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SHORT COMMUNICATION

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Flow mechanisms in the face-centred cubic micellar gel of a diblock copolymer

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Abstract The mechanisms of flow of a face-centred cubic micellar phase were investigated using small-angle X-ray scattering (SAXS) for samples under either steady or oscillatory shear in two different geometries: Couette cell and planar shear sandwich. The system studied was a gel formed by a poly(oxyethylene)–poly(oxypropylene) diblock copolymer in water. SAXS indicated that under steady shear in a Couette cell, flow occurs via sliding of hexagonal close-packed (hcp) layers with a close-packed [110] direction along the shear direction. Under oscillatory shear in the planar shear sandwich, coexistence between this orientation and one in which the hcp layers are rotated by 30° (and flow is in a [211] direction) was observed; however, when subject to oscillatory shear in the Couette cell, flow only occurred along a [110] direction. This observation of flow in a non-close-packed direction may be due to alignment induced by the walls of the shear sandwich.

Key words Block copolymers · Micelles · Gels · Shear · Small-angle x-ray scattering

Introduction

The flow behaviour of soft materials is of both fundamental and practical interest. The former stems from the desire to understand the relationship between thermodynamics and flow dynamics in complex systems and the latter because polymer solutions and colloidal sols are subjected to flow fields during processing. Suspensions of charge- or sterically stabilized colloidal sols have been widely studied in this context because they can behave as ''hard spheres'', for which the interparticle potential can be modelled.

The flow behaviour of sterically stabilized colloidal latex suspensions has been investigated by Ackerson and Pusey [1, 2] using static light scattering. These studies focussed on samples forming stacked hexagonal close-packed (hcp) layers. At rest, in a face-centred-cubic (fcc) structure these layers are arranged in an ABCABC… stacking sequence. Upon increasing the rate of steady shear the following structures are observed for colloidal suspensions forming an fcc structure at rest: zigzag motion between the two possible registration sites for an fcc crystal, sliding layers where there is no registration in the stacking sequence of successive hcp layers, string formation where the hcp ordering within planes is destroyed and ultimately shear melting at high shear rates. Several of these structures were also observed under oscillatory shear, depending on the strain amplitude (only one shear rate was applied) [1]. A model for the structure factor for stackings of hcp planes has been developed to describe these diffraction patterns [3]. Other researchers have also investigated flow-induced stacking transitions of hcp colloidal suspensions via small-angle scattering [4–6] and analysed them using the Loose–Ackerson model [5, 6]. Similar transitions have been reported for body-centered-cubic (bcc) colloidal crystals [7].

It has recently been shown that diblock copolymer micelles can also behave as hard spheres, forming close-packed fcc structures when the micellar corona is small compared to the core, and when the concentration of diblock is low [8, 9]. We are currently investigating the

flow behaviour of these model systems, for which it is possible to vary the effective intermicellar potential by choosing diblocks of different composition [10]. Previous studies of the effect of shear on fcc arrays of block copolymer micelles include the work of McConnell et al. [8] on polystyrene–polyisoprene diblocks in decane. A transition from polycrystallinity to sliding hcp layers was observed on increasing the shear rate. Shear-induced orientation effects in fcc structures have also been investigated using Pluronic [poly(oxyethylene)–poly (oxypropylene)–poly(oxyethylene)] triblock copolymers [11, 12]; this and other work is reviewed elsewhere [10, 13]. Here, we present evidence for a flow mechanism, previously unreported to our knowledge, for an fcc micellar crystal formed by a poly(oxypropylene)–poly(oxyethylene) diblock copolymer in water. Flow is observed to occur in a non-close-packed direction. The gel was subjected to oscillatory shear in a shear sandwich geometry with simultaneous small-angle X-ray scattering (SAXS). For comparison, the same gel was investigated under steady or oscillatory shear in a Couette cell, and the well-known layer sliding mechanism of flow was observed in these cases. The difference in flow mechanism under oscillatory shear in the Couette cell compared to the shear sandwich may be due to preferential alignment induced by the polyimide walls of the shear sandwich.

