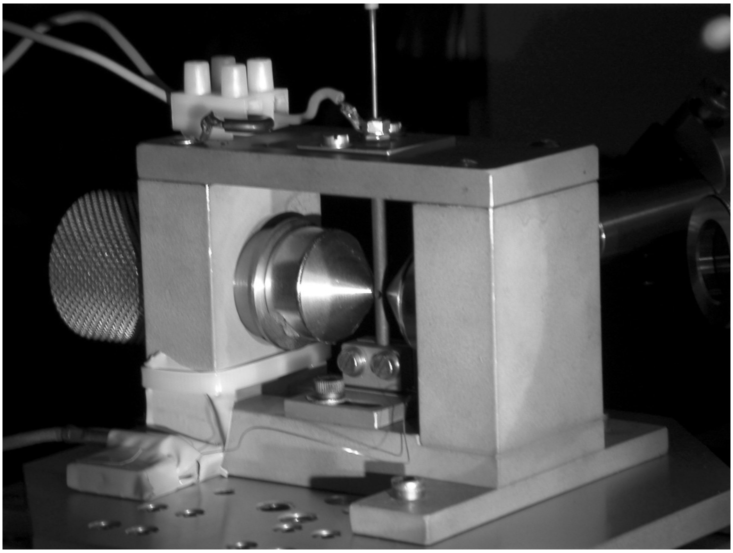

FIGURE 3 Sample holder used in this X-ray study.

Bruker-Nonius D8 Discover with a sample to detector distance set to 29 cm. Using a 2-D detector diffraction patterns were recorded every 30 min. Finally, in order to align the sample a focused permanent magnetic field of approximately 4 T was applied perpendicular to the capillary using NdFeB magnets. The sample holder and magnet as discussed above are shown in Figure 3.

RESULTS AND DISCUSSION

Solutions containing 6 wt% of Sulfo Invert PPTA were studied. Previous investigation has shown that such solutions contain large supramolecular aggregates, estimated to be ~8700 Å long with a cross section of only ~22 Å [7]. The shear applied to the sample during the filling operation of the X-ray capillary gives rise to a rather high level of alignment. We find that the director of the supramolecular polymer aggregates is initially aligned along the axis of the capillary.

During the experiments the temperature was set either to 45°C or 60°C and the X-ray capillary was exposed to a focused permanent magnetic field of about 4 T, applied perpendicular to the axis of the capillary and the incident X-ray beam. The overall process of reorientation of the director of the supramolecular aggregates turns out to be rather slow probably due to their large size. Note that the overall rate

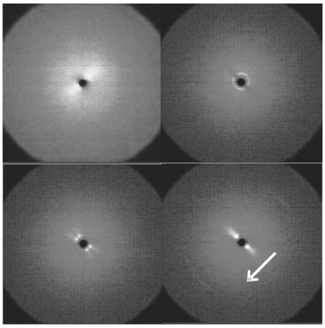

FIGURE 4 X-ray scattering patterns on a 2D detector at different times after application of the external magnetic field. Top left 30 minutes, top right 1 hour, bottom left 2 hours, and bottom right 6 hours. The white arrow represents the direction of the external magnetic field.

of alignment is to first approximation determined by the viscous torque and the magnetic torque. The viscous torque is rather high due to the large dimensions of the supramolecular objects in the solution while the magnetic torque will be relatively small due to the low polymer concentration.

We find that the relaxation process can be divided into four phases as shown in Figure 4, where the X-ray scattering intensity as recorded on a 2-D detector is displayed as a function of time. Initially, the aggregates are still aligned along the capillary resulting from the shear applied during the filling process (Fig. 4a). This can be seen by the presence of the two equatorial scattering peaks perpendicular to the capillary axis. They remain in this orientation for a short period of time depending on the temperature and polymer concentration. Next in the second phase, an isotropic ring, or large croissant, appears at the expense of the two original peaks while no other clear maxima can be detected (Fig. 4b). During this time, no meaningful value of the peak width can been established. In the third phase, a double peak starts to appear at the edges of the croissants (Fig. 4c), which grows at the expense of the croissants intensity. Finally, the double peaks move towards each other, separated by an angle χ, and slowly merge into single strong peaks (Fig. 4d) with a high level of alignment. This indicates that ultimately the director is fully aligned along the magnetic field.

