Dynamic response of block copolymer wormlike micelles to shear flow.

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The flow behavior of giant wormlike micelles consisting of Pb-Peo block copolymers in the vicinity of the isotropic-nematic phase transition concentration is studied. We explain the appearance of shear banding close to this transition by critical slowing down of the rotational diffusion. This is evidenced by a combination of Fourier transform rheology, time-resolved Small Angle Neutron Scattering (SANS), using a microscopic theory for stiff rods to interpret the dynamic response of the system.

Dispersions of surfactant wormlike micelles form a class of systems that has been intensively studied during the past two decades. Wormlike micellar systems sometimes exhibit extreme shear-thinning behaviour, resulting in shear-induced structure formation like shear banding. Strong shear thinning is of practical interest, since often systems are required in practical applications that exhibit extreme differences in viscosity between the sheared and quiescent state. The reason for the popularity of wormlike micelles for physicists lies in their complex rheological behavior like shear banding and chaotic response, which are connected to the thinning behaviour of these systems. It is therefore important to understand the microscopic mechanism underlying the very strong shear-thinning behaviour of wormlike micelles. It is thought that one mechanisms for the occurrence of strong shear thinning is related to the breaking and/or merging of worms. Another possible mechanism for strong shear thinning is connected to the fact that wormlike systems can undergo an isotropic-nematic (I-N) phase transition. Close to the spinodal point, where the isotropic sample becomes unstable against fluctuations in the orientation, the collective rotational diffusion is critically slowing down, which is quantified by

$$D_r^{eff} = D_r \left\{ 1 - \frac{1}{4}\frac{L}{d}\phi \right\}. \qquad (1)$$

Here D_r is the rotational diffusion at infinite dilution, L is the length of the particle, d its thickness and ϕ the volume fraction. The system will show strong shear thinning since the susceptibility of the system to shear depends on the ratio of the applied shear rate to this rotational diffusion coefficient, given by the effective 'dressed' Peclet number $Pe_{eff} = \dot{\gamma}/D_r^{eff}$. Similarly, the dynamic response of the system to oscillatory flow is expected to be non-linear, which depends on Pe and on the scaled frequency, i.e. the effective 'dressed' Deborah number $\Omega_{eff} = f/D_r^{eff}$, with f is the applied frequency.

Here we study the flow behavior of poly(butadiene)-poly(ethylene oxide) (Pb-Peo) diblock copolymer with a $50-50$ block composition in aqueous solution, which are produced by living anionic polymerization in a two-step procedure[1]. This system exhibits many of the properties of surfactant wormlike micellar systems that are responsible for their interesting rheological behaviour. However, in contrast to surfactant systems, the I-N transition can be accessed at a modest concentration of about $5\ \%$[2]. This is due to its stiffness, with a persistence length of around $500\ nm$ and a diameter of $14\ nm$. The contour length of the Pb-Peo worms is around $1\ \mu m$. However, so far the I-N binodal and spinodal I-N transition points have not been determined. A feature of this diblock copolymer system that is probably not shared with micellar systems is that the polymers do not easily break and merge under flow. We thus focus on the microscopic mechanism mentioned above, related to critical slowing down of rotational diffusion close to the I-N transition.

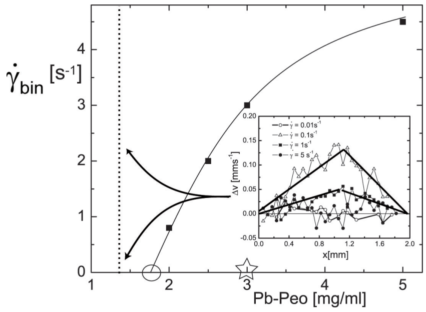

FIG. 1: The binodal points obtained from shear rate quenches. The circle indicates the equilibrium I-N binodal, that is, the binodal point in the absence of flow. The line is a guide to the eye representing the non-equilibrium binodal. The open star indicates the location of the spinodal at zero shear rate. The insert shows banded flow curves.