Experimental

Materials

The copolymer $P_{94}E_{316}$ was identical to the one used earlier [14]. As described elsewhere [14], it has a narrow molecular-weight distribution (i.e. the ratio of mass-average to number-average molar mass), $M_w/M_n = 1.07$, determined by gel permeation chromatography based on poly(oxyethylene) calibrants, where $M_n =$ 5,450 gmol^{-1} was determined from the analysis of ^{13}C NMR spectra [14]. A 50 wt% solution of $P_{94}E_{316}$ in water was prepared by mixing appropriately weighed amounts of copolymer and water by diffusion over a period of days at low temperature (around 5 °C). Optical examination revealed that the gel formed by this sample was clear and not birefringent, consistent with cubic symmetry.

Methods

SAXS experiments on samples subjected to shear were performed on beamline 2.1 of the Synchrotron Radiation Source at the Daresbury Laboratory, Warrington, UK. The beamline is configured for SAXS experiments using monochromatic radiation of wavelength $\lambda = 1.5$ Å. Details of this beamline and the data collection electronics have been given elsewhere [15]. Scattered photons were collected on a multiwire gas-filled area detector. A scattering pattern from a specimen of wet collagen (rat-tail tendon) was used for calibration of the q scale ($|\mathbf{q}| = 4\pi \sin\theta/\lambda$, where the scattering angle is 2θ).

The samples were subjected to either steady or oscillatory shear, using a Couette cell described in detail elsewhere [16]. Briefly, it comprises two concentric polycarbonate cylinders, with an inner stator (radius 25 mm) and an outer rotor, with a 0.5-mm gap for the sample. A cylindrical tube is incorporated in the inner stator, for the X-ray beam to pass through. The cell is mounted on a motorised translation stage, which allows the sample to be aligned in a radial configuration. This orientation corresponds to $\mathbf{q}$ parallel to $\nabla\mathbf{v}$, the shear gradient direction, and enables the SAXS pattern to be recorded in the ($\mathbf{q}_v$, $\mathbf{q}_e$) plane, where $\mathbf{e} = \nabla\mathbf{v} \times \mathbf{v}$ is the neutral direction (v is the shear direction). The temperature of the Couette cell was controlled using a water bath. The measurements were carried out at 20 or 30 °C.

The samples were also subjected to oscillatory strain using a Rheometrics solid analyser RSA II system with a shear sandwich geometry. A detailed description of the rheometer is provided elsewhere [17, 18]. It enables the collection of simultaneous rheology data; however, this was not analysed in the present case because the samples were subjected to large-amplitude oscillatory strain, i.e. in the nonlinear viscoelastic regime. The shear sandwich cell comprises three rectangular plates, the two external plates are fixed, while the central piece oscillates vertically. Apertures were machined into the plates of the shear sandwich assembly to allow transmission of the X-ray beam and were covered by Kapton polyimide windows. The sample is loaded on both sides symmetrically about the insert piece. The shear sandwich plates are perpendicular to the X-ray beam which is incident along $\nabla\mathbf{v}$, so that the ($\mathbf{q}_v$, $\mathbf{q}_e$) plane is accessed in SAXS experiments. Oscillatory shear was applied at 30 °C.

Results

We first discuss the SAXS pattern of the sample at rest. Then we consider the flow behaviour during and after both steady and oscillatory shear.

