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A thermally induced transition from a body-centred to a face-centred cubic lattice in a diblock copolymer gel

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Abstract A transition from a body-centred cubic structure at room temperature to a face-centred cubic structure at higher temperature has been observed in a solution of a poly(oxyethylene)-poly(oxybutylene) diblock copolymer. The ordered micellar structures were confirmed using small-angle X-ray scattering by preparing oriented domains via steady shearing in a Couette cell. The effect of shear in

generating highly oriented, twinned cubic domains is discussed.

Key words Block copolymers – micelles – shearing – rheology – small angle scattering

Introduction

Block copolymers are versatile materials that can be considered as polymer alloys, where the properties of two distinct polymers are exploited by joining chains at their ends. The phase behavior of block copolymers in the melt has been the subject of considerable attention [1–3], and other aspects, such as the effect of crystallization of one of the blocks on the microstructure, have been the subject of recent work [1].

Some of the most important applications of block copolymers arise from their surfactant-like properties. When dissolved in a selective solvent, block copolymers can form micelles above a critical micelle concentration or temperature [1]. At higher concentrations, micelles can self-assemble into ordered arrays such as cubic structures. The cubic phases are stiff gels that do not flow under their own weight, i.e. they are characterized by a finite yield stress. Thermally driven gelation in block copolymer solutions results from the increase in volume fraction of micelles with increasing temperature. The transition to

a hard gel occurs when the volume fraction of spheres in the system reaches a critical value. The corresponding packing fraction is $\Phi_c = 0.74$ for face-centred cubic (fcc) or hexagonal-close packed (hcp) structures, $\Phi_c = 0.68$ for a body-centred cubic (bcc) structure or $\Phi_c = 0.52$ for a simple cubic structure.

The effect of shear on order in micellar phases of block copolymer solutions has been probed by Mortensen and coworkers [4–6]. They investigated Pluronic (poly(oxyethylene)–poly(oxypropylene)–poly(oxyethylene), PEO–PPO–PEO) triblock copolymer gels in aqueous solution, the structure of which was elucidated using small-angle neutron scattering (SANS). The cubic phase in the materials examined was found to be bcc in all cases. Face-centered cubic structures have also been observed in Pluronic copolymers, using small-angle X-ray scattering (SAXS) [7, 8]. The effect of steady shear, applied using a Couette cell, on the orientation of an fcc structure in PEO₁₂₇PPO₄₈PEO₁₂₇ in aqueous solution (Pluronic F108) was investigated using SAXS, and transitions between shearing flows were elucidated [7]. Both bcc and fcc phases have been observed in solutions of

poly(styrene)-poly(isoprene) diblocks in decane [9]. One or other of the two structures was formed below the order-disorder transition depending on the thickness of the micellar corona compared to the core. Thinner coronas lead to more short range inter-micellar repulsions and so favour the fcc structure, whereas the bcc phase is favoured for "softer spheres" with larger coronas [9]. In Kraton copolymers (poly(styrene)/hydrogenated (poly(isoprene) diblocks and triblocks) SANS was used to identify an ABC... stacked hexagonal structure, where the unit cell was distorted from a cubic one [10].

The behaviour of cubic phases in block copolymer solutions (and melts) under shear shows many analogies with the behavior of charge stabilized colloids under shear. In a pioneering series of papers, Ackerson and coworkers have elucidated transitions involving the flow of hcp layers [11–14]. Depending on the shear conditions (steady or oscillatory, shear rate and amplitude) and the volume fraction, it is possible to form two-dimensional hcp layers in which the close-packed direction lies parallel to the flow direction and the layer normal is parallel to the gradient direction. Single crystal fcc structures can also be obtained under suitable conditions.

We have previously reported on the phase behaviour of gels of a poly(oxyethylene)-poly(oxybutylene) diblock, PEO₄₀PBO₁₀ (the subscripts denote the number of repeats) in 0.2 M K₂SO₄, elucidated using SAXS with simultaneous rheology [15]. This work complemented an earlier study where micellar dimensions and association numbers were characterized using light scattering, gel-sol boundaries were mapped via mobility experiments and clouding was observed at high temperatures [16]. The addition of salt was shown simply to lead to a downward shift in the upper gel-sol boundary compared to salt-free solutions. In this letter, evidence is presented for a transition between bcc and fcc structures on heating micellar solutions of this diblock copolymer. SAXS was used to determine the ordered structure in unoriented samples and also samples oriented by continuous shear in a sealed Couette cell. The effect of shear in generating highly oriented, twinned cubic domains is discussed.

