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SHORT COMMUNICATION

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# Small-angle neutron scattering from a hexagonal phase under shear

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**Summary** The shear orientation of a micellar hexagonal liquid crystalline phase was investigated by small-angle neutron scattering. The hexagonal phase in the quiescent state showed a symmetrical scattering pattern typical of a polydomain structure. Enhanced scattering along the flow direction was observed during shear and the anisotropy of scattering intensity became stronger with increasing shear rate. The anisotropic scattering pattern corresponds to an orientation perpendicular to the flow direction and can be interpreted as a log-rolling state. The oriented sample did not relax after cessation of shear. The results from small-angle neutron scattering confirm data obtained previously from rheo-small angle light scattering measurements and are discussed in comparison to shear alignment of lyotropic liquid crystalline polymer solutions.

**Key words** Hexagonal phase – small-angle neutron scattering – shear orientation – nonionic surfactant – lyotropic liquid crystal

## Introduction

Liquid crystalline materials are characterized by a long-range orientational order of anisotropic particles. Rheological properties of such materials are rather complex since mechanical deformation usually leads to a macroscopic orientation of the anisotropic particles [1, 2]. Several studies investigated flow properties of anisotropic phases, in particular solutions of stiff macromolecules that form nematic or cholesteric phases at high concentration. Various rheo-optical techniques have been developed in order to simultaneously obtain information on rheological and structural changes. Flow birefringence, microscopy, rheo-small-angle light scattering (rheo-SALS) and rheo-small-angle neutron scattering (rheo-SANS) proved to be very helpful to obtain information on shear alignment [3–9]. Usually the rodlike particles are aligned in flow direction.

Lyotropic liquid crystalline phases are also found in concentrated surfactant solutions [10]. Lamellar phases with a smectic-like order of surfactant double layers are known, as well as hexagonal phases where rodlike micelles are packed in a hexagonal lattice. However, less is known about shear alignment of mesophases in surfactant/water systems as compared to polymeric systems. Recently, Diat et al. studied the effect of shear on a lamellar phase and Berret et al. studied the shear induced isotropic to nematic phase transition [11, 12]. Lukaschek et al. investigated a micellar hexagonal phase by means of rheo-NMR [13].

Rheo-SALS experiments on a hexagonal phase revealed two different types of orientation [14]. First, an orientation perpendicular to the direction of flow was observed at small deformation. At high shear rates an orientation parallel to the flow direction was found. The orientation perpendicular to the flow direction could correspond to a "log-rolling" state of rodlike micelles. Small-angle light scattering, however, probes dimensions much larger than the size of individual micelles and therefore rheo-SALS provides information on the orientation of domains only. It seems reasonable that the orientation of micelles is the same as the orientation of larger domains, but a smectic-like structure as known from cybotactic clusters is also conceivable [15]. Therefore rheo-small-angle neutron scattering experiments have been performed with the same hexagonal phase in order to obtain information on shear alignment in a different range of scattering vector and hence on a smaller length scale as compared to light scattering.

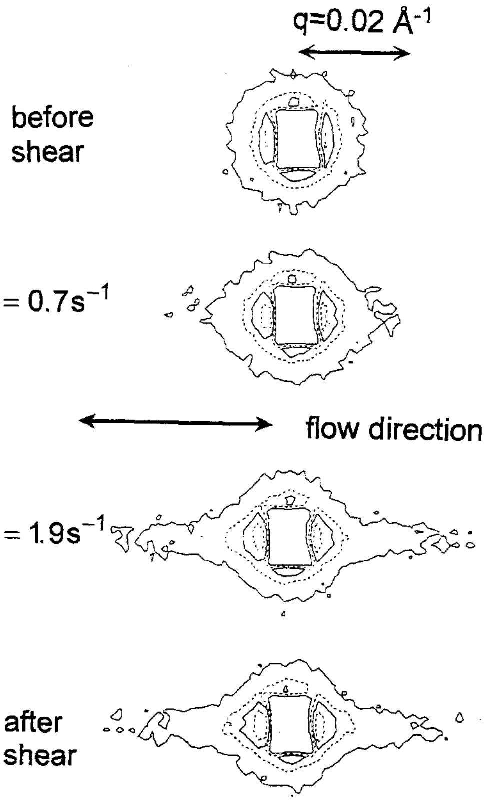

Fig. 1 Contour plots of scattering intensity in the hexagonal phase at 24 °C

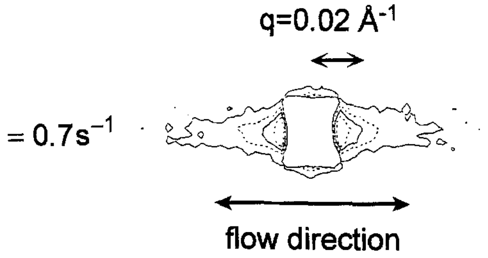

Fig. 2 Contour plot of scattering intensity in the hexagonal phase at 20 °C and $\dot{\gamma} = 0.7\ s^{-1}$

