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Mesoscopic Crystallography: A Small-Angle Neutron Scattering Study of the Body-Centered Cubic Micellar Structure Formed in a Block Copolymer Gel

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ABSTRACT: Gels of a poly(oxyethylene)−poly(oxybutylene) diblock copolymer in an aqueous solution forming a bcc phase have been examined using small-angle neutron scattering (SANS) with simultaneous rheology. Application of large amplitude oscillatory shear was observed to induce macroscopic alignment of twinned bcc crystals. The structure of these crystals was probed in three dimensions using SANS with a shear-oriented sample that was fixed in situ in the shear cell and mounted on a goniometer. This corresponds to a kind of "mesoscopic crystallography" which enabled the eludication of the twinned bcc structure, in which the [111] direction was oriented along the shear direction, this being a 6-fold rotation axis. Flow was found to occur in (110) planes oriented normal to the shear gradient direction. A comparison is made between this twinned structure, probed comprehensively in three dimensions, and those previously reported for block copolymer solutions and melts.

Introduction

Block copolymers in the melt and in concentrated solution in a selective solvent can self-assemble into a variety of structures which are ordered on the mesoscopic length scale (i.e., typically 10−100 nm).[1] In an AB diblock melt[2] or concentrated solution,[3−7] ordered morphologies result from unfavorable interactions between A and B chain units, which often increase on lowering temperatures. In solution, there are additional interactions between the chain units and solvent that can lead to a rich phase behavior that resembles that of conventional amphiphiles, if the blocks are short.

The formation of distinct ordered structures in melts and solutions is often described in terms of interfacial curvature. For melts, it is the compositional asymmetry of the copolymer that determines the morphology in the strong segregation limit, highly asymmetric copolymers leading to curved interfaces such as those in the body-centered cubic spherical phases.[2,8] A description in terms of molecular asymmetry (volume relative to the interfacial area and chain length) has also been applied to account for phases such as the cubic micellar phases formed in solutions of amphiphiles.[9] An additional effect for copolymer micelles arises from the osmotic requirement for the corona blocks to maintain a uniform concentration in the matrix phase (containing solvent and corona segments). This requirement places entropic restrictions on the coronal block conformation and micelles pack in cubic structures to minimize the osmotic constraint.[10] In contrast, the formation of cubic phases of spherical domains in block copolymer melts is controlled by the balance of interfacial free energy and the free energy associated with packing constraints (which tend to favor domains of uniform thickness) with an additional entropic penalty resulting from chain stretching.[8]

The development of cubic ordering in a micellar solution is accompanied by a profound change in the flow behavior. Whereas micellar solutions flow under their own weight and are viscoelastic (or even Newtonian) fluids, cubic phases are elastic solids, with a high-yield stress. Cubic phases in block copolymer solutions have thus been characterized as "hard gels".[3] This type of gel formation in aqueous solutions of poly(oxyethylene)−poly(oxypropylene)−poly(oxyethylene) (commercial name: Pluronic) copolymers in aqueous solution has been extensively studied.[1,11] Mortensen and co-workers[12−14] have used shear to prepare aligned domains of Pluronic block copolymer gels, the structure of which was elucidated using small-angle neutron scattering (SANS).

The influence of shear on the bcc phase in block copolymer melts has also been probed using SANS on samples oriented using reciprocating shear.[15,16] Almdal and co-workers showed that highly twinned bcc single crystals of a poly(ethylene propylene)−poly(ethylethylene) diblock could be obtained by large amplitude shearing.[15] The deformation occurred via slip of close-packed {110} slip planes in the $[\bar{1}11]$ direction. The shear gradient direction was coincident with $[\bar{0}11]$. Epitaxial growth of a bcc structure from an oriented hexagonal structure has been observed for the same class of diblocks.[16] The [111] direction of the bcc structure was found to be coincident with the original cylinder axis, leading to a highly oriented, twinned bcc structure. At high and low shear rates, twinned bcc

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crystals were observed. However, at intermediate shear rates, shear melting occurred as shown by isotropic two-dimensional SAXS patterns. The loss of translational order at intermediate shear rates was ascribed to the generation of numerous defects (i.e., a proliferation of slip of {110} planes).[16]

