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The shear-induced transition between oriented textures and layer-sliding-mediated flows in a micellar cubic crystal

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Abstract. A series of experiments has been performed in order to analyse the shear-induced structures for a micellar cubic phase using small-angle neutron and x-ray scattering techniques. Steady shear was applied in a Couette cell to the (EO)₁₂₇(PO)₄₈(EO)₁₂₇ triblock copolymer system dissolved in water. At rest, the system crystallizes into a long-range ordered mesophase of face-centred symmetry (lattice parameter ~ 300 Å). The good resolution of the x-ray technique enables us to study in detail the transition between shearing flows dominated by oriented textures at low shear rates ($\dot{\gamma} < 1$ s⁻¹) and flows mediated by the mechanisms of layer sliding at higher rates ($\dot{\gamma} > 100$ s⁻¹).

Since the pioneering work of Hoffman [1] and Ackerson and Clark [2] on shear-induced transitions in suspensions of charged particles, much effort has been made to identify the structural properties of sheared colloidal crystals [3, 4]. More recently, it has been shown that large-size monodisperse particles can be prepared by using the selective solvent properties of diblock or triblock copolymers [5–7], yielding ordered mesophases of cubic symmetry. As far as the structure under shear flow is concerned, a link has been established between the former conventional (charge-stabilized) colloidal crystals and the latter micellar cubic phases [7].

When a colloidal crystal is subjected to a shearing field, layers of maximum compacity and hexagonal symmetry (hereafter referred to as 2D hcp layers) are formed in such a way that the close-packed direction is parallel to the flow velocity v , whereas the layers are stacked perpendicular to the shear gradient ∇v . For a face-centred cubic (fcc) symmetry, the 2D hcp layers are the (111) planes and the close-packed direction is the [110] twofold axis [3]. During the last decade, neutron scattering at small angles has proven to be a very powerful tool in the identification of sheared structures. However, the major drawback of such experiments is the poor resolution (limited by the 10% accuracy on the incident neutron wavelength), which is not sufficient to characterize quantitatively ordered structures.

The system that we have investigated under shear is a ‘soft solid’, resulting from the aggregation of self-assembling triblock copolymers and crystallizing in an fcc structure. In this communication, we report on shear-induced structures observed using both neutron (SANS) and x-ray (SAXS) scattering at small angles. The resolution of the SAXS spectrometer located on the ‘high-brilliance beam line’ (BL4) at the European Synchrotron Radiation Facility (ESRF) [8] enables us to distinguish between shear flows mediated by oriented textures or by layer sliding.

