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Influence of the Shear Rate on the Small-Angle Neutron Scattering Pattern of Polyelectrolyte Solutions: The Xanthan Example

M. Milas, P. Lindner,[†] M. Rinaudo, and R. Borsali*

CERMAV−CNRS and Joseph Fourier University,
P.O. Box 53, F-38041 Grenoble Cedex 9, France

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Introduction

It is well established that polyelectrolytes in salt-free solutions present a peak in light, neutron, and X-ray scattering.[1−3] This peak is ascribed to electrostatic interactions between charged linear[4] or spherical[5] molecules.

Neutron scattering results were first discussed on poly(styrenesulfonate) solutions (NaPSS).[6] The position of the peak, characterized by $q_{\max}$, is shifted toward higher values as the concentration increases. The variation of the peak position generally obeys the scaling law $q_{\max} \sim C^{1/2}$, which is characteritic of semidilute solutions.[7] The existence of such maxima in salt-free polyelectrolyte solutions is related to a type of "electrostatic order". The addition of salt screens the electrostatic interactions, and the maximum disappears progressively, reaching the neutral behavior. Data were previously described on xanthan[8] in the same experimental conditions as presented in this work but in the absence of shear.

In this work, a polyelectrolyte solution of a wormlike charged polysaccharide (xanthan molecule) was investigated in a Couette type shear apparatus in order to better characterize the so-called organization in the solution.

Experimental Section

Two xanthan samples were used in this work. The first was supplied by Shell (Sittingbourne, U.K.) and obtained from an unpasteurized broth.[9] Its weight-average molecular weight is 8×10^6. The second was a xanthan sample (P100) produced by Rhône-Poulenc (France) which was depolymerized by enzymic treatment followed by fractionation.[10] The fraction used in this work corresponds to the sample F3[10] and has a weight-average molecular weight equal to 2.35×10^5. The samples were dissolved in D_2O.

The xanthan solutions were sheared in a Couette type shear apparatus for SANS measurements at the D11 instrument of the ILL.[11] The samples are confined in the gap between two concentric quartz cylinders, with the outer one rotating. The inner, static cylinder is temperature controlled. The incoming beam which encounters the sample normal to the axis of rotation of the outer cylinder is parallel with respect to the shear gradient $\dot{\gamma}$ and perpendicular with respect to the flow direction $\mathbf{v}$.

Results and Discussion

(1) Static Scattering. In order to better understand the effect of shearing, it is useful to present first SANS at zero shear rate (scattering at rest). In the range of investigated concentrations, $3.5 \times 10^{-3} < C_P < 15 \times 10^{-3}$ g/mL, for the two samples $M_w = 8 \times 10^6$ and $M_w = 2.35 \times 10^5$, a very distinct and broad peak is observed at certain $q_{\max}$ whose values depend on the polyelectrolyte concentration. To be more complete, in our observation, no secondary peak was detectable.

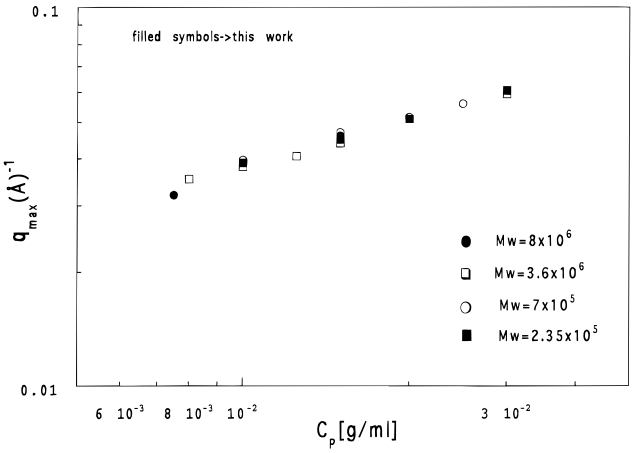

Figure 1. log−log variation of $q_{\max}$ as a function of the polyelectrolyte concentration: (●) $M_W = 8.0 \times 10^6$; (□) $M_W = 3.6 \times 10^6$; (○) $M_W = 7.0 \times 10^5$; (■) $M_W = 2.35 \times 10^5$. The filled symbols represent this work, the empty symbols those from ref 12.