We determined the equilibrium and non-equilibrium I-N binodal point by performing shear rate quenches and measuring the rheological response using a

ARES, TA instruments, with couette geometry. As in earlier work on rod like viruses[3], we define the binodal by the shear rate at which no increase of the viscosity can be detected after the shear rate is quenched from a high shear rate, where the nematic phase is stabilized, to some lower finite shear rate. This is a good measure since the isotropic phase is more viscous than the nematic phase. The resulting points are plotted in Fig. 1. Extrapolation to zero shear also yields the quiescent binodal point with a high precision. Having located the I-N transition and keeping in mind the strong shear thinning in this part of the phase diagram (data not shown) we also determined the flow profile in a couette shear cell in this part of the phase diagram, using spatially resolved Heterodyne dynamic light scattering. A few typical velocity profiles relative to the applied shear rate within the gap of the couette cell are plotted in the inset of Fig. 1. Shear banding is only observed between $0.1\ s^{-1}$ and $0.75\ s^{-1}$. As such this is the first system that shows shear banding as a result of the critical slowing down at the I-N transition.

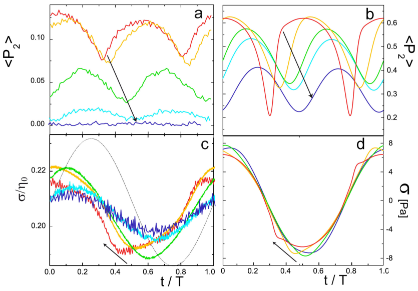

FIG. 2: Time-dependent response of the orientational order parameter $\langle P_2 \rangle$ (a,b) and the stress σ (c,d) to an oscillatory shear flow for experiments ($\dot{\gamma}_{max} = 1.0\ s^{-1}$, a concentration of $2\ \%$Pb-Peo, frequency between 0.025 and $1.0\,Hz$) (a,c) and theory ($Pe_{eff} = 75$, concentration is $\frac{L}{d}\varphi = 3.3$, frequency varying between $\Omega_{eff} = 3$ and 60). The thin dotted curves indicate the applied shear rate. The arrows indicates increasing frequency. The time t is scaled with the period T of oscillation.

Having evidenced the appearance of shear bands close to the binodal, we still need to prove that the system actually shows critical slowing down. Theoretical calculations for hard rods show how rheological as well as structural signatures can be obtained performing perform dynamic, i.e. oscillatory, experiments[4]. These experiments we perform using a combination of $in\ situ$ time-resolved SANS (SINQ spallation source at the PSI in Villigen, Switzerland) in combination with Fourier Transform Rheology. In the SANS experiments we obtain the orientational distribution of the Kuhn segments of the worm-like micelles due to the observed q-range. This distribution is characterized by the order parameter $\langle P_2 \rangle$, which can be obtained with a time resolution of up to $5\ ms$. Such curves are plotted in Fig.2a for increasing frequency, while similar theoretical curves are plotted in Fig. 2b. Since the stress is directly related to the order parameter also the stress response is monitored. Thus we make the link between the microscopic order parameter, which is in general difficult to obtain, and the standard macroscopic stress, see Fig. 2c and d.

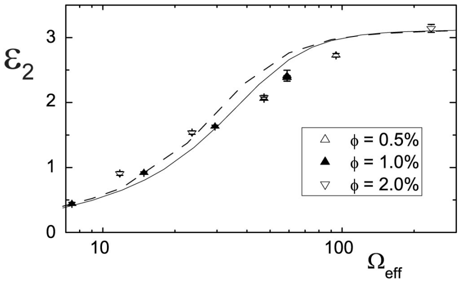

FIG. 3: The phase shift of the orientational response as a function of the effective Deborah number for different scaled concentrations.

The first feature to note is that the order parameter oscillates with twice the frequency of the applied shear rate, even for low shear rates where the stress response is linear in the shear rate. The reason for this is that the scattering experiments probe the flow-vorticity plane, so that the measured order parameter characterizes the orientational order within that plane for which the leading response is quadratic in the shear rate. Second, and more interestingly, we see both with theory and experiments that with increasing frequency the response becomes more linear, i.e. more sinusoidal, but also more phase-shifted. In order to predict the phase shift, one has to relate the frequency with the collective rotational diffusion coefficient, which is given in Eq. 1. This means that the experiments can be scaled with the concentration, using the spinodal point, i.e. $\frac{1}{4}\frac{L}{d}\phi$ as a fit parameter. Performing this scaling, as shown in Fig. 3, and calculating the actual volume fraction of the wormlike micelles from the average length and thickness leads to two separate determinations of the spinodal point that are not further apart than about $30\ \%$. In view of the poly-dispersity and flexibility of the system, this is a surprisingly good comparison. This equilibrium spinodal point is plotted as a star in Fig. 1. More information can be found in reference [5].

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