The relaxation time of the final phase mentioned above, that is, merging of the double peaks, may be evaluated by the measurement of the time dependence of the angle, $\Delta\chi$, between the double peaks

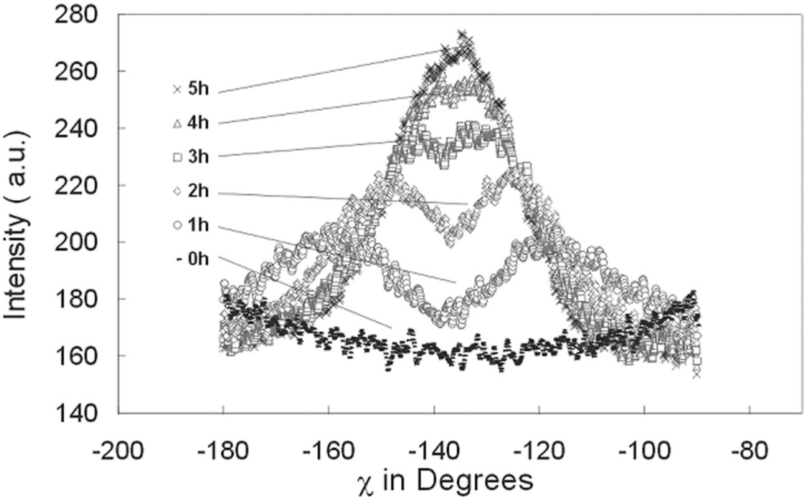

FIGURE 5 Azimuthal χ dependence of the scattering peaks of a 6 wt% solution at 60°C during the peak-merging phase.

positioned at angles χ_1 and χ_2, respectively. Grouped scattering data along 2θ are represented in Figure 3 as a function of χ for a 6 wt% solution in water at different times during relaxation, and at 45°C or 60°C. As can be observed from the figure, the initially separate peaks merge into a single one as a function of time.

A bimodal Maier-Saupe function (Eq. (1)) was fitted to the experimental data in order to extract the two peak positions, χ_1 and χ_2, the intensities A_1 and A_2 and the peak widths, α_1 and α_2.

$$i(\chi) = i_0 + A_1 \exp(\alpha_1 \cos^2(\chi - \chi_1)) + A_2 \exp(\alpha_2 \cos^2(\chi - \chi_2)) \qquad (1)$$

In expression (1), i_0 is an arbitrary baseline. The angles related to the peak positions, χ_1 and χ_2, as well as the angles between the two peaks, $\Delta\chi = |\chi_1 - \chi_2|$, are plotted in Figure 5, for both temperatures. Also, inspection of Figure 6 reveals that the first phases of the relaxation mentioned above occur much faster at 60°C than at 45°C, the scattering peaks related to χ_1 and χ_2, appearing only after 3.5 hours after the beginning of the experiment for the sample at 45°C while they are already visible after 0.5 hours for the sample at 60°C.

An exponential decay function was used to fit $\Delta\chi$ as a function of time and as a result, characteristic orientation times of about 2.4 hours and 1.3 hours were found for 45°C and 60°C, respectively. It is interesting to recall that the order of magnitude found for the response times here is much larger than those found for lyotropic systems