We have previously investigated the effect of oscillatory shear on gels of poly(oxyethylene)−poly(oxybutylene) (E_mB_n, where the subscripts are numbers of repeats) diblock copolymers in aqueous salt solution. Structures were elucidated using SAXS with simultaneous rheology for diblocks $E_{40}B_{10}$[17] and $E_{86}B_{10}$.[18] Salt was added to reduce the temperature of the sol−gel boundary. In addition, the effect of steady shearing in a Couette cell has been examined using SAXS[19] and SANS.[20] For $E_{40}B_{10}$ solutions in 0.2 M K_2SO_4, both face-centered cubic (fcc) and bcc phases were identified using SAXS, with the bcc phase observed for concentrations greater than 30 wt % polymer at low temperatures. Gels of $E_{86}B_{10}$ in the same salt solution in the concentration range 25−40 wt % were shown to exhibit a bcc phase alone.[18] On the basis of the SAXS data, a macroscopically aligned twinned structure, obtained following large-amplitude, high-frequency shear was found to have the [111] direction aligned along the shear flow direction, with flow occurring in the {110} and {211} planes which intersect along the same [111] direction. Gels formed by the poly(methylene)−poly(oxyethylene) (CE) diblocks $C_{11}E_{40}$, $C_{15}E_{39}$, and $C_{17}E_{40}$ in aqueous solution have also been shown to correspond to bcc structures, some of which can be oriented to produce patterns with the same symmetry as those observed for $E_{86}B_{10}$ gels.[21]

Here, large-amplitude oscillatory shearing (with simultaneous SANS and rheology to study the alignment process) was used to produce a macroscopically oriented bcc phase formed from gels of the diblock copolymer $E_{210}B_{16}$ in D_2O. The orientation of the resulting twinned "mesoscopic" crystal was then investigated by mounting the sheared sample in a goniometer (contained within the rheometer oven). The sample was rotated about the shear direction (and rocked out of the shear direction) and SANS patterns were obtained for different crystallographic orientations. This enabled a systematic investigation where the orientation of a cubic micellar phase in a mesoscopic system was probed by in situ crystallography. A similar technique has previously been reported for a shear-oriented Pluronic copolymer, where SANS was used to probe the crystal structure of a bcc phase oriented by hand-shearing between parallel plates.[22] The orientation of the structure identified here differs from that previously reported for Pluronic triblocks in aqueous solution[7,8] and our previous results from SAXS/rheology experiments,[18,21] all of which were limited, however, to the acquisition of diffraction patterns in the plane defined by shear and neutral directions. However, the orientation we observe has previously been reported for block copolymer melts[15,16] and polystyrene−polyisoprene (PS−PI) diblocks in a selective solvent.[23]

Experimental Section

1. Materials. The copolymer was prepared by sequential anionic polymerization of ethylene oxide followed by 1,2-butylene oxide.[24] The initiator was 2-(2-methoxyethoxy)-ethanol activated by reaction with the potassium metal (mole ratio [OH]/[K] = 15). Characterization of the final copolymer with gel permeation chromatography (GPC, calibrated with poly(oxyethylene) standards) gave $M_w/M_n = 1.03$. Comparison of the intensities of resonances from backbone and end group carbons in the ^{13}C NMR spectrum gave M_n = 10 400 and the composition 92.9 mol % E. These results are consistent with the molecular formula $E_{210}B_{16}$. The intensities of resonances from end and EB-junction carbons were identical within experimental error, so confirming the diblock structure. Combination of the GPC and NMR results gave M_w = 10 700 g mol^{-1}.

