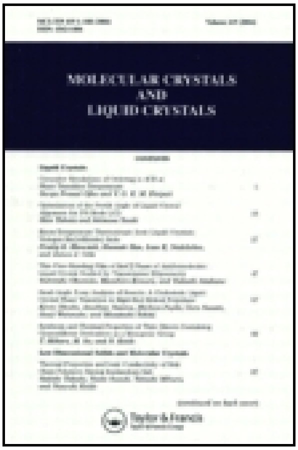

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Water Soluble Rigid Rod Polymers: A SANS Study of Shear-Induced Alignment and Relaxation

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WATER SOLUBLE RIGID ROD POLYMERS: A SANS STUDY OF SHEAR-INDUCED ALIGNMENT AND RELAXATION

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In this paper, we report the effect of shear and relaxation on low concentration solutions of a synthetic water-soluble rigid rod polymer in deuterated water using small angle neutron scattering (SANS). The polymer used is sulfo poly p-phenyleneterephtalamide (Sulfo-PPTA). At rest, a 1wt% solution of Sulfo-PPTA presents a scattering maximum at small angles that is related to the interaction between rods. Under the action of very small shear rates, a high alignment is observed. The scattering maximum, initially isotropic, strongly increases upon shear in the direction perpendicular to the applied shear while it is suppressed in the direction parallel to the shear. After cessation of shear the alignment remains for a considerable period of time. The $\langle P_2 \rangle$ *order parameter has been determined from the SANS data during application of shear and during relaxation. The formation of needle-like aggregates in solution is suggested as a possible explanation of our results.*

Keywords: molecular aggregates; SANS; shear, relaxation; Sulfo PPTA; water soluble polyaramides

INTRODUCTION

Alignment under shear of polyelelectrolyte solutions as well as of wormlike ionic micelles has been reported in the literature [1–8]. In the second

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*Corresponding author. Fax: +31 15 2787415, E-mail: s.j.picken@tnw.tudelft.nl system, because of the semi-rigid nature of the micellar assemblies and the long-range nature of the electrostatic interactions, alignment can easily be induced by shear. Because of the same nature of the interactions, similar effects can also occur in solutions of semi rigid natural polyelectrolytes [9] and alignment of the polyelectrolyte molecules can be induced by shear on those systems. In order to induce alignment in concentrated high molecular weight polymers only very *high shear rates* have been used and reported so far [3].

In this paper, we report on the effect of shear on low concentration solutions of a water-soluble rigid rod synthetic polymer (sulfopoly p-phenylene-terephtalamide) (Sulfo-PPTA) in deuterated water (Fig. 1).

We show below that *relatively small shear rates* are needed to align the dispersion even at low polymer concentrations such as 1 wt%. The experimental technique used here is small angle neutron scattering. By fitting a Maier-Saupe distribution, we were able to measure the $\langle P_2 \rangle$ order parameter. After shearing, the system has been allowed to relax during a long period of time (30 hours), and this relaxation has also been determined via the time dependence of $\langle P_2 \rangle$. The obtained results will be discussed taking the nature of the polymer solutions into account.

EXPERIMENTAL SECTION

Polymer Synthesis

The sulfo poly-phenyleneterephtalamide (Sulfo-PPTA) polymer sample has been synthesized as described in the literature [9,10] (Fig. 2).

The molecular weight was determined by viscosimetry and SEC in concentrated sulfuric acid. The polymers have an Mw of 18 000 $g.mol^{-1}$ and the polydispersity index is about 1.4 to 1.8. The contour length is approximately 700 Å for this molecular weight. During the synthesis, we made use of LiCl. Some of this remains in the polymer samples and acts as a counter-ion. In the present sample, the Li^+ content is 0.28 wt% which means that 15% of the sulphonic groups contain lithium. The amount of lithium present in the sample has been determined by Flame Absorbance Atomic Spectroscopy (FAAS).

