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## Relaxation of Shear-Aligned Wormlike Micelles

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Received: October 23, 2001; In Final Form: December 31, 2001

We report on the first time-resolved small-angle neutron scattering (SANS) study of the structural relaxation from a shear-induced aligned state back to the isotropic state in a system of giant wormlike reverse micelles. The micelles are formed by lecithin and small amounts of water in cyclohexane. A liquid sample with the micellar volume fraction  $\phi = 0.3$  was exposed to a steady shear of  $\dot{\gamma} = 10 \text{ s}^{-1}$  in a Couette shear cell. This was sufficient to transform the whole sample into an aligned state with the polymer-like micelles preferentially oriented parallel to the velocity direction. After cessation of shear, the sample relaxes back to the equilibrium liquid phase. By time-resolved SANS we could follow the relaxation process, which is characterized by a continuous decrease of the order parameter.

Amphiphilic molecules, like surfactants or lipids, self-associate in solution into aggregates of various size and shape. In certain systems very long wormlike aggregates are formed.<sup>1</sup> Such systems have properties in common with polymer solutions although there exist some important differences. In the self-assembly system the aggregate molecular weight is not a constant but varies with, e.g., temperature and composition. In addition, the self-assembly aggregates have a finite lifetime and can break and reconnect;<sup>2,3</sup> hence they are often referred to as “living polymers”. There has been considerable interest in these systems due to their spectacular viscoelastic properties,<sup>4,5</sup> their partial resemblance to polymer solutions,<sup>6,7</sup> and more recently, to their particular flow behavior.<sup>8–12</sup>

In this study we focus on the structural relaxation of a sample from a shear aligned state back to the disordered liquid state after cessation of shear. The relaxation process was followed by time-resolved small angle neutron scattering (SANS). The rheo-SANS experiments were performed at Risø National Laboratory, Denmark, using a temperature-controlled Couette shear cell of the small angle instrument at the DR3 reactor at Risø, which allows for the recording of small angle neutron scattering under shear.<sup>13</sup> We also compare the structural relaxation kinetics with the stress relaxation kinetics. Rheology data were obtained in rate-controlled experiments performed on a Physica UDS 200 rheometer using a Couette geometry. The sample is made up of the biological amphiphile phosphatidylcholine (lecithin), which forms giant polymer-like reverse micelles in cyclohexane in the presence of small amounts of water.<sup>14–16</sup> The Soybean lecithin (Epicuron 200) was a generous gift from Lucas Meyer A.G. Cyclohexane (p.a.) for rheological measurements were purchased from E. Merck, Darmstadt, Germany. For SANS measurements we used perdeuterated cyclohexane purchased from Dr. Glaser, Basel. All chemicals were used as received. Water was Millipore filtered. Here we

have used a water-to-lecithin molar ratio  $W_0 = 10$  and the volume fraction,  $\phi$ , of micelles (sum of water and lecithin) is 0.3.

For  $W_0 = 10$ , the system forms, around room temperature, a liquid phase,  $L_2$ , up to approximately  $\phi = 0.35$ , followed by a nematic phase,  $N_2$ , which is stable up to approximately  $\phi = 0.45$ .<sup>17</sup> Increasing the concentration further, translational order is obtained as the micelles are packed on a two-dimensional hexagonal lattice ( $H_2$ ).<sup>17</sup> The  $L_2$  phase has been well characterized by light<sup>16,18</sup> and small angle neutron scattering<sup>19</sup> and NMR self-diffusion.<sup>14,20,21</sup> Except at very low concentrations the micelles are longer than micrometers.<sup>14</sup> They do not form branches and the lecithin molecules have a lifetime in the micelles that is longer than 1.5 s.<sup>14</sup>