System at rest

The as-mounted sample at 25 °C in the rheometer showed a nearly spherically averaged powder diffraction pattern (results not shown), consisting of three diffraction rings in the positional ratio $1:(4/3)^{1/2}:(8/3)^{1/2}$, corresponding to the reflections 111, 200 and 220 respectively of an fcc lattice ($Fm\bar{3}m$ symmetry) [19]. It is possible to calculate a cell parameter $a = (460.9 \pm 13.7)$ Å, from the first order reflection at $q^* = (0.0236 \pm 0.0007)$ Å^{-1}. The cell parameter yields a distance between nearest neighbours $d = (326 \pm 10)$ Å, from which it is possible to calculate a micellar radius $r_m = (163 \pm 5)$ Å. This value is in good agreement with the hydrodynamic micellar radius $r_h = 200$ Å, obtained from dynamic light scattering [14]. Assuming a hard-sphere structure, the radius of gyration in dilute solution is obtained as $r_g = \sqrt{3/5}r_h$, leading to a radius in substantial agreement with that determined via SAXS. Correspondence between r_g(dilute solution) and r_m(gel) has been noted for other micellar systems [20].

Shear-flow behaviour: steady shear

The sample was subjected to shear at a rate $\dot{\gamma} = 20$ s^{-1}. Fig. 1 The 2D SAXS patterns obtained in the ($\mathbf{q}_v$, $\mathbf{q}_e$)

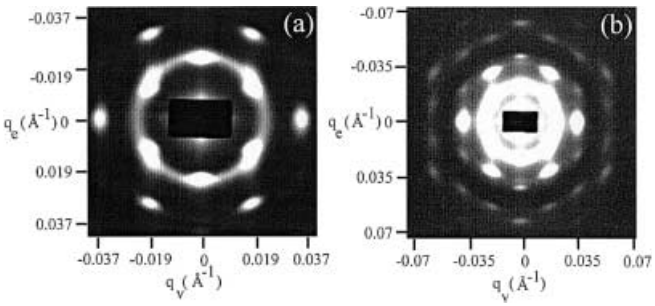

Fig. 1a, b Small-angle X-ray scattering (*SAXS*) pattern in the ($\mathbf{q}_v$, $\mathbf{q}_e$) plane obtained at 20 °C for the sample under steady shear in the Couette cell at $\dot{\gamma} = 20\ s^{-1}$. The scattering patterns are shown on a larger q scale in **b** to highlight higher order reflections (the highest intensity inner reflections are oversaturated). The shear direction is horizontal

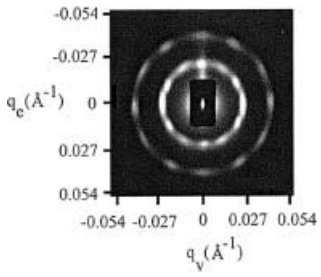

Fig. 2 SAXS pattern in the ($\mathbf{q}_v$, $\mathbf{q}_e$) plane obtained at 30 °C for the sample at rest after oscillatory shear in the shear sandwich at a frequency, ω, of 100 s^{-1} and associated strain amplitude, A, of 200%. The SAXS pattern has been rotated through 90° so that the shear direction is horizontal, to facilitate comparison with Fig. 1

plane are shown in Fig. 1. The main effect of the shear flow is to induce an orientation of the crystal planes. The first- and third-order rings of the reflections observed for the as-mounted sample change, under shear flow, to Bragg spots arranged with sixfold symmetry.

The Bragg spots are distributed in five concentric rings, which correspond to 111, 220, 311, 331 and 422 reflections of 2D hcp layers aligned parallel to the cell walls. The simultaneous presence of 111 and 220 reflections in the diffraction patterns shows that the fcc stacking sequence is irregular, probably owing to a combination of ABAB..., ACAC... and ABCABC... stacking [3, 8, 9, 21]. Four additional weak reflections are also observed in Fig. 1a, at $\pm 45°$ with respect to q_v, at scattering angles corresponding to the second-order diffraction ring of the as-mounted sample. These correspond to 200 reflections of fcc grains oriented with {100} planes parallel to the shear plane and the [110] direction aligned parallel to **v**, as discussed elsewhere [9, 21, 22].