The copolymer PEO₄₀PBO₁₀ was identical to the one used earlier [15]. As described elsewhere [16] it has a narrow molecular weight distribution, $M_w/M_n = 1.04$ determined by GPC based on poly(oxyethylene) calibrants. The material used in this study was a 38 wt% solution of the copolymer in 0.2 mol dm⁻³ K₂SO₄, which was prepared by mixing at $T = 60-70^\circ\text{C}$, followed by several days storage in a refrigerator. Examination in an optical microscope revealed that gels formed by this sample were clear and did not show birefringence, consistent with cubic symmetry.

Small-angle X-ray scattering experiments were performed on the high brilliance beamline at the European

Synchrotron Radiation Facility. Further details of the instrument are provided elsewhere [17]. Pinhole optics were employed to collimate a monochromatic incident X-ray beam (1 Å wavelength) to a cross-section $0.2 \times 0.2 \text{ mm}^2$ at the sample position. The SAXS patterns were recorded on a two-dimensional gas detector in an evacuated tube. The detector was located 3 m from the sample. Samples were sheared in a homemade Couette cell, made of polycarbonate, that is described in detail elsewhere [18]. The rotor is the outer cylinder and the size of the annular gap between both cylinders of the cell is 1 mm. The cell is mounted on a motorized translation stage which allows the sample to be aligned in any beam position between the so-called radial and tangential orientations. These configurations are illustrated in Fig. 1. Denoting the incident wavevector by \mathbf{q}_0 , the radial orientation corresponds to \mathbf{q}_0 parallel to \mathbf{V} , the velocity gradient direction. The tangential orientation corresponds to \mathbf{q}_0 parallel to \mathbf{v} , the shear velocity direction. The third direction $\mathbf{e} = \mathbf{V} \times \mathbf{v}$ is the vorticity direction. These two configurations provide the SAXS pattern in two orthogonal planes in reciprocal space, namely $(\mathbf{q}_v, \mathbf{q}_e)$ and $(\mathbf{q}_v, \mathbf{q}_e)$.

SAXS patterns from the gel at 25°C are shown in Fig. 2. For the as-mounted sample, the diffraction patterns in both planes are essentially isotropic, with rings in the positional ratio $1:\sqrt{2}:\sqrt{3}$ (Fig. 2: top). This is consistent with the bcc (spacegroup $Im\bar{3}m$) structure observed for block copolymer melts and surfactant micellar solutions. On increasing the shear rate to $\dot{\gamma} = 8 \text{ s}^{-1}$, the diffraction pattern in the $(\mathbf{q}_v, \mathbf{q}_e)$ plane (Fig. 2c) develops a pronounced two-fold symmetry, with the inner 110 reflections tending to be oriented along the meridian (the $\{110\}$ planes are the closest packed planes in this bcc structure). This indicates that the $\{110\}$ planes in this direction are predominantly oriented in the (\mathbf{v}, \mathbf{V}) plane, although the presence of significant intensity elsewhere on the ring indicates that the sample is by no means a monodomain. This is also evident from the presence of 200 reflections on the equator, which are assigned to separate grains in which $\{200\}$ planes are oriented in the (\mathbf{v}, \mathbf{e}) plane. The diffraction pattern in the $(\mathbf{q}_v, \mathbf{q}_e)$ plane under the same shear conditions (Fig. 2d) reveals four orthogonal 110 reflections on the inner ring and four 200 reflections on the second ring. The two equatorial reflections indicate that a fraction of $\{110\}$ planes must be oriented in the (\mathbf{v}, \mathbf{e}) plane as well as the (\mathbf{v}, \mathbf{V}) plane giving rise to the meridional reflections, i.e. the $\{110\}$ planes are oriented both parallel and perpendicular to the shear plane (\mathbf{v}, \mathbf{e}) . These patterns from oriented samples provide strong evidence for a bcc structure of the gel at low temperature.