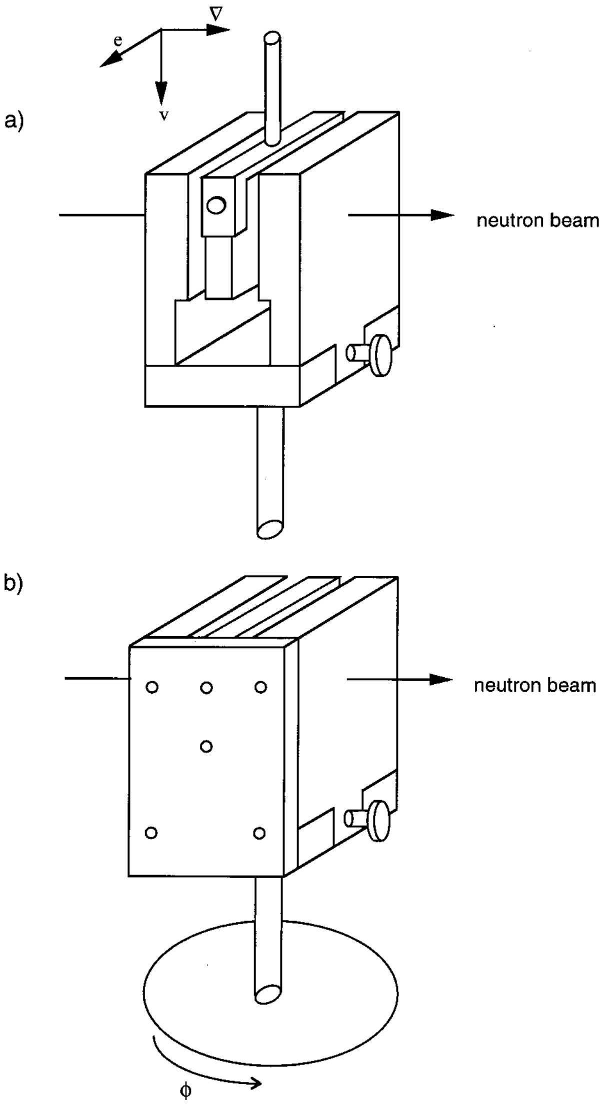

Figure 1. Schematic of the shear sandwich tool (a) in the rheometer, as configured for rheology experiments, (b) detached from the transducer and actuator, plates being fixed together with the sample in situ, the entire assembly then being mounted on a two-circle goniometer for SANS experiments to probe the structure as a function of the rotation angle, ϕ, about the shear direction.

The materials studied were concentrated solutions of the copolymer in D_2O, (chosen to enhance the contrast and reduce the background for SANS experiments) which were prepared by mixing at T = 60−70 °C, followed by storage of the gel in a refrigerator for several weeks. The phase diagram for $E_{210}B_{16}$ in H_2O shows that the gel phase extends to low concentrations, ≈7 wt % at 45 °C,[25] and SAXS and SANS on gels in H_2O or D_2O confirm a bcc structure, at least for concentrations in the range 25−70 wt %.[26] All experiments reported in this paper were conducted on a 40 wt % gel at 25 °C.

2. Simultaneous Small-Angle Neutron Scattering and Rheology. Neutron-scattering experiments were conducted at the SANS facility at Risø National Laboratory, Denmark. Neutrons with wavelength λ = 5.6 Å and $\Delta\lambda/\lambda$ = 0.09 were

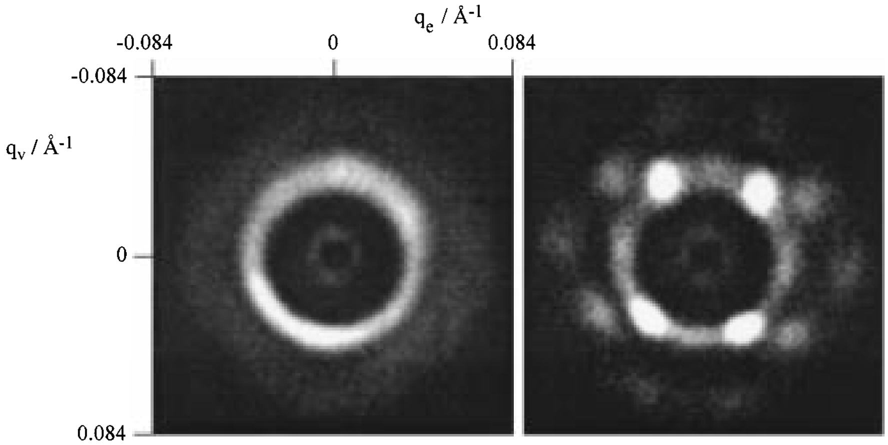

Figure 2. SANS pattern obtained for a 40 wt % solution of $E_{210}B_{16}$ in D_2O at 25 °C, (left) sample as mounted, (right) following shear at $\omega = 10$ rad s^{-1} and $\lambda = 150\%$ for 5 min.