Our results show that the shear-flow mechanism under steady shear in the range $10 \leq \dot{\gamma}/s^{-1} \leq 400$ is predominantly layer sliding, where hcp layers slide over each other, with their close-packing direction parallel to the shear. It must be mentioned that $q^* = (0.0232 \pm 0.0007)$ Å^{-1} was not significantly reduced under shear flow, although this is expected in the sliding-layer regime [5, 8]. The partial orientation of the as-mounted sample might have led to a reduction in q^* prior to shearing.

Shear-flow behaviour: oscillatory shear

Using the shear sandwich tool in the rheometer, the sample was sheared at a frequency, ω, of 100 rads^{-1} and a strain amplitude, A, of 200%. The 2D SAXS pattern obtained under quiescent conditions following shear is shown in Fig. 2. The SAXS pattern is characterised by 12 Bragg spots symmetrically distributed on each of the first- and third-order rings of the reflections observed for the as-mounted sample. This pattern was obtained reproducibly for this gel under these conditions of shear and strain in the same run at 60 °C and in another run at both 25 and 70 °C.

The SAXS pattern in Fig. 2 can be understood as a superposition of two hexagonal diffraction patterns from uncorrelated hcp layers rotated with respect to each other by 30°. This unusual observation led us to consider possible inhomogeneous flows induced, for example, by wall effects. In particular, the set of six reflections in the inner ring of the SAXS pattern shown in Fig. 2 that are rotated by 30° with respect to those in Fig. 1 correspond to flow in a [211] direction (defined with respect to an fcc unit cell), which is rotated 30° from the most closely packed [110] direction. This would appear to be a less favourable flow direction, one possible explanation for which is preferential orientation induced by the walls in the shear sandwich, made from polyimide. Fig. 3 shows the profile of the scattered intensity as a function of the

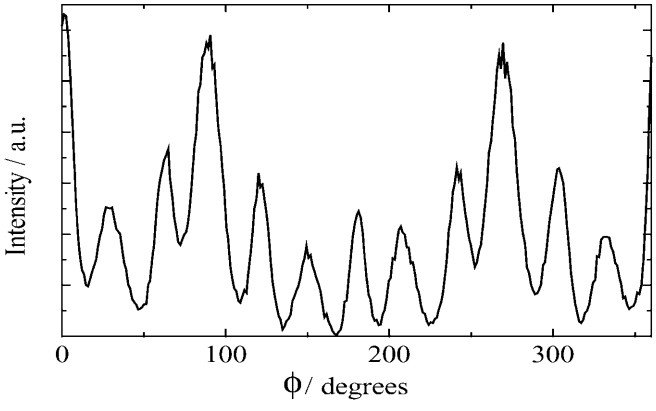

Fig. 3 Profile of the scattered intensity as a function the azimuthal angle (defined with respect to the vertical) obtained from the SAXS pattern in Fig. 2 by integration in a narrow band centered on q^*

azimuthal angle obtained from the SAXS pattern in Fig. 2, by integration in a narrow band centred in q^*. The mosaicity of the peaks corresponding to flow in a [110] direction is $\Delta\phi \sim 11.2°$, while $\Delta\phi \sim 14.4°$ for the other set of peaks. The higher mosaicity for the peaks arising from planes flowing with a [211] direction in the shear direction indicates that the planes are more misoriented, one possible explanation for which is that a different flow mechanism occurs in the vicinity of the polyimide-covered shear tools owing to wall slip (caused, for example, by microscopic scratches or specific surface interactions due to the hydrophobic nature of the polyimide film). The coexistence of two orientations of hcp planes is illustrated in Fig. 4 (which is schematic, since the shear sandwich consists of two fixed outer plates and an inner oscillating one).