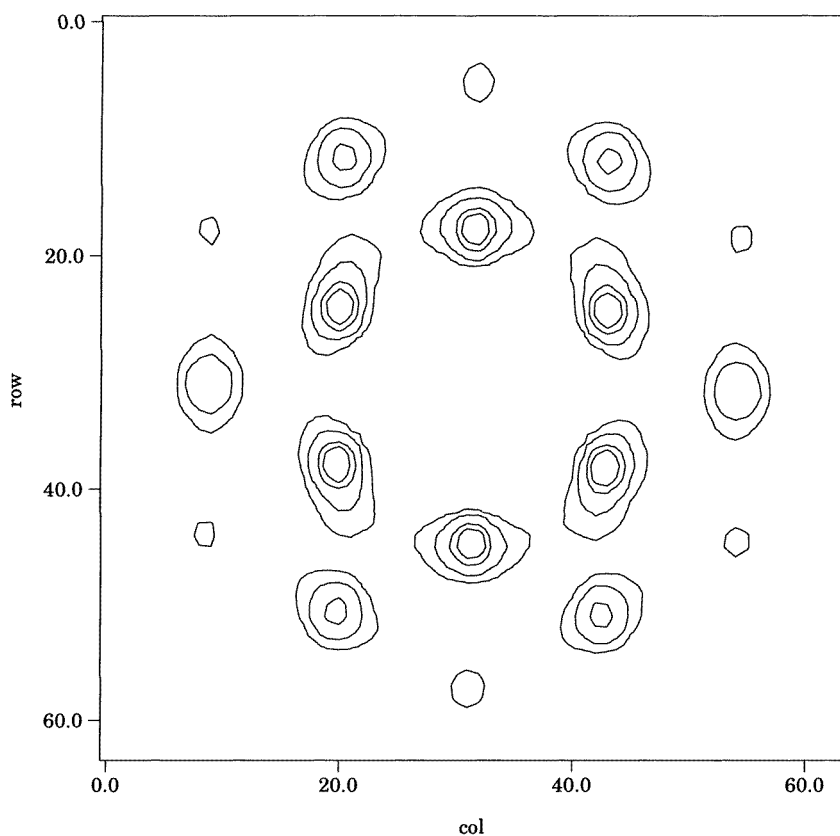


Figure 1. The SANS pattern of an $(\text{EO})_{127}(\text{PO})_{48}(\text{EO})_{127}/\text{D}_2\text{O}$ gel at $\phi = 35\%$ at $\dot{\gamma} = 18 \text{ s}^{-1}$. The shearing device is located 4 m away from the (64×64) -cells multidetector and the wavelength of the neutrons is 6 \AA .

The block copolymers investigated here are $(\text{EO})_{127}(\text{PO})_{48}(\text{EO})_{127}$ where EO denotes a polyethylene oxide chain of 127 monomers and PO a polypropylene oxide chain of 48 monomers. They were purchased from the company Serva, which sells them under the commercial name of pluronics F108 ($M_W = 14\,000 \text{ Da}$). At low polymer concentrations ($\phi < 5\%$ in molecular weight), light scattering measurements corroborate the aggregation of copolymers into spherical micelles above 30°C . With increasing concentration but keeping $\phi < \phi_c = 18\%$, the transparent solutions remain fluid up to boiling water temperature. Above ϕ_c , a liquid-to-solid transition occurs as T is increased. The liquid-to-solid boundaries $T_{ls}(\phi)$ are strongly ϕ dependent, in good agreement with the findings of Wanka *et al* on triblock copolymers with similar block lengths of the EO and PO chains [9]. Data shown here are for deuterated and hydrogenated solutions at $\phi = 35\%$, for which $T_{ls}(\phi) = 10^\circ\text{C}$. The shearing apparatus used for neutron and x-ray scattering was a Couette cell using a 1 mm gap. The shear rate range explored extends from 10^{-2} to 1000 s^{-1} .

The structure of the ‘soft solid’ phase at rest for the $\phi = 35\%$ system was identified to be polycrystalline. The 2D x-ray pattern displays well defined scattering rings (see [10] for details). Once integrated radially, the scattered intensity gives rise to a series

