Orientation and twins separation in a micellar cubic crystal under oscillating shear

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A series of experiments has been performed in order to analyze the shear orientation effect on a micellar cubic phase using small-angle x-ray-scattering techniques. In a Couette cell, an oscillating shear of strain amplitude less than unity was applied to the crystal. Using a x-ray synchrotron beam, the reciprocal planes perpendicular to the flow velocity and velocity gradient, respectively, were probed. Length and angle correlations were well characterized in both planes and full separation of twinned fcc single crystals was evidenced in some cases, each of them being coherent at millimeter scale. [S0163-1829(96)02446-0]

Since the pioneering work of Hoffman[1] and also of Ackerson and Clark[2] on shear-induced transitions in suspensions of charged particles, many efforts have been made to identify the structural properties of sheared colloidal crystals.[3,4] In this respect, some recent rheological studies have focused on searching for a correlation between the mechanical response of colloidal suspensions and their structures in shearing fields.[5–9] In addition to conventional colloidal crystals, large-size monodisperse particles can also be prepared by using the selective solvent properties of di- or triblock copolymers. Recently, a correlation between flow and structural properties for polystyrene/polyisoprene diblock copolymers as constituents of polymeric micelles in decane, has been clearly pointed out for two different types of crystalline arrangement.[8]

In almost all the cases mentioned above, when a colloidal crystal is subjected to a shearing field, layers of maximum density and hexagonal symmetry are formed in a way that the close-packed direction is parallel to the flow velocity, whereas they are stacked perpendicular to the shear gradient. During the last decade, neutron scattering at small angles has proven to be a very powerful tool in 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. There have been several attempts to determine the correlation between sheared layers stacked in the direction of the velocity gradient,[10,11] and only in a few cases could an estimation of the stacking fault distribution be given.[8,11–15]

The system that we have investigated under shear is a physical gel, resulting from the aggregation processes of associating triblock copolymers into spherical micelles which crystallize in a face-centered-cubic (fcc) structure. In this paper, we report on the clear evidence of the shear orientation of this micellar cubic phase in a monocrystal, and of the complete separation of the two twinned fcc structures. Applying an oscillating shearing field with a strain amplitude less than 50% results in a layered structure fully correlated along the velocity gradient axes. These correlations were analyzed by recording small-angle diffraction patterns on the high brilliance beamline (BL4) at the European Synchrotron Radiation Facility (ESRF).[18]

The block copolymers investigated here are the $(EO)_{127}(PO)_{48}(EO)_{127}$ 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 Da). At low polymer concentrations ($\phi<5\%$ in molecular weight), light-scattering measurements[16] corroborate the aggregation of monomers into spherical micelles above the so-called critical micellar temperature. 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. In the solid phase, the spherical micelles are arranged in a compact manner on the sites of a three-dimensional (3D) lattice with a fcc symmetry. The liquid-to-solid boundaries $T_{ls}(\phi)$, as well as the biphasic region are strongly ϕ dependent and are in a good agreement with the findings by Wanka, Hoffman, and Ulbricht on triblock copolymers with similar block lengths of the EO and PO chains.[17] The phase diagram as well as the comprehensive structural characterizations will be reported later in a more detailed article.[16]

A series of small-angle x-ray-scattering (SAXS) experiments was performed on the high brilliance beamline at the ESRF. The SAXS setup is based on a pin-hole camera with a beamstop placed in front of a two-dimensional (2D) gas-filled detector. The x-ray-scattering patterns were recorded on the detector which was located at 7 m from the sample, using a monochromatic incident x-ray beam (1 Å wavelength) with a cross section of 0.2×0.2 mm^2 ($V\times H$) at the sample position. The shearing device was a homemade polycarbonate Couette cell which has already been described in Ref. 19. The rotor is the outer cylinder and the size of the annular gap between both cylinders of the cell is 1 mm. Of major importance for the present experiment is that the shearing cell is mounted on motorized translation stages which allow the sample to be aligned in any beam-path positions between the so-called radial and tangential positions.