On heating to 52°C , an fcc structure (probable space-group $Fm\bar{3}m$) develops. The structure of this phase was most clearly revealed by the application of shear to

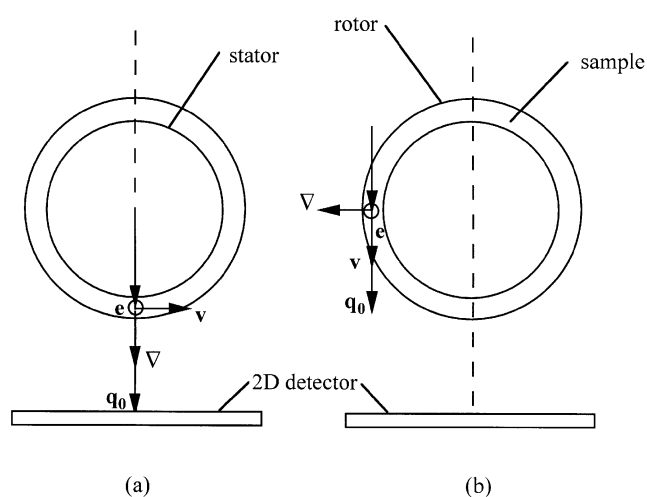
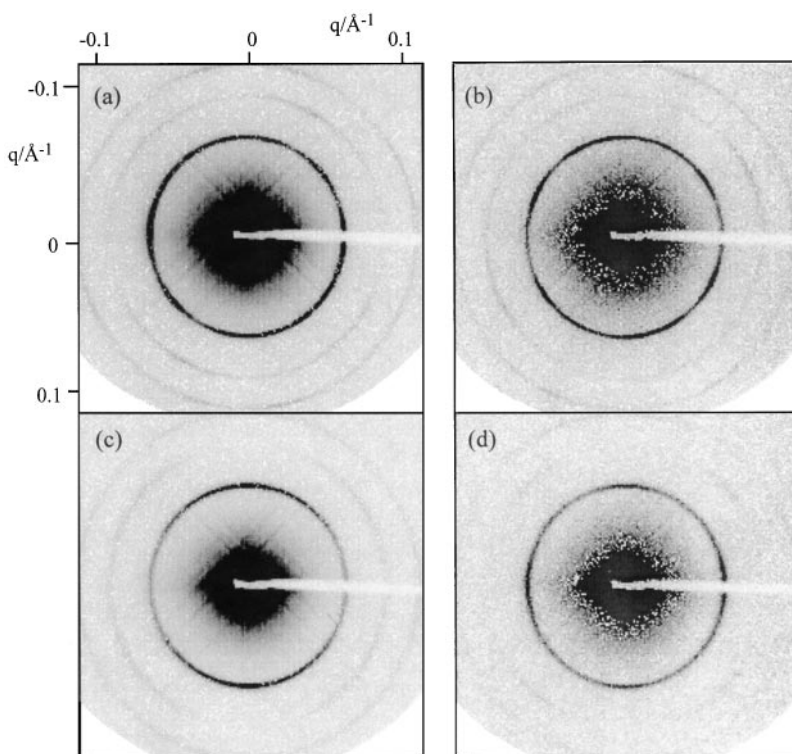


Fig. 1 Top view of the Couette cell showing the two geometries for the SAXS experiments. Here \mathbf{v} is the velocity (shear) direction, ∇ is the shear gradient direction and $\mathbf{e} = \mathbf{v} \times \nabla$ is the neutral (vorticity) direction. (a) $(\mathbf{q}_v, \mathbf{q}_e)$ plane, (b) $(\mathbf{q}_v, \mathbf{q}_e)$ plane