## Experimental

The nonionic surfactant $C_{14}G(E_4M)_2$ with the chemical structure $H_3C(CH_2)_{13}OCH[CH_2O(CH_2CH_2O)_4CH_3]_2$ was used. Synthesis and purification was performed as described in ref. [16]. A solution of 60% (w/w) in $D_2O$ was prepared, which had an isotropic to hexagonal phase transition at 29 °C.

Small-angle neutron scattering measurements were performed at the instrument D11 at the Institut Laue–Langevin. A couette cell made out of quartz glass was used for the shear experiments. The gap size was 1 mm and the primary beam was parallel to the velocity gradient and perpendicular to the flow direction [17].

## Results and discussion

The couette cell was always loaded above 30 °C, i.e., with the sample being in the isotropic phase. Then the sample was cooled into the hexagonal phase and annealed at 24 °C. Figure 1 shows contour plots of the scattered intensity of the hexagonal phase at rest and at two different shear rates $\dot{\gamma} = 0.7\ s^{-1}$ and $\dot{\gamma} = 1.9\ s^{-1}$, respectively. A symmetrical scattering pattern was observed with the sample in the quiescent state. Such a scattering picture is typical of a polydomain structure. During shear flow, however, the scattering pattern on the two dimensional multidetector became anisotropic and increased scattering in flow direction as compared to the direction perpendicular to the flow was found. After cessation of flow, this anisotropic pattern did not relax (Fig. 1 bottom). Figure 2 shows the same behavior at 20 °C and in a different range of scattering vector.

In Fig. 3 the scattering intensity radially averaged in a sector along the flow direction is plotted vs. the scattering vector $q$ for different shear rates. $q$ is given as:

$$q = \frac{4\pi}{\lambda} \sin(\theta/2) \qquad (1)$$

with $\lambda$ the wavelength of the neutrons ($\lambda = 6$ Å) and scattering angle $\theta$.

The scattering intensity parallel to the direction of flow increased with increasing shear rate, but no change of scattering intensity was observed perpendicular to the flow direction.

Scattering experiments probe dimensions in reciprocal space. Therefore scattering in flow direction corresponds to an anisotropic particle that is aligned perpendicular to the flow direction. The same shear orientation was observed before in rheo-SALS experiments from the same system.

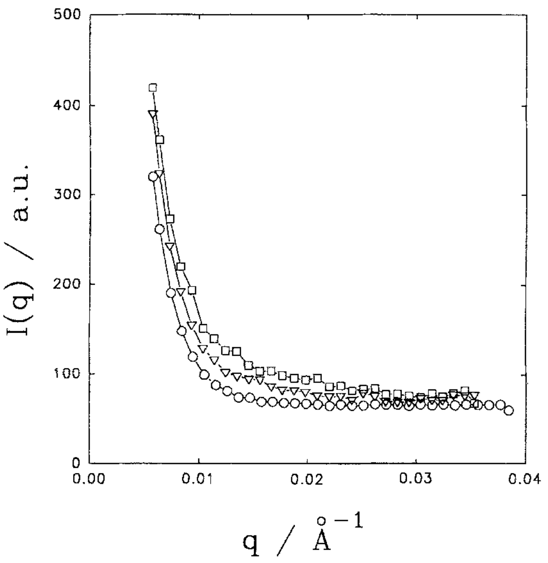

**Fig. 3** Scattering intensity in the hexagonal phase vs. scattering vector in flow direction. (○) at rest, (▽) at $\dot{\gamma} = 0.7\ s^{-1}$, (□) at $\dot{\gamma} = 1.9\ s^{-1}$. Lines are guides to the eye