Solutions of wormlike micelles are, like polymer solutions, in general, shear thinning because the micelles disentangle and align in the flow direction. In Figure 1, top left, we show the two-dimensional SANS pattern obtained at  $\dot{\gamma} = 10 \text{ s}^{-1}$ . In the SANS experiments, the primary beam goes through the center of the cell perpendicular to the neutral cylinder axis. The primary beam is thus parallel to the velocity gradient direction and the scattered intensity is recorded in the plane defined by the neutral direction (vertical  $y$ -direction) and the velocity direction (horizontal  $x$ -direction). At this shear rate the sample scatters essentially only in the neutral direction, showing that the sample is a monodomain of micelles aligned in the horizontal flow direction. The structure factor has a peak at  $Q \approx 0.08 \text{ Å}^{-1}$ ,  $Q$  being the scattering vector. The peak positions are essentially identical in the shear induced aligned state and in the isotropic state at rest.

The anisotropy of the scattering pattern can also be analyzed by plotting the scattered intensity obtained in a narrow  $Q$ -range around the peak position, as a function of the azimuthal angle,  $\varphi$ , in the  $(Q_x, Q_y)$  plane. Using the  $Q$ -range  $0.06 \text{ Å}^{-1} \leq Q \leq 0.09 \text{ Å}^{-1}$ , such plots are also shown in Figure 1, bottom. Defining the positive  $x$ -direction as  $\varphi = 0$  the structure factor peaks occur at  $90^\circ$  and  $270^\circ$ , respectively.

The orientational order can be quantified in terms of the second rank order parameter  $P_2 = \langle 3 \cos^2 \theta - 1 \rangle / 2$ , where  $\theta$  is the local angle between the tangent of the micellar contour

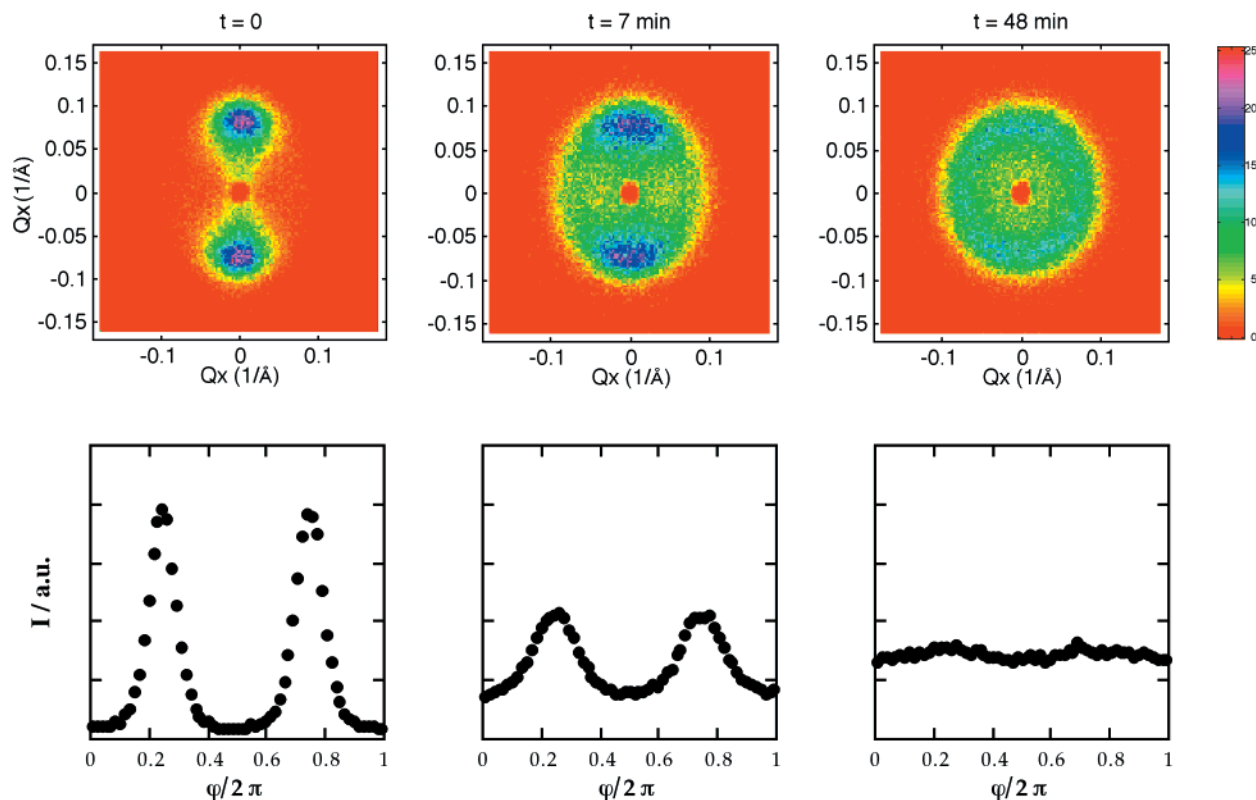
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**Figure 1.** (Top) two-dimensional scattering patterns obtained during shear,  $\dot{\gamma} = 10 \text{ s}^{-1}$  (left), 7 min after cessation of shear (middle), and 48 min after cessation of shear (right). The temperature was  $16.7^\circ \text{C}$ .  $Q_x$  and  $Q_y$  correspond to the velocity and neutral directions, respectively. (Bottom) azimuthal angular dependence of the scattered intensity in the  $Q$ -range  $0.06\text{--}0.09 \text{ \AA}^{-1}$ .