Sample Preparation and Shear Cell

The polymer powders were dissolved in D_2O (1wt%). The solutions were heated at 100°C during 5 min in sealed tubes and then ultrasonicated for at least 2 hours at 60°C. The polymer solutions were re-heated to 100°C prior to use and the temperature of the Couette cell was set to 75°C before the solution was poured into it. The Couette cell has a 2 mm gap and its

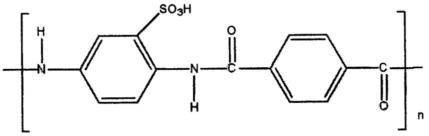

FIGURE 1 Sulfo PPTA, sulphonated poly(p-phenyleneterephtalamide).

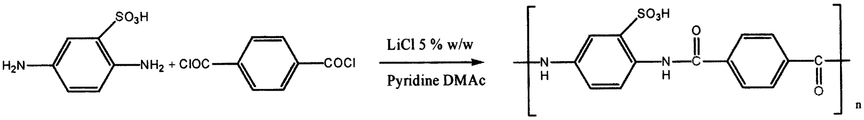

FIGURE 2 Synthesis route of Sulfo PPTA.

temperature was controlled with a thermal bath. After sample preparation and conditioning, all SANS experiments were carried out at 25°C. Before application of shear, the sample rested in the Couette for at least 2 hours at 25°C.

The incident neutron beam passes through the Couette cell perpendicular to the axis of rotation, parallel to the shear gradient and perpendicular to the flow direction.

Sans Experiments

The scattered neutrons were detected by the 128 × 1282D detector of spectrometer PAXY at Laboratoire Leon Brillouin, CEA-CNRS, Saclay (France). A sample-detector distance of 2.5 meters and incident neutron wavelength of 8 Å were used. The standard procedure of data treatment

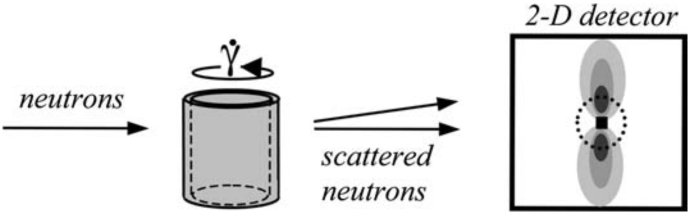

FIGURE 3 Schematic couette setup at the LLB PAXY beamline.

was applied to the data, such as division by the flat incoherent scattering of water to obtain the detector response and subtraction of empty cell scattering and incoherent background. The data has also been regrouped in the direction parallel and perpendicular to the shear direction using angular sectors of 15 degrees. Three different shear rates were applied to the samples: 12.5 s^{-1}, 125 s^{-1} and 2500 s^{-1}.

RESULTS AND DISCUSSION

Shearing

At rest, a 1 wt% solution of Sulfo-PPTA presents a scattering maximum at small angles, which is related to the interaction between charged rods. On a 2D detector, such a maximum of scattering corresponds to a ring of stronger intensity in the centre of the observable window (Fig. 4a). At this stage the system is isotropic and no significant value of $\langle P_2 \rangle$ was found. Under the action of even *relatively small shear rates*, the scattering ring at small angles transforms into two spots in the direction perpendicular to the applied shear (Fig. 4b). Initially isotropic at $\gamma = 0\,s^{-1}$, a strong intensity increase in the direction perpendicular to the applied shear is observed while it is dramatically suppressed in the direction parallel to the shear. The increase of shear rate does not effect the radial position of the peak. In the azimuthal direction, however, the peak becomes narrower, reflecting an increase of alignment in the direction parallel to the applied shear. This can be easily seen from the set of curves in Figure 4 showing the increase of orientation with increasing shear rate.

As mentioned above, an intensity decrease in the direction parallel to the applied shear is also observed. It can be better seen in Figure 5, where the intensities at rest and those in parallel and perpendicular directions are plotted as a function of the scattering vector for the lowest shear-rate ($\gamma = 12.5\,s^{-1}$). The large intensity increase in the perpendicular direction is clearly shown in the figure. Considering the low polymer concentration, the degree of alignment, already occurring at low shear rates, is very high.