In Figure 1, we have plotted the log−log variation of $q_{\max}$ as a function of C_P. These results are in good agreement with those already reported on xanthan solutions obtained on other samples having different molecular weights.[12] This shows that the position of the peak is independent of the molecular weight of xanthan and still agrees with a hexagonal packing of the molecules or the existence of an isotropic structure with a preferential distance between the nearest polyion neighbors as described previously.[12,13]

The exponent of the scaling law (about $^1/_2$) above $C_P = 15 \times 10^{-3}$ g/mL, where the xanthan is under its order conformation, is consistent with the notion of a correlation hole effect[2−5] and liquid-like correlations of cylindrical scatterers.[13−15] In the absence of salt and in the semidilute regime, although a polyelectrolyte cannot be considered as a rod particle, it is locally stiff enough to have a rodlike type behavior.

(2) Scattering under Shear. The evolution of the structure was investigated at different shear rates in the range of $\dot{\gamma} = 500$ to $\dot{\gamma} = 12\,000$ s^{-1}. The first observation is that when $\dot{\gamma}$ increases, the peak position remains constant whereas its height increases progressively and becomes sharper with $\dot{\gamma}$.[8] This result indicates an increase of the degree of the order in the solution as $\dot{\gamma}$ increases. Figure 2 illustrates this behavior where a typical intensity contour plot is given for static measurement (a) and after shearing of the solution at $\dot{\gamma} = 12\,000$ s^{-1} (b) for the xanthan in salt-free semidilute solution ($M_W = 2.35 \times 10^5$ and $C_P = 15 \times 10^{-3}$ g/mL). This figure demonstrates clearly the transition from isotropic to anisotropic character of the solution. Figure 2a represents the scattering under static conditions ($\dot{\gamma} = 0$ s^{-1}) and shows the isotropic nature of the solution with randomly oriented polyions. Figure 2b represents the scattering intensity at the important shear gradient of $\dot{\gamma} = 12\,000$ s^{-1}, where the flow direction is indicated by the arrow. It shows clearly an anisotropy of the system which is a direct consequence of preferential orientation of the polyelectrolyte chains in the shear field. Consequently, a certain degree of order exists in solution which has been highlighted by the effect of shearing. Similar observations were previously reported on, for instance, smectite

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* To whom correspondence should be addressed.

[†] Institut Laue Langevin, BP 156, Grenoble Cedex 9, France.

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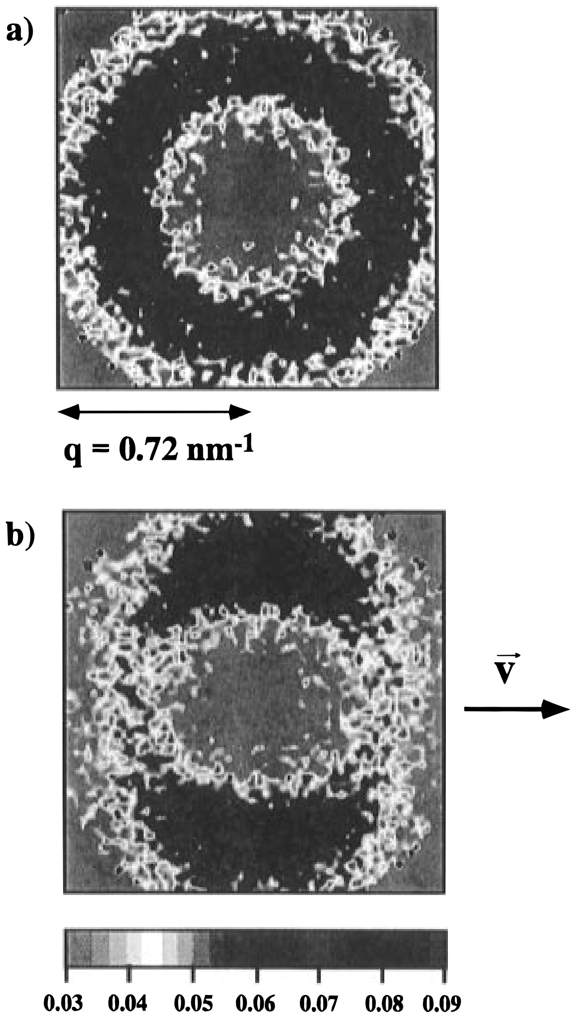