and the director of the phase. This order parameter can be obtained from an analysis of the anisotropic structure factor peak according to<sup>22</sup>

$$P_2 = 1 - \frac{3}{2N} \int_0^{\pi/2} d\varphi I(\varphi + \pi/2) \left[ \sin^2 \varphi + \sin \varphi \cos^2 \varphi \ln \left\{ \frac{1 + \sin \varphi}{\cos \varphi} \right\} \right] \quad (1)$$

where  $N$  is the normalization constant

$$N = \int_0^{\pi/2} d\varphi I(\varphi + \pi/2) \quad (2)$$

and  $\varphi$  is the azimuthal angle. From performing this analysis on the scattering pattern of Figure 1, top left, we obtain an order parameter  $P_2 = 0.57$ .

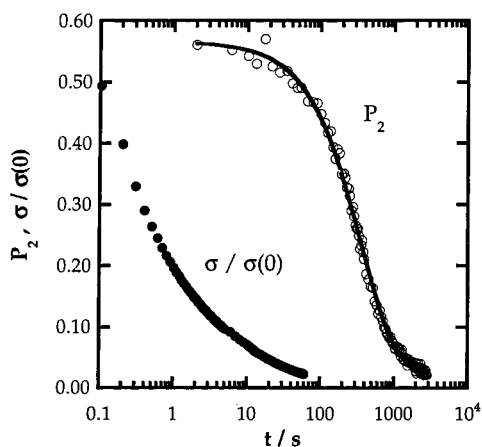
We also followed the evolution of the SANS pattern after the cessation of shear, where the sample had been pre-sheared for 18 min at  $10 \text{ s}^{-1}$ . In Figure 1, middle and right, we show scattering patterns recorded 7 min and 48 min after cessation of shear, respectively. As can be seen, the anisotropic pattern of the sheared state relaxes to the isotropic state, where the scattering is independent of the angle  $\varphi$ .

The relaxation from the aligned state with two peaks in the two-dimensional scattering pattern to the isotropic state with no azimuthal angular dependence occurs gradually. If the relaxation mechanism would be nucleation and growth of the liquid phase, we would expect the development of a circular scattering pattern, the intensity of which would grow in time at the expense of the peak intensities. The two peaks should also decay with a constant width. However, this is not observed. Rather, the relaxation is characterized by a continuous increase of the angular width, finally resulting in a ring on the two-dimensional detector.