incident on samples mounted in a parallel plate shear sandwich geometry, illustrated in Figure 1a. The plates are made from aluminum to allow passage of the neutrons. The shear sandwich fixture was mounted in a Rheometrics RSA II rheometer, adapted for neutron-scattering experiments at Risø. The plates were contained within an oven, with temperature control to within ±1 °C, with cylindrical tubes inserted in the oven walls to allow passage of the beam. With the rheometer in situ at the neutron beamline the shear direction **v** was vertical and the neutron beam was incident along the horizontal shear gradient direction ∇, the neutral direction $\mathbf{e} = \nabla \times \mathbf{v}$ also being horizontal.

For the experiments where the crystal structure was probed as the sample was rotated, the shear sandwich tool shown in Figure 1a was clamped as shown in Figure 1b, forming a rigid assembly in which the sample was held in position between the plates. The central insert was then disconnected from the transducer. The assembly was then mounted on a custom-made goniometer, contained, for convenience, within the oven of the rheometer. Details of the goniometer design are provided elswehere.[27] Rotation about the angle ϕ shown was achieved manually, in addition rocking of the sample by an angle χ in the range $0° < \chi < 30°$ away from the vertical was possible. A final experiment was performed with the sample placed with the assembly positioned in the beam with the fixing plate horizontal, so that the diffraction pattern with the beam along the shear direction was obtained. This was possible, despite the large path length of sample and aluminum, due to their relatively high neutron transmission.

Results and Discussion

SANS patterns obtained from the 40 wt % gel of $E_{210}B_{16}$, either as mounted in the rheometer at 25 °C or by following large-amplitude shear at the same temperature, are shown in Figure 2. For the sample as mounted, the SANS pattern shows a ring of scattering centered on $q^* = 0.038$ Å^{-1} (corresponding to a lattice parameter $a = 234$ Å) with some weak anisotropy resulting from compression of the sample during mounting. In contrast, the pattern obtained following the cessation of shear (at a frequency $\omega = 10$ rad s^{-1} and a strain amplitude $\lambda = 150\%$ for 5 min) displays sharp Bragg spots, arranged in “layer lines”. This pattern was found not to change with time following the cessation of shear, thus indicating that the macroscopic orientation had been locked in. The pattern of reflections can be indexed to a twinned bcc structure, as will be discussed shortly.

The structure of the macroscopically oriented crystal was then investigated in three dimensions, by rotation of the sample fixed in the shear sandwich cell and placed on the goniometer in the rheometer. The sample was rotated about the shear direction through an angle ϕ and also rocked away from the shear direction through an angle χ. Figure 3 shows selected SANS patterns from one-half of a full rotation scan around ϕ. SANS patterns were also acquired at numerous intermediate angles, but only the patterns corresponding to projections of the structure along symmetry directions are shown in Figure 3. This experiment revealed 6-fold symmetry around the shear direction, with the original pattern at $\phi = 0°$ also recovered at 60°, 120°, 180°, etc., as shown in Figure 3. However, at intermediate angles