Figure 2. Interpolated image of the normalized two-dimensional SANS multidetector spectrum of xanthan solution ($M_W = 2.35 \times 10^5$, $C_P = 15 \times 10^{-3}$ g/mL, sample-to-detector distance $L = 2.60$ m, neutron wavelength $\lambda = 12$ Å): (a) solution at rest; (b) solution in Couette flow at a shear gradient of $\dot{\gamma} = 12\,000$ s^{-1}. The flow direction is indicated by an arrow.

clay colloids.[16] One notes that the position of the scattering peak remains unchanged, corresponds to the static behavior, and shows that the interparticle distance is unperturbed by the applied shear to the solution. An important and new result is the emergence, although weak, of a shoulder which mimics a secondary order scattering whose position is between $1.7q_{\max}$ and $1.9q_{\max}$ and is illustrated in Figure 3. This value may correspond to locally hexagonal packing ($1.7q_{\max}$) or liquid-like behavior ($1.9q_{\max}$), but the accuracy of this value does not allow us to draw a definitive conclusion. These results indicate a progressive development of an anisotropic locally ordered structure corresponding to a preferential alignment of the ionic polymers in the direction of the shear when $\dot{\gamma}$ increases. It also demonstrates clearly that the main peak is related to electrostatic interactions which impose a preferential distance between the locally ordered chain under shear or at rest.

Conclusion

This paper discusses neutron scattering data on xanthan salt-free solutions under shear. It demonstrates clearly that the peak observed in neutron scattering is related to locally ordered packing of the polymers induced by electrostatic repulsions. Particularly, shear stress increases this degree of ordering of the molecules and gives rise to a weak second-order scattering shoulder. Under shear, the position of the peak ($q_{\max}$) remains at the same position as at rest but the solution becomes anisotropic (preferential orientation of the chains in one direction). Compared with data obtained on synthetic polyelectrolytes, one may emphasize in this case that the stiffness of the xanthan (persistence length about 350 Å in the simple chain helical conformation) favors such strong correlations under shear leading to easily oriented semiflexible polyelectrolyte chains.

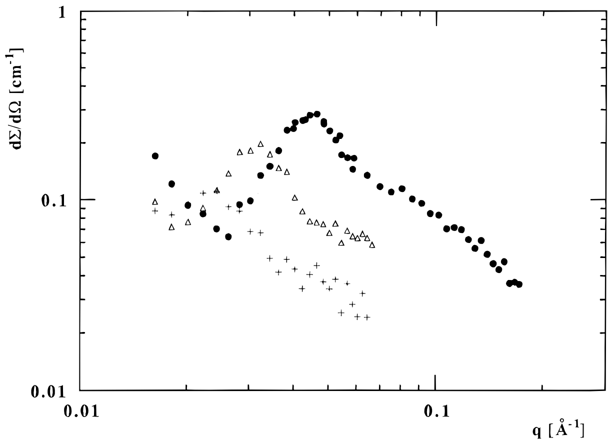

Figure 3. Differential scattering cross section of sheared xanthan solutions as a function of momentum transfer q (at shear gradient $\dot{\gamma} = 12\,000$ s^{-1}). The intensity distribution on the detector is evaluated in the direction perpendicular with respect to the flow direction (sample-to-detector distance $L = 2.60$ m, neutron wavelength $\lambda = 12$ Å, $M_W = 8.0 \times 10^6$): (●) $C_P = 15 \times 10^{-3}$ g/mL; (△) $C_P = 7.5 \times 10^{-3}$ g/mL; (+) $C_P = 3.5 \times 10^{-3}$ g/mL.

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