The effect of the shear rate on the alignment is shown in Figures 6 and 7 where the curves of I(Q) in the perpendicular and parallel directions are plotted for different shear rates. Basically, a further increase of intensity in the perpendicular direction and a suppression of intensity in the parallel direction are observed with increasing shear rate. Also, it seems that the alignment stops increasing beyond a certain shear rate value. This is clear by comparing the last two shear-rates 125 and $2500\,s^{-1}$.

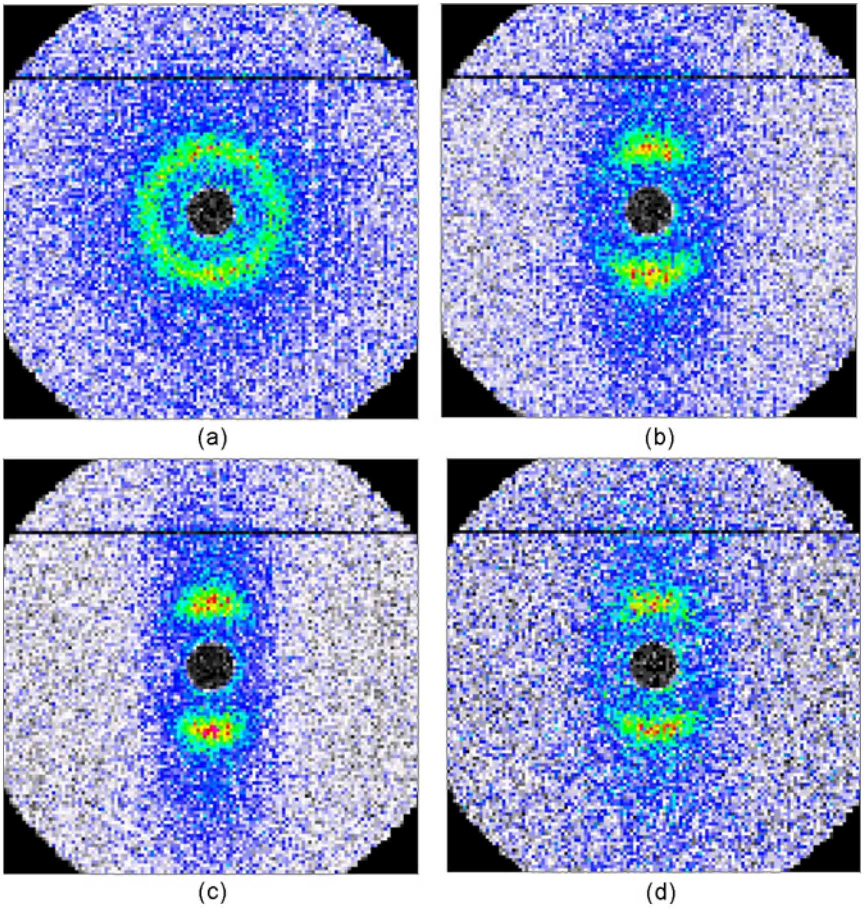

FIGURE 4 2-dimension SANS spectra of Sulfo PPTA at 1% (sample to detector L = 2.5 m, neutron wavelength $\lambda = 8\,\text{Å}$: (a) zero shear; (b) shear rate of $\gamma = 12.5\,\text{s}^{-1}$; ; (c) shear rate of $\gamma = 125\,\text{s}^{-1}$; (d) shear rate of $\gamma = 2500\,\text{s}^{-1}$. (See COLOR PLATE XIV)

Further analysis was performed in order to estimate the orientation induced by shearing. The $\langle P_2 \rangle$ order parameter was calculated by fitting a Maier-Saupe distribution to our data. To do this the data were integrated around a ring as shown in Figure 8.