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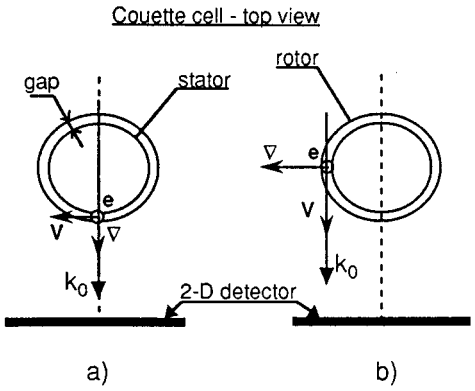

FIG. 1. (a) and (b) Top view of shear cell showing the orientation of the main scattering geometries: V is the velocity, ∇ is the shear, and e is the vorticity. The width of the annular gap between the rotor (outer cylinder) and the stator is 1 mm and the inner diameter of the rotor is 21 mm.

Both experimental configurations are illustrated in Figs. 1(a) and 1(b), respectively. The first one (radial configuration) corresponds to $\mathbf{k}_0 \| \boldsymbol{\nabla}$, the velocity gradient and the second one (tangential configuration) to $\mathbf{k}_0 \| \mathbf{V}$ the shear velocity, where $\mathbf{k}_0$ is the incident x-ray wave vector. The third direction is defined by the unit vector $\mathbf{e}=\mathbf{V}\times\boldsymbol{\nabla}$ which is usually called vorticity. These configurations are essential since for layered structures or ordered systems they provide the static structure factor in two perpendicular planes of the reciprocal lattice, namely the $(\mathbf{k}_v,\mathbf{k}_e)$ and the $(\mathbf{k}_{\boldsymbol{\nabla}},\mathbf{k}_e)$ planes. The set of these three vectors $\mathbf{k}_i$ is actually fixed by the flow conditions of the cell. The beam size being smaller than the gap size, we can also scan through the gap in the gradient velocity direction.

The results presented in the following concern a water solution sample with a weight fraction of 35% of polymer in water, at 30 °C. The corresponding diffraction pattern on Fig. 2 is the signature in the Fourier space of a polycrystalline sample with a fcc symmetry and we have determined a lattice parameter $b=302$ Å from the radial position of the diffraction rings. On a freshly loaded solution in the Couette cell, a preshear of $\dot{\gamma}=100\ \mathrm{s}^{-1}$ is applied during a few seconds at a controlled temperature of 30 °C. In Figs. 3(a) and 3(b) diffraction patterns are shown for radial and tangential

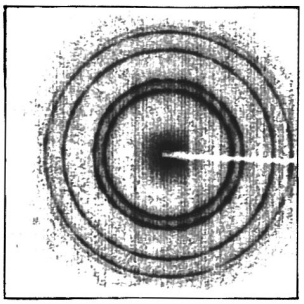

FIG. 2. Powder spectrum of 35% (in weight) of $(EO)_{127}(PO)_{48}(EO)_{127}$ in water, at $T=30$ °C. This spectrum has been recorded with a sample-detector distance equal to 8 m. The positions of the diffraction rings match perfectly the predicted position for a fcc crystal with a lattice parameter b equal to 302 Å.

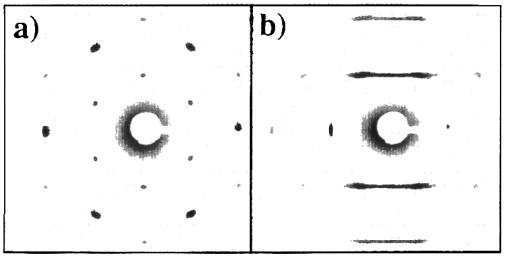

FIG. 3. The sample is subjected to a laminar shear characterized by a shear rate $\dot{\gamma}=100\ \mathrm{s}^{-1}$. The x-ray-diffraction pattern is recorded (a) in the $(\mathbf{k}_v,\mathbf{k}_e)$ plane of the reciprocal and (b) in the $(\mathbf{k}_{\boldsymbol{\nabla}},\mathbf{k}_e)$ plane with a distance sample detector equal to 7 m.