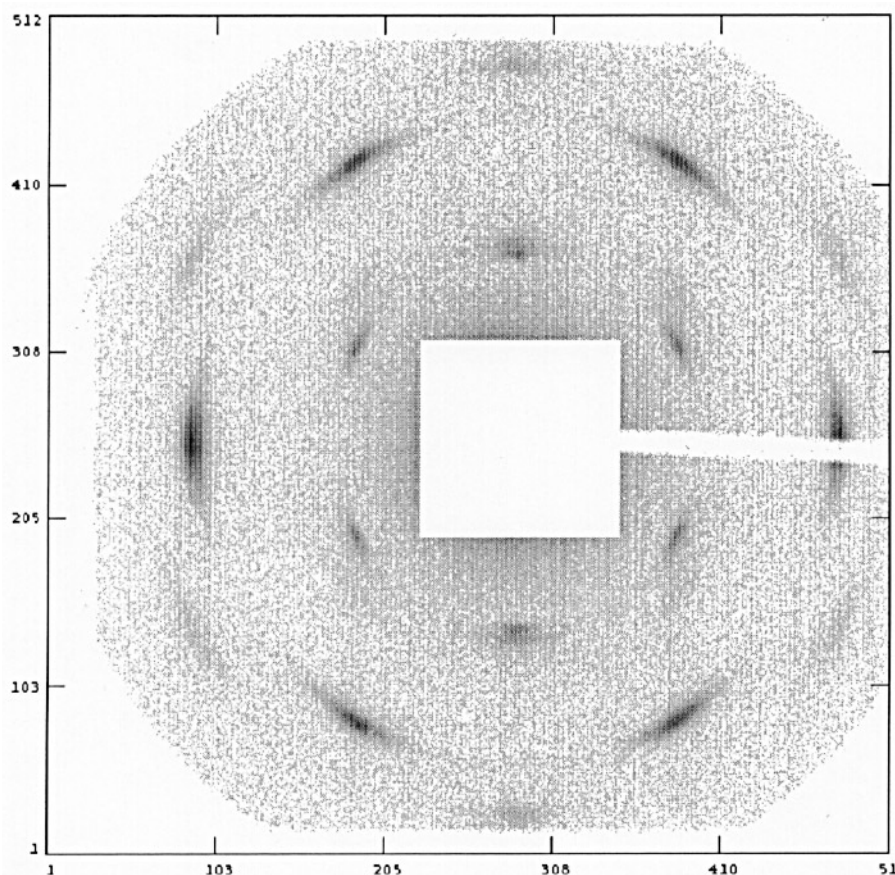


Figure 2. The SAXS pattern as taken in the same shearing configuration as in figure 1. The solution was prepared from the same $(EO)_{127}(PO)_{48}(EO)_{127}$ batch with H_2O at $\phi = 35\%$, ($\dot{\gamma} = 10 \text{ s}^{-1}$). The (512×512) -cell multidetector is at 7 m from the sheared sample and the x-ray wavelength is 1 Å.

of five diffraction peaks, which have been checked to be resolution limited. The first peak observed for $Q_1^p = 0.037 \text{ \AA}^{-1}$ (the index p stands for powder) is regarded as the first diffraction order and the symmetry is determined with respect to this first-order peak. The Q_i^p/Q_1^p sequence for $i = 1-5$ reads 1, 1.13, 1.63, 1.90, 2.0, which is in excellent agreement with the predicted Q_i^p/Q_1^p values for an fcc structure. Recall that, for this structure, $Q_i^p/Q_1^p = \sqrt{(h^2 + k^2 + l^2)}/3$, where (h, k, l) are the Miller indices for Bragg reflections. The lattice parameter, derived with good accuracy, is $a = 294 \text{ \AA}$, corresponding to a nearest-neighbour distance between particles of 208 \AA .

Figure 1 displays the 2D scattering pattern of the $(EO)_{127}(PO)_{48}(EO)_{127}/D_2O$ system at $\phi = 35\%$ under shear, in terms of contour plots of iso-intensity. Measurements were made under shear flow at $\dot{\gamma} = 18 \text{ s}^{-1}$ on the D11 spectrometer located at the Institute Laue-Langevin (Grenoble). Horizontal and vertical axes correspond to wave-vector Q_{\parallel} and Q_{\perp} , parallel and perpendicular to v and in the range $[-0.084 \text{ \AA}^{-1}; 0.084 \text{ \AA}^{-1}]$. Both Q_{\parallel} and Q_{\perp} are perpendicular to ∇v . The scattering patterns exhibit the typical diffraction spots of hcp layers which have been found in numerous colloidal crystals [3, 5, 7]. This result is

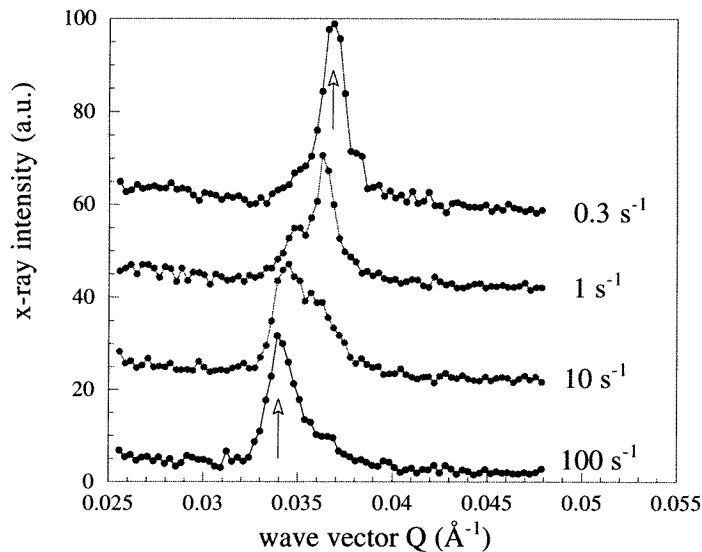


Figure 3. The x-ray intensity (in arbitrary units) as received in the Q_{\perp} direction for the $(EO)_{127}(PO)_{48}(EO)_{127}$ sample at $\dot{\gamma} = 0.3, 1, 10$ and 100 s^{-1} . The diffraction peaks at 0.034 and 0.037 \AA^{-1} are related to the first-order diffraction in layer sliding conditions and oriented textures, respectively.