The continuous relaxation is characteristic of a melting process. While a liquid phase can be supercooled, an ordered phase can, in general, not be superheated. Melting occurs instantaneously, starting from defects in the ordered structure. The relaxation in the present system is expected to involve a stretched-to-coil transition, where the micelles in the aligned state are stretched with an end-to-end distance significantly larger than in the relaxed coil state. It is also expected to involve micellar breaking since this creates free ends with a larger motional freedom compared to inner segments of a micelle.

The relaxation process was followed by time-resolved SANS by repeated recordings of scattering patterns after cessation of shear. An acquisition time of 2 s was found to give a sufficient signal-to-noise, and this was used in the first part of the relaxation. The time window was then stepwise increased to 30 s at long times. The process was followed for a total of 48 min corresponding to an almost complete relaxation of the sample. From each scattering pattern the order parameter was evaluated according to eq 1, and the results are presented in Figure 2. Initially,  $P_2$  decays exponentially; however, we observe a slow tail at longer times. To capture the main features of the relaxation the data can be fitted with a biexponential decay,  $P_2(t) = P_2(0)(\alpha \exp\{-t/\tau_1\} + (1 - \alpha) \exp\{-t/\tau_2\})$ , and the fit is shown as a solid line. The fit parameters are  $P_2(0) = 0.57$ ,  $\alpha = 0.92$ ,  $\tau_1 = 360 \text{ s}$  (6 min) and  $\tau_2 = 4900 \text{ s}$  (82 min). Hence, we conclude that the relaxation is dominated by a mode with a time constant of 6 min. The full significance of the nonexponential relaxation, however, remains unclear.

In Figure 2 we also present the results from a stress relaxation experiment. Here, we have plotted  $\sigma(t)/\sigma(0)$  versus  $t$ , where  $\sigma(t)$  is the stress and  $\sigma(0) = 130 \text{ Pa}$  its steady state value in the sheared state. Clearly, the two processes occur on completely different time scales. While the structure relaxes on the time scale of minutes, the stress relaxes on the time scale of seconds.



**Figure 2.** Variation of the second rank order parameter  $P_2$  (open circles) and the normalized shear stress,  $\sigma(t)/\sigma(0)$  (filled circles) with time after cessation of shear. A fit to the  $P_2$  data with a biexponential decay is shown as a solid line (see text).

The reason for the very rapid stress relaxation is that the micelles in the aligned state are not entangled, as they are in the isotropic liquid state.

Here we should not be confused by the fact that stress relaxation times of the order of seconds, and even shorter, are often observed in wormlike micellar systems. In those cases, the breaking time is apparently very short and the micelles may also be branched. Branching is difficult to quantify, but it can be done from analyzing the surfactant self-diffusion.<sup>14,23</sup> In the present system, the micelles are not branched and the breaking time appears to be very long. Stress relaxation times of minutes from the entangled state have indeed been observed in the present system at lower concentrations.<sup>24</sup>

To summarize, we have demonstrated that the relaxation of shear-aligned wormlike micelles back to the isotropic state can be followed using time-resolved SANS. We found the relaxation to be characterized by a gradual decay of the orientational order. The time scale of this structural relaxation is of the order of minutes, in contrast to the stress relaxation that occurs on the time scale of seconds. The structural relaxation is expected to involve a stretched-to-coil transition of the micelles, with additional influence of micellar breaking and recombination. The fact that the structural relaxation is found to be slow is important, and consistent with the view<sup>14,23</sup> that micellar

breaking in this lecithin system is an unusually rare event. The present experiments were carried out at high concentrations where interactions influence the structural relaxation rate. The work is as such related to the phenomenon of a shear-induced nematic state. It would be interesting to extend the measurements to lower concentrations to separate interaction effects and single chain properties.<sup>25</sup> Such attempts are in progress. In dilute solutions, however, stretching and alignment is expected to require significantly higher shear rates.

**Acknowledgment.** This work was supported by the Swedish Research Council, the Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase (CSGI-Firenze), and the European Large Scale Program under TMR.

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