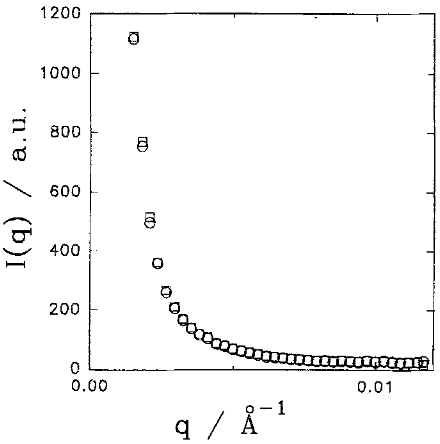

**Fig. 4** Scattering intensity in the isotropic phase at 31 °C vs. scattering vector (○) at rest, (□) at $\dot{\gamma} = 33\ s^{-1}$

Recently, Larson and Öttinger discussed the effect of molecular elasticity on shear alignment of liquid crystalline polymers [18]. They found that two stable orientations can be achieved if a shear deformation is applied to a monodomain: i) an in-shear-plane orientation that can be time-period tumbling or wagging or ii) an out-of-shearing plane orientation which can be a "log-rolling" steady state or a time-period "kayaking" state. In particular their calculations revealed a strong dependence of orientation on elasticity and strength of the nematic potential. Thus the shear alignment perpendicular to flow direction which is observed in the hexagonal phase can be interpreted as a log-rolling state.

In lyotropic liquid crystalline polymer solutions, e.g., poly($\gamma$-benzyl *L*-glutamate) in *m*-cresol, usually shear orientation in flow direction was observed in small-angle light scattering experiments [6]. A log-rolling orientation was recently found by rheo-SANS from the same liquid crystalline polymer in shear flow, however, a different solvent was used [19]. The solvent used in the neutron scattering experiments lead to an aggregation of the macromolecules and the measurements were performed close to a gelation threshold. This might indicate that elastic properties of the sample could be responsible for the log-rolling orientation. The micellar hexagonal phase is extremely viscous and a storage modulus of the order of $10^4$ Pa was observed in low amplitude oscillatory shear experiments [20]. This value is much higher compared to nematic liquid crystalline polymer solutions [21] and might be a reason for the unusual behavior of the hexagonal phase.

Figure 1 also shows a contour plot of the scattering intensity after cessation of flow. The anisotropic scattering pattern did not change after the shear flow was stopped i.e. the oriented state was rather stable and the sample did not relax to polydomain structure. Similar behavior was observed before in rheo-SALS and indicates that the aligned state is stable on the length scales observed in light and neutron scattering. This observation suggests that the anisotropic interaction potential in the hexagonal phase is higher compared to nematic polymer solution which showed a relaxation to a polydomain structure within a few seconds.

Structures with hexagonal order are also known from block copolymer melts, and shear alignment can be observed [22]. Neutron scattering measurements revealed that various orientations can be achieved by shear. One study found that different planes of the hexagonal microstructure were aligned in the shear plane depending on the temperature difference to the order–disorder transition [23]. A shear induced change of cylinder size and spacing was also observed recently [24]. However, the rods were always oriented along the direction of shear and to our knowledge, a log-rolling orientation has not yet been observed in block copolymer melts. Thus different behavior is observed in micellar and polymeric hexagonal phases, respectively, and further experiments are necessary in order to understand this difference.

Figure 4 displays the small-angle neutron scattering intensity from the sample in the isotropic phase at 31 °C. Rheological measurements in the isotropic phase revealed a maximum of viscosity at 60% (w/w), i.e., above the hexagonal phase. Such a maximum could be caused by a change of micellar shape, e.g., a sphere-to-rod transition [25]. However, the solution showed Newtonian flow behavior and no indications of shear orientation were detected by rheo-SALS in the isotropic phase. These results are confirmed by small angle neutron scattering. The scattering pattern was always symmetrical and the radially averaged scattering intensity was not affected by the shear flow. Figure 4 shows that no difference in scattering intensity was observed between the sample in the quiescent state and at a shear rate of $\dot{\gamma} = 33\ \mathrm{s}^{-1}$, respectively, indicating that the viscosity maximum was not caused by a sphere-to-rod transition.

In summary, we observed an orientation perpendicular to the direction of flow by rheo-small-angle neutron scattering measurements from a micellar hexagonal phase under shear. The results confirm data obtained previously by rheo-small-angle light scattering from the same system. Obviously, the log-rolling orientation is a stable flow mechanism of the hexagonal phase at low shear rates. The fact that the orientation perpendicular to the flow direction was observed both in light and neutron scattering demonstrates the stability of the log-rolling state on different length scales. A comparison with results found in nematic solutions of liquid crystalline polymers indicates that elastic properties, i.e., a high elastic shear modulus, might be a reason for a log-rolling orientation under shear.

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