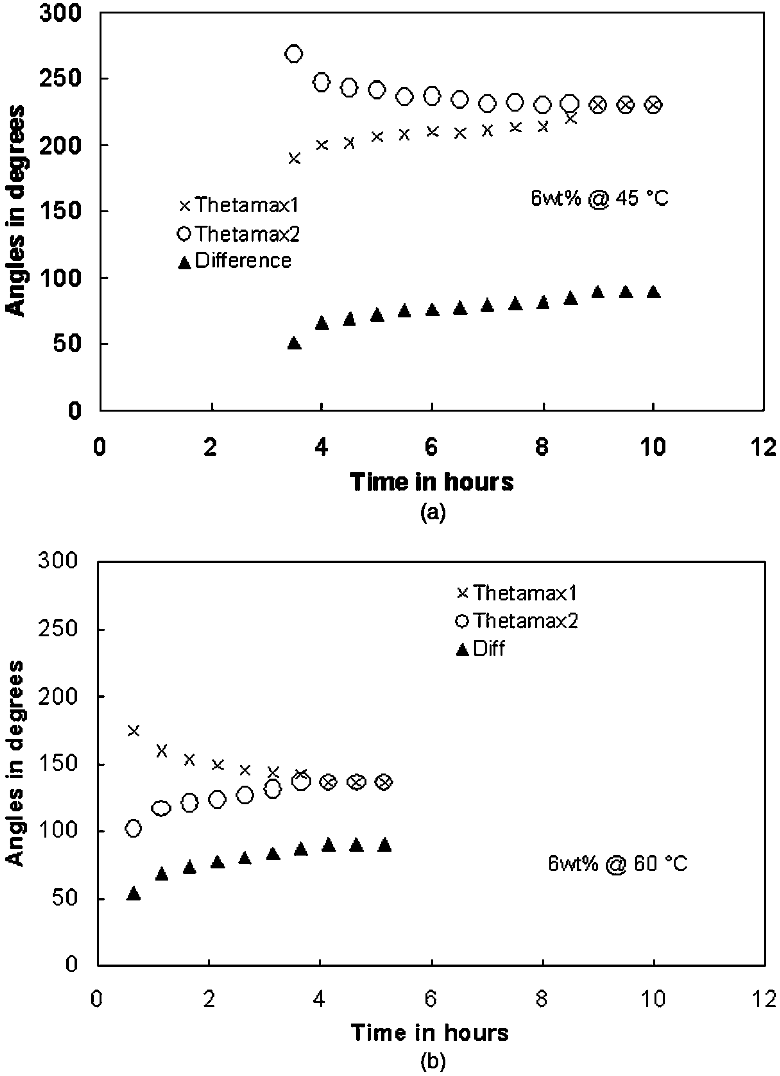

FIGURE 6 Peak positions, χ_1 and χ_2, and difference $\Delta\chi = |\chi_1 - \chi_2|$, as a function of with time, during the peak-merging phase.

formed by small molecules. Such systems exhibit typical response times of seconds and the impact of the size of the nematic molecules on the response time may be quantified [8]. In the present system, the fact that we are dealing with supramolecular aggregates, explains the observed rather large response time.

From the α values obtained from the fitting of the peaks with Eq. (1), a value of the order parameter $\langle P_2 \rangle$ was obtained by using the following expression, where x is the cosine of the molecular alignment angle, and $P_2(x) = 1/2(3x^2 - 1)$:

$$\langle P_2 \rangle = \frac{\int_{-1}^{1} P_2(x) e^{\alpha x^2} dx}{\int_{-1}^{1} e^{\alpha x^2} dx} \qquad (2)$$

Because the solutions studied here have a rather high viscosity, the method used to fill the X-ray capillary is very efficient to align the director (or the molecular aggregates) along the capillary. The evolution of the $\langle P_2 \rangle$ order parameter, during the final stage of the alignment process has been determined for the two temperatures and the results are displayed in Figure 7.

As already mentioned, the typical value of the order parameter for a similar system Sulfo-PPTA in H_2O is particularly high and remains constant, independent of time and temperature [9]. This apparently also is the case for Sulfo Invert PPTA, both at rest and during the transient reorientation. The average value we find is around 0.93 which confirms the view that the supramolecular aggregates form an Onsager type liquid crystal system. This is further supported by the observed athermal nature of the phase diagram, i.e., the critical concentration for forming the nematic phase does not show appreciable temperature dependence.