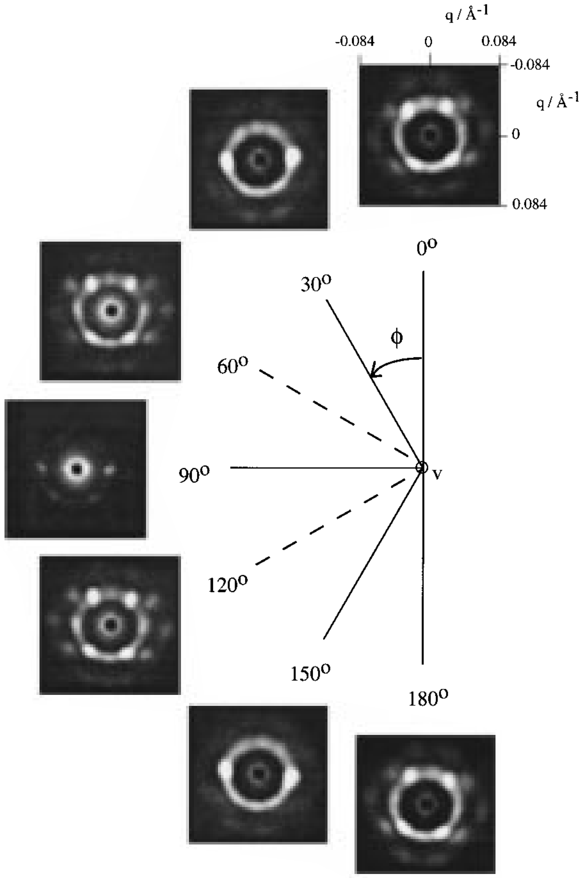

Figure 3. SANS patterns obtained by rotating the “crystal” of the gel about the shear direction through the azimuthal angle ϕ. Symmetric diffraction patterns were obtained for $180° \le \phi \le 360°$.

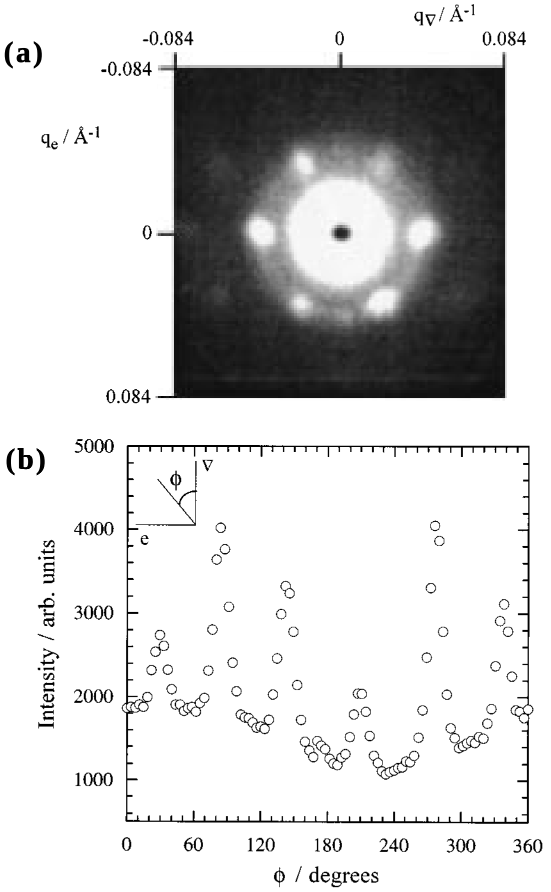

Figure 4. (a) SANS pattern obtained with the neutron beam incident along the shear direction, (b) azimuthal intensity profile.

$\phi = 30°$, 90°, 150°, etc., a projection of the structure corresponding to 2-fold symmetry was obtained as shown by SANS patterns with only a pair of equatorial reflections. The pattern obtained at 90°, shown in Figure 3 is weak due to the lower transmission at this angle. Nevertheless, two equatorial reflections are apparent, along with weaker off-equatorial reflections at ±60° with respect to the equator, which are assigned to a small fraction of misoriented sample. For all ϕ accessed, rocking in the range $\chi = \pm 30°$ away from the shear direction did not lead to other symmetry projections of the structure, merely producing patterns reminiscent of those obtained for $\chi = 0°$ (for example, those shown in Figure 3) but with asymmetric distributions in Bragg peak intensities, as certain spots moved away from the diffraction condition. We return to a discussion of the indexation of the SANS patterns in Figure 3 shortly.

Confirmation of the 6-fold symmetry of the twinned structure about the shear direction was obtained directly by placing the sample cell such that the neutron beam was incident along the shear direction, with the fixing plate shown in Figure 1b horizontal. The resulting SANS pattern in the (∇,**e**) plane, together with a plot of intensity as a function of azimuthal angle (ϕ) is shown in Figure 4. Strong forward scattering in this pattern results from background scattering from the cell. The SANS pattern contains six 110 reflections arranged hexagonally (Figure 4a), and weak higher order 200 reflections also arranged hexagonally (not apparent in Figure 4a). The scan of azimuthal intensity in a circular band centered on the 110 reflections, shown in Figure 4b, confirms quantitatively the hexagonal pattern, the average angle between peaks being 61 ± 3°. The peak intensities are not uniform due to asymmetric transmission through the shear sandwich tool (with different thicknesses of aluminum in different directions).