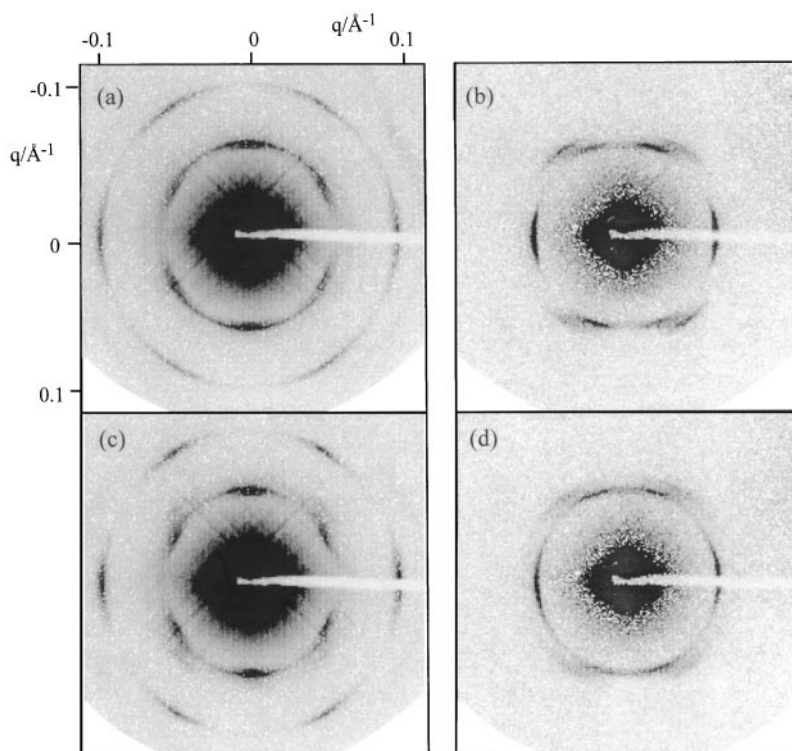
generate oriented SAXS patterns. Figure 3 shows SAXS patterns under the same shear conditions as for the bcc phase patterns in Fig. 2. The primary effect of increasing the shear rate is to increase sharpness of the Bragg spots in the $(\mathbf{q}_v, \mathbf{q}_e)$ plane (compare (c) and (a)) at the expense of the spread of the reflections in the $(\mathbf{q}_v, \mathbf{q}_e)$ plane (d) versus (b)).

Fig. 2 SAXS patterns at 25 °C. (a) $(\mathbf{q}_v, \mathbf{q}_e)$ plane, sample as mounted, (b) $(\mathbf{q}_v, \mathbf{q}_e)$ plane sample as mounted, (c) $(\mathbf{q}_v, \mathbf{q}_e)$ plane, during shear at $\dot{\gamma} = 8 \text{ s}^{-1}$, (d) $(\mathbf{q}_v, \mathbf{q}_e)$ plane during shear at $\dot{\gamma} = 8 \text{ s}^{-1}$. The neutral direction (e) is vertical



There is evidence for additional scattering at $\sqrt{\frac{4}{3}} q^*$ (second order reflections) in (c) which is not present in (a), and this pattern is similar to that obtained by us previously for a 30 wt% gel subject to oscillatory shear [15]. The outer hexagon of reflections in Fig. 3a and (c) are 220 reflections from hcp layers. This indicates that a proportion of these layers are oriented in the (\mathbf{v}, \mathbf{e}) plane, i.e. parallel to the shear plane. However, the presence of an inner hexagon of reflections indicates that the structure cannot simply be an ABCABC ... stacking of hcp layers (i.e. a monodomain fcc structure), because in this case these 111 reflections from the close-packed planes would be absent. This can be ascribed to irregularities in the stacking sequence, i.e. sequences of random stacking of a high density of slip planes (parallel to the $\{111\}$ planes) between grains with regular ABCABC ... stacking. (These alternatives are, of course, not mutually exclusive). However, the structure does not consist solely of hcp layers parallel to the shear direction because the meridional 111 reflections are approximately twice as intense as the other four, and the intensity of the 220 and 220 equatorial reflections is similarly enhanced compared to the other four 220 reflections. This suggests an appreciable fraction of $\{111\}$ planes oriented in the (\mathbf{v}, ∇) plane, i.e. perpendicular to the shear plane. Thus “parallel” and “perpendicular” orientations of close-packed $\{111\}$ planes (with respect to the (\mathbf{v}, \mathbf{e}) plane) coexist. The weak

Fig. 3 SAXS patterns at 52 °C. (a) ($\mathbf{q}_v, \mathbf{q}_e$) plane, during shear at $\dot{\gamma} = 0.8 \text{ s}^{-1}$, (b) ($\mathbf{q}_v, \mathbf{q}_e$) plane during shear at $\dot{\gamma} = 0.8 \text{ s}^{-1}$, (c) ($\mathbf{q}_v, \mathbf{q}_e$) plane, during shear at $\dot{\gamma} = 80 \text{ s}^{-1}$, (d) ($\mathbf{q}_v, \mathbf{q}_e$) plane during shear at $\dot{\gamma} = 80 \text{ s}^{-1}$. The neutral direction (e) is vertical



second order 200 reflections in Fig. 3c can be ascribed to a small population of grains with $\{2\ 0\ 0\}$ planes at $\pm 45^\circ$ to the shear direction. Thus, the SAXS patterns in the ($\mathbf{q}_v, \mathbf{q}_e$) plane arise from domains in several orientations.