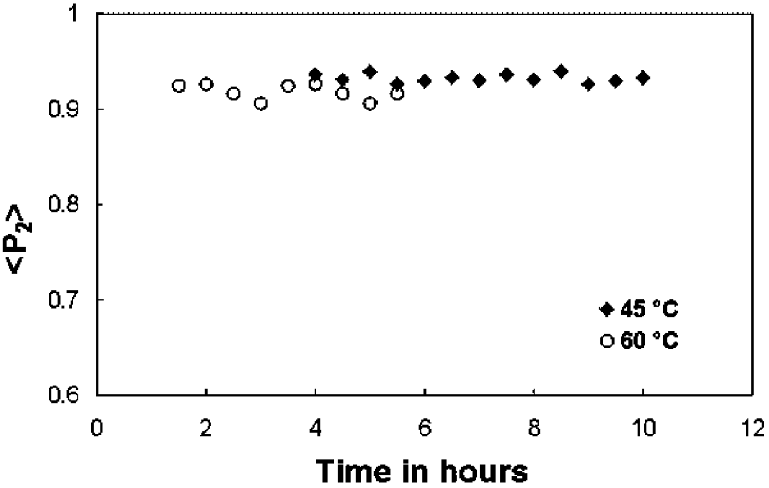

FIGURE 7 Time dependence of the $\langle P_2 \rangle$ order parameter during the latter stage of the reorientation process, for temperatures 45°C and 60°C.

We note that a molecular nematic system, such as 8.8 wt% non-sulfonated PPTA (Mw ~30.000) in sulphuric acid, also exhibits relaxation times in the range of hours [10] at 25°C. It should be realised that the relaxation time scales are governed by the size of the molecules or molecular aggregates and also by temperature and the viscosity of the solvent. Similar time scales are, therefore, a coincidence.

Finally, since the liquid crystal system studied here is formed by supramolecular aggregates, it is of interest to examine the effect of the reorientation on the integrity of the aggregates. We observe experimentally that during the reorientation the position of the scattering peaks does not change. From this we conclude that the supramolecular aggregates apparently are not severely disturbed. When the final equilibrium state is reached, the aggregates remain ordered, without any change in the scattering peak radial position. This was monitored for more than 192 hours at 25°C, and it confirms that no destruction or reorganization phenomena occur during the transient rotation process of the supramolecular aggregates.

CONCLUSIONS

We report on the magnetic field-induced transient reorientation in a supramolecular liquid crystal formed by the self-assembling of a sulfonated polyaramide. X-ray scattering (XRD) has been used to directly monitor the transient phenomenon in real time. It was shown that the very long supramolecular aggregates (~8700 Å) initially oriented along the capillary direction due to the filling process, reorient along a magnetic field perpendicular to the initial alignment in a process that may be divided into four stages. Those stages translate into different scattering patterns on the 2D X-rays detector. First, the aggregates are still aligned along the capillary by shear at the early stages of the experiment and remain in this orientation for a short period of time depending on the temperature and polymer concentration. Second, an isotropic ring, or large croissant, appears at the expenses of the two previous peaks while no other peaks can be detected. In a third phase, double peaks start to appear at the edges of the croissants at the expenses of the croissants intensity and finally these double peaks are aligned along the capillary direction, slowly merging into two single strong peaks. This indicates that the supramolecular aggregates are finally oriented along the magnetic field. The time dependence of the double-peak merging process shows a strong dependence on temperature. Characteristic times of the order of 2.4 hours and 1.3 hours, respectively at temperatures of 45°C and 60°C , were found using a 6 wt% solution in water of a $M_w = 15.000\,g \cdot mol^{-1}$ polymer sample.

Finally, the extremely high values of the $\langle P_2 \rangle$ order parameter, characteristic of such large supramolecular aggregates in solution, remains practically constant during reorientation. This fact, together with the constant value of lateral spacing, provides evidence that no disruption or recombination of the supramolecular aggregates occurs during the reorientation of the director field.

The experimental results for the orientation dynamics can in principle be analysed using the Martins model [2], which should enable us to determine the complete set of Leslie coefficients. This requires additional investigation of the realignment at smaller angles of the applied field, so as to be able to check the consistency of the results.

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