confirmed by the sixfold symmetry of the first three diffraction orders. According to the SANS data and by analogy with earlier neutron reports, figure 1 would represent the form factor of the 2D hcp layers [4]. With respect to the Q_1^l -value (where l stands for layer), we find that $Q_i^l/Q_1^l = \sqrt{(h^2 + k^2 + hk)}$, where h and k can take any positive integer values. The second and third orders observed with SANS in figure 1 are thus at 1.73 and 2 in units of Q_1^l .

It is outside the scope of the present paper to discuss the relative intensity of the Bragg spots within a ring in order to infer eventual correlations between the 2D hcp layers in the ∇v direction [4, 7]. Rather, we aim here to compare the result of figure 1 with the scattering pattern obtained on an $(EO)_{127}(PO)_{48}(EO)_{127}/H_2O$ system at $\phi = 35\%$ under similar shear conditions and using SAXS (figure 2). The resolution of the SAXS spectrometer on the ID2 beam line at the ESRF (Grenoble) is $\Delta Q/Q \sim 1\%$ instead of the 10% for SANS. At first sight, the scattering pattern of figure 2 resembles strongly the previous one. Diffraction spots of hexagonal symmetry are again observed for each of the first diffraction orders. However, a closer inspection reveals the following.

(i) The diffraction intensities for each peak are now distributed into arcs, along the azimuthal direction. This is particularly clear for the third-order powder peak at $Q_3^p = 4\pi/d$ for which the broadening (FWHM) has been estimated to be about 10° .

(ii) More interestingly, the first-order neutron diffraction peak is found to be split into two contributions (most noticeable in the Q_{\perp} direction). The wave-vector values for these two peaks are 0.034 and 0.037 \AA^{-1} .

In order to visualize this splitting more clearly, we have displayed in figure 3 the integrated x-ray intensity in the Q_{\perp} direction at different shear rates, from 0.3 to 100 s^{-1} . At low shear rates, the scattering pattern is a maximum for the wave vector measured in the

powder polycrystalline sample, $Q_1^p = 0.037 \text{ \AA}^{-1}$. With increasing $\dot{\gamma}$, this first-order peak shifts to a lower value, $Q_1^l = 0.034 \text{ \AA}^{-1}$, i.e. that recorded for the layer-sliding-mediated flow. For intermediate shear rates, both peaks can be resolved (figure 3).

This shift confirms the transition between two extreme scenarios of flow behaviour. The first one occurs at high shear rate, $\dot{\gamma} > 100 \text{ s}^{-1}$, and is related to the layer sliding flow mechanism. The first-order peak observed at 0.034 \AA^{-1} yields the Q_i^l/Q_1^l sequence 1, 1.73, 2 etc in agreement with that of the form factor of the 2D hcp layers. The second extreme case is at low shear rates, $\dot{\gamma} < 1 \text{ s}^{-1}$. The system flows as a polycrystal made of oriented textures. Textures are understood here as domains of fcc structure which are able to roll over each other or eventually tumble [7]. Within these oriented crystallites, the fcc stacking order is preserved, yielding a Bragg peak sequence identical to that of the powder. This suggests finally that the shear gradient is localized at the interfaces between the textures, defects (e.g. dislocations) playing an important role in the flow mechanisms. The transition between these two kinds of flow behaviour is progressive, and, for intermediate $\dot{\gamma}$, the two populations (layers and textures) coexist, as indicated by the data at 1 and 10 s^{-1} in figure 3.

It is important to recognize that this latter result could not have been found using SANS only. In a forthcoming publication [10], a more detailed analysis of the different flows in an $(\text{EO})_{127}(\text{PO})_{48}(\text{EO})_{127}$ crystal made of spherical aggregates of associative polymers will be provided, as well as a direct connection with mechanical responses.

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