The resulting curve was then fitted to a Maier-Saupe equation distribution with a free baseline and position of the maximum:

$$I = I_0 + Ae^{\alpha \cos^2(x-\theta_0)}$$

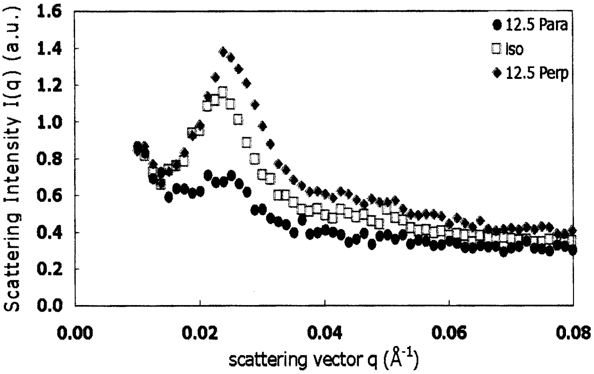

FIGURE 5 Comparison between scattered intensity in parallel and perpendicular directions for the solution submitted to shear and the intensity in the isotropic state. (●) Parallel direction, (◆) Perpendicular direction and (□) isotropic.

The fitting procedure gives the parameter α. The $\langle P_2 \rangle$ value was obtained by the following equation:

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

The $\langle P_2 \rangle$ values obtained for the different shear rates are shown in Figure 9.

The result confirms the trend discussed before: at a low shear rate of $12.5\,\mathrm{s}^{-1}$, $\langle P_2 \rangle$ already reaches a value of 0.3. Further increasing the shear rate causes $\langle P_2 \rangle$ to reach a plateau value around 0.55.

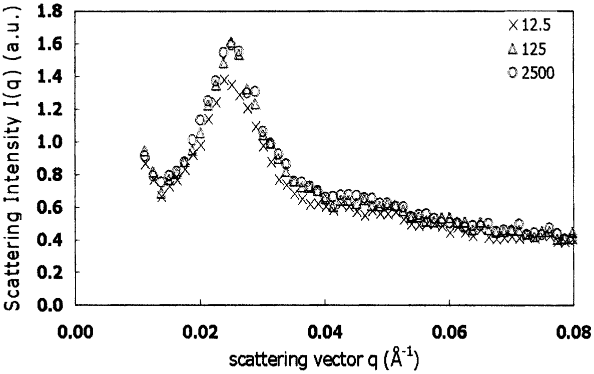

FIGURE 6 Scattering intensity in the perpendicular direction for shear rates of: (X) $\gamma = 12.5\,\mathrm{s}^{-1}$; (Δ) $\gamma = 125\,\mathrm{s}^{-1}$; (○) $\gamma = 2500\,\mathrm{s}^{-1}$.

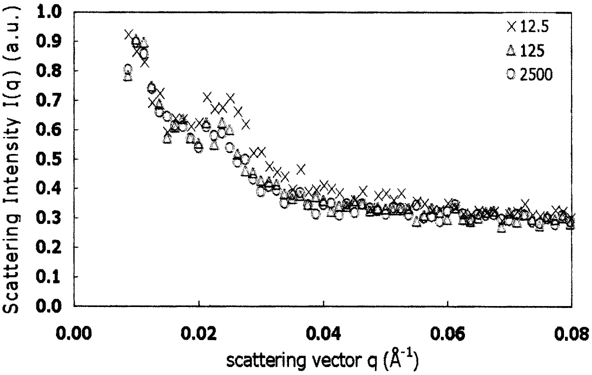

FIGURE 7 Scattering intensity in the parallel direction for shear rates of: (X) $\gamma = 12.5\,\mathrm{s}^{-1}$; (Δ) $\gamma = 125\,\mathrm{s}^{-1}$; (○)$\gamma = 2500\,\mathrm{s}^{-1}$.

We note that the $\langle P_2 \rangle$ values are rather high for such a dilute low molecular weight polymer solution. By comparison, a normal PPTA solution with molecular weight around 30 000 to 40 000 g.mol^{-1} forms a nematic phase from around 8–10 wt%. At this point, $\langle P_2 \rangle$ reaches a value of 0.4. Therefore, in the present case, $\langle P_2 \rangle$ is abnormally high. A possible explanation for this is the formation of rod-shaped supramolecular aggregates