The patterns in Fig. 3b and d are simpler to index, they correspond to a twinned structure. The diffraction pattern for one of the twins has a pair of reflections ($\bar{1}\ \bar{1}\ 1$ and $1\ 1\ \bar{1}$) on the equator and $1\ 1\ 1$, $\bar{1}\ \bar{1}\ \bar{1}$ reflections at an angle with respect to the meridian $\alpha = \sin^{-1}(1/3) = 19.5^\circ$ and $00\ 2$ and $00\ \bar{2}$ reflections at $\beta = \sin^{-1}(1/\sqrt{3}) = 35.3^\circ$. The presence of these off-equatorial reflections indicates a substantial fraction of ABCABC ... stacking. The fact that the equatorial reflections in the SAXS patterns in the ($\mathbf{q}_v, \mathbf{q}_e$) plane are approximately twice as intense as the others indicates that some of the planes have a random stacking sequence, consistent with the interpretation of the data for the ($\mathbf{q}_v, \mathbf{q}_e$) plane. These data provide convincing evidence for an fcc phase in this diblock gel (extending from 50–60 °C), obtained upon heating from a bcc phase.

On further heating a hexagonal (hex) structure was observed above 75 °C (with a biphasic region between 60 °C and 75 °C). The SAXS pattern in the absence of shear (not shown) showed unoriented rings in the positional ratio $1:\sqrt{3}:2$. This phase was cloudy and birefringent, providing further evidence for a structure of

hexagonal-packed cylinders. The hex phase persisted up to the highest accessible temperature (95 °C) [15].

The observation of a transition between bcc and fcc structures is attributed to the thinning of the coronal layer that occurs on heating. This is apparent from the data shown in Table 1, which contains micellar parameters from light scattering experiments on dilute solutions [16]. The thermodynamic radius and thermodynamic volume reduced with respect to the association number give a measure of the volume of the PEO corona, and these are decreasing function of temperature for PEO₄₀PBO₁₀ in 0.2 M K₂SO₄ [16]. The observed increase in association number and micellar radius with increasing temperature (Table 1) implies that more PEO blocks are needed to cover the surface of the micelle to compensate the reduction in coronal volume. Thus the packing fraction must increase from $\Phi_c = 0.68$ in the bcc phase to 0.74 in the fcc phase. The presence of a thinner corona at higher temperatures is consistent with the interactions between micelles being more “hard sphere-like”, thus favouring an fcc structure.

A theory for the formation of micellar phases in block copolymer melts was developed by Semenov [19] by calculating the interaction energy between micelles using an electrostatic energy for the chain distribution [20]. In this way, a sequence of transitions between fcc and hex structures and ultimately a bcc structure was predicted as

Table 1 Micellar characteristics for PEO₄₀PBO₁₀ in 0.2 M K₂SO₄ (from [16])

<i>T</i> (°C)	<i>p</i> ^{a)}	<i>r</i> _t [nm] ^{b)}	<i>r</i> _h [nm] ^{c)}
20	32	4.6	4.6
30	45	5.1	5.1
45	55	6.1	5.3

^{a)} Association number.^{b)} Thermodynamic radius = equivalent hard-sphere radius.^{c)} Hydrodynamic radius.

a function of a reduced χ parameter and the volume of the core relative to that of the total micelle. Unfortunately, this theory is not straightforward to extend to the case of block copolymer micelles in solution and furthermore the sequence of phases observed here: bcc–fcc–biphasic–hex is not anticipated. Density functional theory has recently been developed for block copolymer micelles, however this

only predicts a simple liquid–fcc transition [21]. Thus, accounting for our results theoretically remains an outstanding challenge.

Thermally driven transitions between bcc and fcc phases are known in metals. For example in the iron–carbon phase diagram, at a given carbon content, a bcc phase (α form or ferrite, coexisting with Fe₃C) is stable below 725 °C, whereas the γ (or austenite) fcc structure is stable at higher temperatures [22]. Our results thus provide further evidence for the remarkable analogies between the phase behavior of soft solids such as those formed by block copolymer micelles and conventional solids such as metals.

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