beam positions, respectively. At a first glance, the pattern of Fig. 3(a) (displaying the diffracted intensity in the $(\mathbf{k}_v,\mathbf{k}_e)$ plane of the reciprocal space) is dominated by six intense diffraction spots with an hexagonal symmetry. Two other sets of Bragg peaks with the same symmetry but exhibiting a weaker intensity are also visible on the detector. The diffraction patterns of Fig. 3(b), obtained by sending the x-ray beam tangentially to the cell through the gap, is quite different and is organized in four horizontal scattering ''tubes,'' so called by Loose and Ackerson,[11] parallel to the $\mathbf{k}_{\nabla}$ direction and located away from the $\mathbf{k}_e=0$ axis. They are smoothly modulated in intensity with some spreading over the azimuthal direction.

After checking that these scattering patterns are fully reproducible, the polymeric gel-like solution was then subjected to an oscillating shearing field with a deformation amplitude of 40% and a frequency $\omega=10\ \mathrm{rad\,s}^{-1}$.[20] The obtained diffraction patterns are shown in Figs. 4(a) and 4(b), again for radial and tangential geometry, respectively. The scattering pattern remains identical after switching off the oscillating shear indicating that the obtained structure is frozen. The general aspect of the patterns is quite similar to the previous ones except that the Bragg spots are more

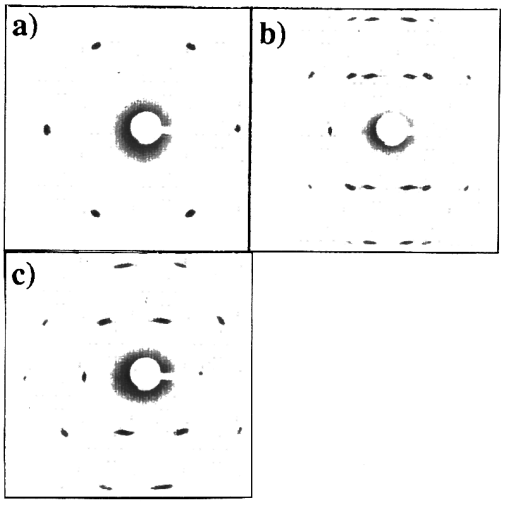

FIG. 4. The sample is subjected to an oscillating shear characterized by an amplitude of strain equal to 40% and a frequency of $10\ \mathrm{rad\,s}^{-1}$. The x-ray-diffraction pattern is recorded (a) in the $(\mathbf{k}_v,\mathbf{k}_e)$ plane of the reciprocal and (b) in the $(\mathbf{k}_{\boldsymbol{\nabla}},\mathbf{k}_e)$ plane. In (c) the x-ray-diffraction pattern is recorded in the $(\mathbf{k}_{\boldsymbol{\nabla}},\mathbf{k}_e)$ plane but when the beam is sent close to the outer cylinder (the rotor).

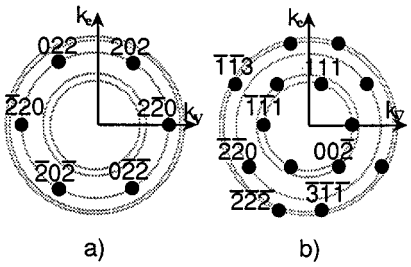

FIG. 5. Positions and indexations of Bragg spots expected for a single fcc arrangement (a) in the $(\mathbf{k}_v,\mathbf{k}_e)$ plane and (b) in the $(\mathbf{k}_\nabla,\mathbf{k}_e)$ plane. With respect to clarification, all the spots in (b) are not labeled but correspond to those indexed and the dashed rings correspond to the positions of the powder rings.

peaked. Some of the spots have almost vanished in the $(\mathbf{k}_v, \mathbf{k}_e)$ plane and the intensity modulation along the ''tubes'' in the $(\mathbf{k}_\nabla, \mathbf{k}_e)$ plane is now by far sharper and concentrates into well separated diffraction spots. Moreover, after having moved the beam through the gap towards the outer cylinder, half of the spots initially visible on each ''tube'' in Fig. 4(b) actually disappear: Fig. 4(c). This means that different well defined structures occupy different macroscopic portions of the gap.