To investigate further possible wall effects, a $P_{94}E_{316}$ gel was subjected to oscillatory shear in the Couette cell (polycarbonate) walls. The SAXS pattern obtained under similar conditions of shear ($\omega = 100$ rads^{-1}, $A = 200\%$) as in the shear sandwich cell in the rheometer is shown in Fig. 5. It is clear that only one set of six reflections is obtained on the inner ring, and the pattern resembles that obtained under steady shear (Fig. 1), although the peaks are less sharp. Thus, in the Couette cell, oscillatory shear leads to flow of hcp layers with the close-packed [110] direction along the shear direction. This gives support to our conjecture that the 12-spot pattern with two sets of six reflections rotated with respect to each other by 30° shown in Fig. 2 is due to inhomogeneous flow in the shear sandwich geometry, possibly due to slip in the neighbourhood of the walls. Another possible explanation for the coexisting orientations is that it is due to differences in the geometry of the two shear configurations (Couette versus shear sandwich); however, this seems unlikely in view of the fact that we have never seen the 12-spot pattern in other experiments using the shear sandwich (with polyimide windows) to orient other diblock copolymer fcc micellar gels, such as those formed by poly(oxyethylene)–poly(oxybutylene) diblocks in water [9, 23]. It should be noted here that the gap in the shear sandwich (0.2 mm) was comparable to that in the Couette cell (0.5 mm), so the effect is unlikely to be due to differences in sample thickness.

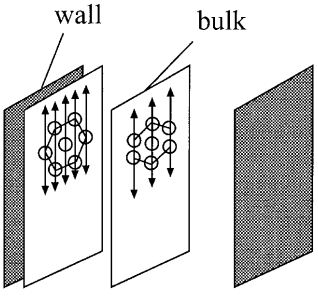

Fig. 4 Model for flow of hexagonal-close-packed layers in two orientations with respect to the oscillatory shear direction (here vertical). It is proposed that near the wall, flow occurs with a [211] direction coincident with the shear direction, whereas in the bulk the more favourable flow mechanism with a [110] direction parallel to the shear direction predominates

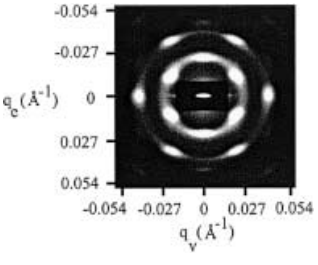

Fig. 5 SAXS pattern in the ($\mathbf{q}_v$, $\mathbf{q}_c$) plane obtained at 30 °C for the sample in the Couette cell under oscillatory shear at a $\omega = 100$ s^{-1}, $A = 200\%$. The shear direction is horizontal

Discussion

The observation of flow in a [211] direction is unexpected, since it is not the most closely packed direction in an fcc structure. Previous work on bcc gels of block copolymer micelles has shown that flow can occur in different planes depending on shear rate [10, 13, 20, 24–26]; however, to our knowledge in all previous reports flow has been reported to occur with the close-packed direction along the shear direction, the same being true for fcc gels [8–13, 17].

It is interesting to note that [211] directions correspond to those for slip caused by Shockley partial dislocations in an fcc crystal, whereas edge dislocations have a Burgers vector in the [110] direction, these being the most energetically favoured defects. It is possible that the [211] direction is selected for flow in some crystal grains (possibly in the vicinity of the wall) in the shear sandwich geometry owing to a proliferation of Shockley partial dislocations, which can form by dissociation of perfect dislocations in [110] directions.

Summary

Steady or oscillatory shear in a gel formed by diblock copolymer $P_{94}E_{316}$ in water in a Couette cell led to the familiar layer sliding mechanism of flow of hcp layers with the close-packed direction along the shear direction, as confirmed by SAXS; however, under oscillatory shear in a shear sandwich geometry, a more complex flow behaviour was observed in which grains of hcp layers are rotated by 30° with respect to the flow

direction, which is now along a [211] direction. A possible explanation of this is wall slip, however further measurements using a microfocussed X-ray beam to obtain SAXS patterns in a scan across the gap of the shear sandwich are required to confirm this.

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