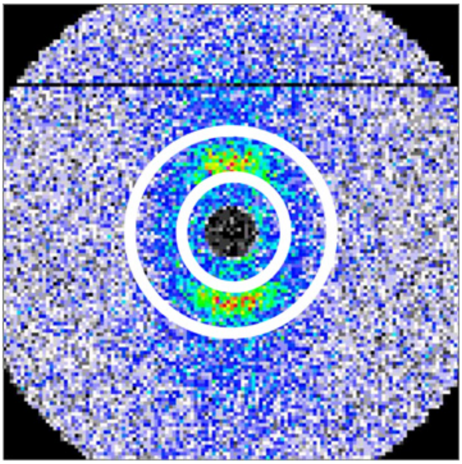

FIGURE 8 Schematic representation of the integration area for the data on the 2D detector. (See COLOR PLATE XV)

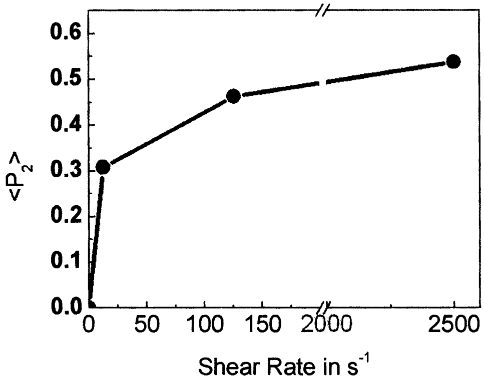

FIGURE 9 $\langle P_2 \rangle$ order parameter as a function of different shear rates.

that align under shear. Similar supramolecular aggregation was previously observed in similar systems and characterized with viscosimetry studies [11].

From the present results, we can now estimate the dimensions of the supramolecular rods. Assuming that the scattering maximum is associated to the distance between rod-like particles (~260 Å) and using a square lattice we obtain a diameter of the molecular aggregates of about d = 30 Å. The use of a hexagonal lattice does not significantly change the estimated value.

Then, applying the Onsager [12] relation $\Phi^* = 4d/L$ for the critical I-N concentration for polydisperse rods, the length of the aggregates is estimated to be about 12,000 Å. Here we are assuming that we are not far from the critical concentration Φ^*, i.e. that $\Phi^* \approx 0.01$. The contour length for an average Sulfo-PPTA chain is 700 Å with a diameter of 5.4 Å. By comparing these values, we find that each needle-like aggregate should contain about 500 polymer chains.

It has been suggested that the driving force of the formation of such molecular aggregates in charged rigid-rod molecules, could be counter-ion-induced attraction [13–16], as has been reported in the condensation of bio polymers such as DNA [17], F-actin fibers and microtubules [18] with the presence of added salts. An additional mechanism that can contribute to the creation of molecular aggregates is the formation of hydrogen bonding between the sulfonic group and the neighboring amide group [19–20]. The question about the exact mechanism responsible for such supramolecular aggregation remains open for the present system as well as for the other bio-molecules and synthetic polymers cited above.