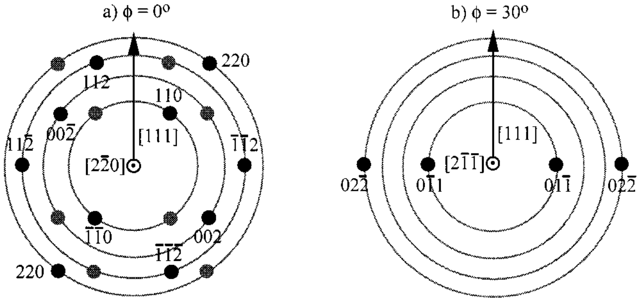

Figure 5. Indexation of the SANS patterns obtained during the rotation experiment. A [111] direction in the crystal orients along the shear direction. Patterns were obtained by rotating around this direction.

Figure 5 summarizes the indexation of the patterns obtained for symmetry projections of the structure at different azimuthal angles ϕ. The Bragg reflections can be indexed on the basis that a [111] direction lies along the shear direction. This is the close-packed direction in bcc crystals, and flow along this direction thus occurs readily. The pattern obtained at $\phi = n60°$ (where n = 0, 1, 2, ..., 6) is indexed as shown in Figure 5a. This corresponds to a twinned structure, with reflections for one of the twins (black spots) indexed as shown, and the reflections from the other twin indicated by gray spots. This arrangement of reflections confirms a twinned bcc structure, the pattern not being obtainable from fcc or hexagonal close-packed structures. The patterns obtained at $\phi = (30 + n60)°$ (n = 0, 1, ..., 5) are indexed in Figure 5b.

These patterns differ from those obtained previously by our group using simultaneous SAXS and rheology on bcc gels formed by copolymers such as $E_{86}B_{10}$[18] and $C_{15}E_{39}$[21] (We have investigated other bcc gels and SAXS/rheology experiments have always revealed SAXS patterns with the symmetry described in ref 18). However, a pattern resembling that obtained by us at $\phi = n60°$ has been reported for a bcc micellar phase formed by a polystyrene−poly(ethylene-*co*-butylene)−polystyrene triblock in a midblock selective solvent.[28] In our earlier experiments, only the (**v**,**e**) plane was accessed, and patterns corresponding to a superposition of Figure 5a, b resulted from large-amplitude shearing at $\omega = 10$ or 100 rad s^{-1} and $\lambda = 100\%$. These patterns clearly differ from that obtained at $\phi = 0°$ (and symmetry related angles) in the present case, due to the presence in the former case of equatorial 110 reflections in addition to the four off-equatorial peaks at ±54.7° with respect to the equator. Those patterns were indexed on the basis of a highly twinned structure with a 3-fold rotation axis about the [111] (shear direction) with flow in the {110} and {211} planes, which intersect along the same [111] direction. Symmetry projections of the structure which brought higher order reflections into the diffracting condition were observed for a number of intermediate angles ϕ ($\neq n30°$) as described in ref 18. One possible reason for the difference in the previously reported patterns compared to those obtained for $E_{210}B_{16}$ in the present work is the higher strain amplitude employed in the current experiments. Further work is in progress