Before analyzing all these scattering patterns, let us note some definitions: a fcc fault-free crystal is commonly characterized by the sequence of compact 2D layers *ABCABCA* (where *A* is the reference layer and corresponds to a (111) plane). The fcc structure exists also in a fully equivalent twin arrangement, *ACBACBA* and a stacking fault will feature the interface between two twin domains. Following the rich literature on layered structures obtained from a fcc-type assembly of spherical particles, we expect the layers which are aligned parallel to the Couette cylinders (i.e., perpendicular to the velocity gradient ∇ direction) to be the (111) planes, i.e., the planes of maximum density and hexagonal symmetry in such a way that the close-packed direction (in the layer) is parallel to the flow velocity. We have accordingly drawn in Figs. 5(a) and 5(b) the Bragg spots positions that we have identified and indexed for only one of the twin fcc arrangements in the $(\mathbf{k}_v,\mathbf{k}_e)$ and $(\mathbf{k}_\nabla,\mathbf{k}_e)$ plane, respectively. The diffraction pattern for the other twin arrangement is obviously the same in the $(\mathbf{k}_v,\mathbf{k}_e)$ plane and simply symmetrical with respect to the $\mathbf{k}_e$ axis in the $(\mathbf{k}_\nabla,\mathbf{k}_e)$ plane. Coming back to the experimental data, when the sample is subjected to an oscillating shear, the Bragg peaks observed in Figs. 4(a) and 4(c) are exactly at the same positions expected for a single twin fcc arrangement (say twin1 for example) and this over the whole volume probed by the x-ray beam. When the beam is closer to the center of the cell but still tangential to the gap [see Fig. 4(b)], we observed the Bragg spots from both arrangements (twin1 and twin2). From the intensity ratio between one spot (belonging to one twin) and its homologous (belonging to the other twin) we can estimate the volume ratio of both arrangements along the beam path. For example, in Fig. 4(b), we found it to be 2/5. Then, knowing the position of the beam with respect to the center of the cell we estimated that half of the gap (in thickness) is occupied by one fcc arrangement and the other half by the second twin arrangement. It should be noticed that in Fig. 4(a) some other peaks are still slightly visible and might correspond to the projection of the [111] and [311] series onto the scattering plane. Actually, these traces result from the broadening of the Bragg peaks along the ''tubes'' visible in Fig. 4(b).

On the other hand when the sample is subjected to a permanent and higher shear rate, the scattering intensity along the ''tubes'' is differently distributed [see Fig. 3(b)]; according to the assumptions of Loose and Ackerson in Ref. 11, the stacking order along the ∇ direction is almost completely lost due to the presence of many stacking faults which allow the flow of the (111) planes parallel to the cylinders of the cell. The slight spread of the diffraction peaks in the azimuthal direction in the $(\mathbf{k}_v,\mathbf{k}_e)$ plane [see Fig. 3(a)] indicates the formation of an orientational texture which remains however relatively well oriented in the layer planes.

Finally, it should be pointed out that a strain amplitude of 10%, after a first oscillating shear of 40% can improve the correlation between the layers but if applied directly after a permanent shear it cannot cause such an ordering. We found a couple of optimum values for amplitude and frequency (0.4 and 10 rad s^{-1}), respectively in order to observe a perfect separation of the twin arrangements. These values are in agreement with the rheological measurements given which will be reported in Ref. 16.

In conclusion, we have shown that a polymeric micellar fcc cubic crystal $(EO)_{127}(PO)_{48}(EO)_{127}$/water, is obtained polycrystalline at rest. Subjected to a laminar stationary shear at high rate, it orients with the compact (111) layers parallel to the shear plane. The flow is obtained through layer sliding, resulting into a highly twinned fcc structure with very high density of stacking faults. An oscillatory strain of moderate amplitude (40%) actually anneals almost all stacking defects and one gets large homogenous single crystals of either twin but well separated at millimeter scale. Further investigations are in progress in order to fully understand the reasons why the twin degeneration is solved solely under the conditions described above.

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