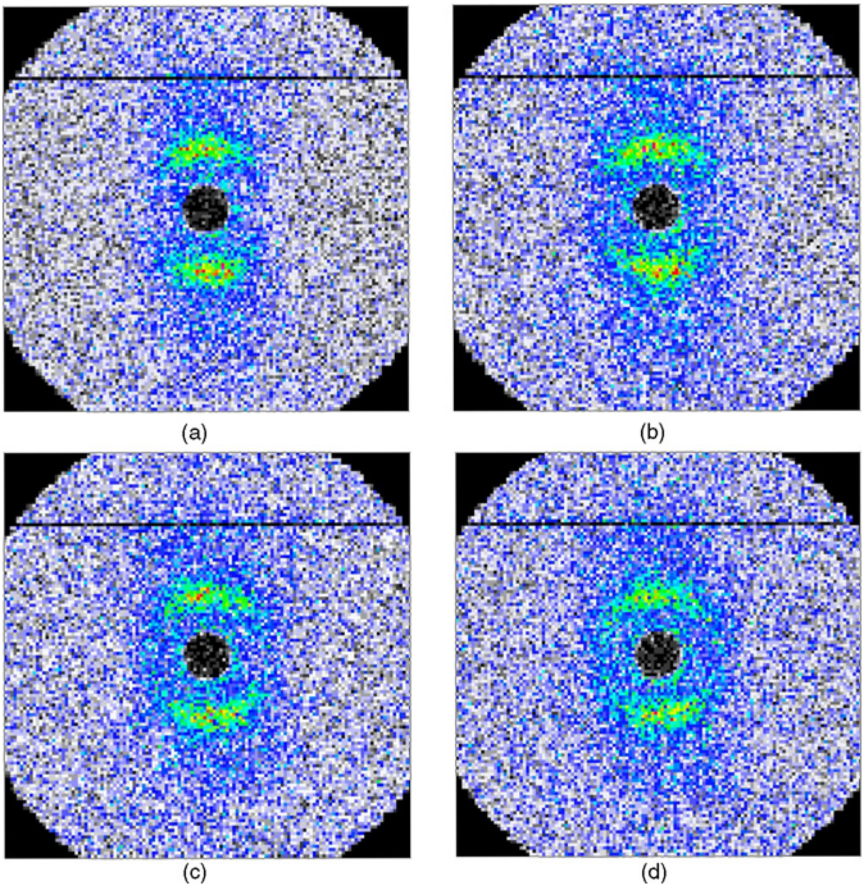

FIGURE 10 2-dimensional SANS patterns of Sulfo PPTA at 1% (sample to detector L = 2.5 m, neutron wavelength $\lambda = 8\,\text{Å}$: (a) 5 hours; (b) 10 hours; (c) 15 hours; (d) 20 hours. (See COLOR PLATE XVI)

Relaxation

The system is allowed to relax after shearing during 30 hours at room temperature. Spectra were recorded every 30 min. As a preliminary observation, the system seems to remain aligned, but the isotropic ring starts to grow and the intensity of the peak decreases. This can be illustrated with the set of spectra taken at four different times (5, 10, 15, 20 hours) as displayed in Figure 10.

The calculation of the order parameter $\langle P_2 \rangle$ reveals more information on the relaxation process. Following the same procedure as described above,

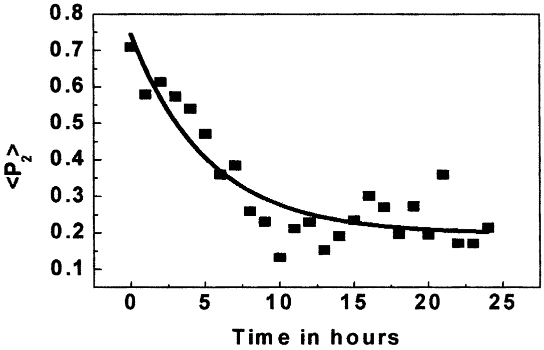

FIGURE 11 $\langle P_2 \rangle$ order parameter as a function of time after cessation of shear.

the $\langle P_2 \rangle$ parameter has been calculated for different times and the results are shown in Figure 11.

The order remains high for a long period of time and only decreases slowly. Again, this seems to confirm the idea of needle-like supramolecular aggregates. Fitting the relaxation curve with a single exponential with a free baseline, a relaxation time of $\tau = 5.1$ hours is found (with a baseline of 0.2). The striking result is that for long times, the system remains oriented, possibly due to the formation of a physical gel that immobilizes the molecular aggregates in an ordered fashion. Molecular relaxation in solution is a far quicker process than that observed here with relaxation occurring over much longer time scales.

SUMMARY & CONCLUSIONS

In this paper, we report the effect of shear on a low concentration solution of a synthetic rigid ionic polymer in deuterated water. The alignment under shear was studied by small angle neutron scattering (SANS). We have shown, by measuring the value of the $\langle P_2 \rangle$ order parameter as a function of the applied shear rate, that a high degree of alignment was obtained even for a relatively low shear rates ($12.5\,s^{-1}$). Alignment is found to increase with shear rate and it seems to saturate as the shear rate increases. The relatively high $\langle P_2 \rangle$ obtained cannot be attributed to the alignment of individual polymer chains but appears to be related to the alignment of molecular needle-like aggregates. After cessation of shearing, the $\langle P_2 \rangle$ value of the solutions remains high with a relaxation time of about 5 hours, revealing that molecular aggregates remain highly oriented over a long period of time. The size and shape of the supramolecular aggregates has been estimated, but the exact mechanism of their formation is still unclear.

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