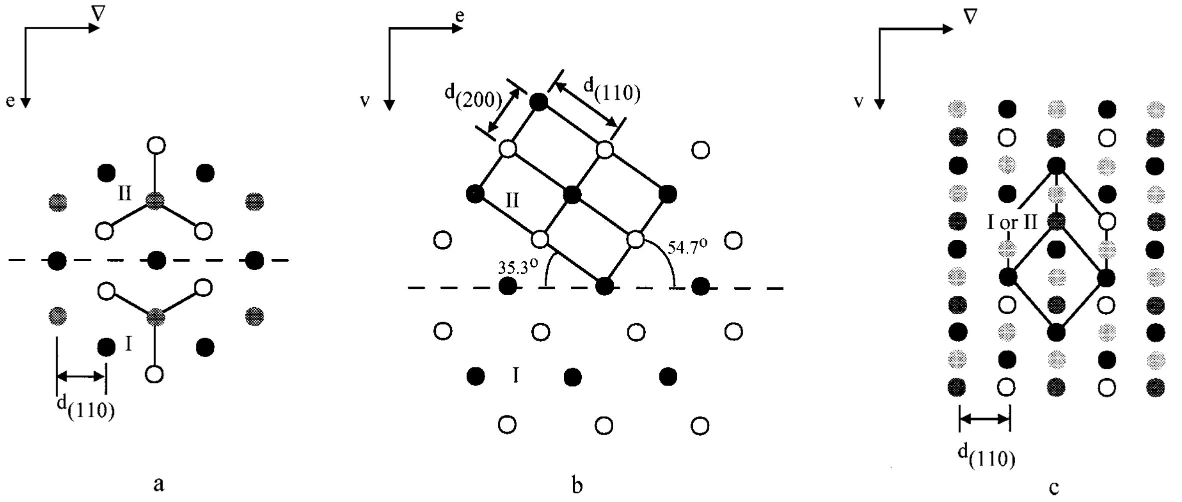

Figure 6. Projections of the twinned bcc structure in three orthogonal planes. Twins I and II are indicated, as are interplanar spacings, *d* (modified from Figure 3 in ref 15).

to investigate the dependence of the orientation of the crystal on strain amplitude.

The SANS patterns presented here also differ from those obtained for the bcc micellar phase formed by Pluronic triblocks in aqueous solution subjected to steady shear in a Couette cell.[12,13] However, similar patterns to that indexed in Figure 5a were obtained for a PS−PI diblock in concentrated solution in decane (a selective solvent for PI),[23] again studied using SANS on samples sheared in a Couette cell. In that case, SANS data were obtained only in the (**v**,**e**) plane, with transitions in orientation observed depending on the shear rate.

Almdal et al.[15] developed a model for a twinned bcc structure formed by a block copolymer melt oriented by reciprocating shear[15] and subsequently cut up to provide SANS patterns in three orthogonal planes. In this model, the bcc crystal is twinned with the twinning plane perpendicular to (110)-type planes, and the twins are oriented at 35.3° with respect to the shear ([111]) direction, as also observed by us, being indicated by the 110 reflections at this angle with respect to the [111] direction in Figure 5a. This model also indicates that (110) planes are stacked along the shear gradient direction. The (110) planes contain three close-packed [111] directions, so that flow in these planes is easy; indeed this is the mechanism for slip in bcc metals[29] and has also been observed for sheared colloidal suspensions.[30] This mechanism leads to a SANS pattern in the (**v**,∇) plane with a pair of reflections along the ∇ direction, as also observed by us (pattern at 90° in Figure 3, also observed at 30°, 150°, etc). Finally, Almdal et al.[15] obtained a hexagonal pattern in the (∇,**e**) plane, similar to that shown in Figure 4. Thus, our crystal orientation is identical to that previously observed for a bcc block copolymer melt. For convenience, Figure 3 from ref 15 is redrawn in Figure 6, indicating projections of the oriented crystal structure. The key point in our case is that SANS patterns in three dimensions were obtained with the gel mounted in situ in the shear cell; clearly cutting the sample in different planes is inappropriate for a gel!

Summary

We have performed "mesoscopic" crystallographic studies on a block copolymer gel, using SANS to probe the structure of a bcc crystal oriented by large-amplitude shearing, mounted in a specially designed cell, and rotated on a goniometer stage. This has enabled a comprehensive characterization of the three-dimensional structure of the "mesoscopic" structure. A structure was deduced in which a [111] direction is oriented along the shear direction (which also corresponds to a 6-fold rotation axis) and slip occurs in (110) planes. This is the same orientation of a bcc crystal previously identified for a sheared block copolymer melt,[15] but differs from previous results for poly(oxyethylene)-based copolymers in solution.[12,13,18,21] This might reflect differences in the slip mechanism as a function of strain amplitude, or result from differences in flow behavior due to the copolymer molecular weight (which could affect chain entanglements and hence the local viscoelasticity). In particular, the hydrodynamic radius of $E_{210}B_{16}$ micelles is $r_h \approx 22$ nm, similar to those for the PS−PI diblocks in decane studied by Gast and co-workers (18−49 nm at room temperature),[31] whereas $E_{40}B_{10}$ micelles are much smaller, having $r_h \approx 8$ nm under comparable conditions.[32] The technique of mesoscopic crystallography on shear-oriented samples should be widely applicable to investigate the structure of other micellar and bicontinuous cubic gels.

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