

In Situ SAXS Studies of Transformations from Close-packed to BCC in Symmetry in Block Copolymer Solutions

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Introduction

Block copolymers often form spherical micelles in a selective solvent. Under appropriate conditions of concentration and temperature, these micelles pack onto a lattice. In this case, the ordered symmetry is either close packed (face-centered cubic [fcc] or hexagonal close-packed [hcp]) or body-centered cubic (bcc), depending on the intermicellar potential. For example, the interaction between micelles with a short corona is short-ranged and repulsive, and the micelles adopt the close-packed fcc structure, similar to hard spheres. The interaction between micelles with a long corona becomes long-ranged, and the micelles favor the less dense bcc structure [1].

One interesting feature is the transformation between fcc and bcc lattices upon changing temperature. Remarkably, we found the region in the phase diagram where a fcc transforms to a bcc lattice upon heating. This transition is driven by a decrease in solvent selectivity with increasing temperature [2]. The detailed transition mechanism and associated epitaxial relationships were investigated by *in situ* small-angle x-ray scattering (SAXS).

Methods and Materials

A symmetric poly(styrene-*b*-isoprene) diblock copolymer with block molecular weights of 8,000 and 7,000 g/mol, designated SI(8-7), was prepared by living anionic polymerization. Diethyl phthalate (DEP) was used as a styrene-selective solvent. Solution samples of SI(8-7) in DEP with a polymer volume fraction ϕ of 30% and 35% show an fcc-to-bcc transition at 35°C and an order-to-disorder transition at 50°C.

SAXS experiments were performed by using two *in situ* shear cells to access two orthogonal axes (the shear gradient ∇ and the vorticity \mathbf{e} directions). A Rheometrics DMTA rheometer, modified to allow x-rays to pass through along the gradient direction (∇), was installed on the 6-m SAXS line at the University of Minnesota. For the vorticity direction, a novel cone and plate shear cell [3] was installed in the APS beamline 5-ID-D.

In both experiments, the solutions were sheared at 30°C to produce single crystal-like diffraction patterns, then heated to 40°C without shear. From the changes in the diffraction patterns during the fcc-to-bcc transition, the mechanism and epitaxial relationships could be deduced.

Results

The sample was sheared in the DMTA rheometer at 30°C (fcc phase) by applying a frequency of 1 rad/s and a strain amplitude of 100% for about 1 hour. Clear hexagonal patterns at the first-order and second-order positions were developed, as shown in Fig. 1(a). It has been well-established in many colloidal crystal and micellar systems that shearing an fcc solution produces a mixture of hcp and fcc phases as a result of the random stacking of the densest {111} planes. As indexed in Fig. 1(c), the first-order spots came from the hcp stacking (i.e., 10 $\bar{1}$ 0 reflections), while the second-order spots came from both the hcp and fcc structures (10 $\bar{2}$ 0 and 220 reflections, respectively). This implies that hcp-to-bcc transformation, as well as fcc-to-bcc transformation, was involved in this system. More details are provided in Ref. 4. After the shear was turned off, the sample was heated to 40°C, and the bcc

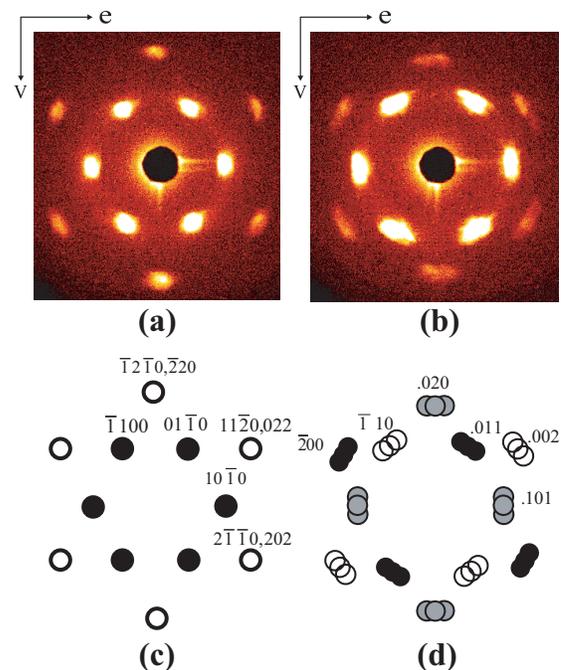


FIG. 1. SAXS patterns for SI(8-7) in DEP $\phi = 0.30$ in the gradient direction (a) after shearing at 30°C (fcc/hcp) and (b) after heating to 40°C without shear. (c) and (d) represent the corresponding index of SAXS patterns for (a) and (b).

phase was grown epitaxially [Fig. 1(b)]. All the spots clearly remained, although they were significantly smeared azimuthally. Also, note that the intensity of the first-order peaks increased. Considering these features, the bcc scattering patterns are indexed in Fig. 1(d). The azimuthally smeared peaks are indexed as a group of three spots, which indicates a multiplicity in the bcc unit cells after transformation. Furthermore, the increase in the intensity of the first-order peaks can be explained by the additional contribution from the hcp-to-bcc transformation.

To investigate scattering in the vorticity direction, a modified cone and plate shear cell were installed at the APS. The protocol was the same as that in the previous experiment. Figures 2(a) and 2(b) are the corresponding SAXS patterns along the vorticity direction for fcc/hcp and bcc phases, respectively. Because of the higher flux and superior collimation for the synchrotron, there are more higher-order reflections than those in Figs. 1(a) and 1(b). Figure 2(a) shows the superposition of fcc and hcp patterns viewed in the $[11\bar{2}]$ and $[10\bar{1}0]$ beam directions, respectively. The scattering patterns in these directions for fcc and hcp are identical, as indexed in Fig. 2(c). After the was turned off shear and the sample was heated to 40°C , the bcc pattern developed [Fig. 2(b)]. There are also a number of higher-order peaks, and they can be assigned as a superposition of the bcc scattering patterns viewed along the $\langle 110 \rangle$ and $\langle 11\bar{2} \rangle$

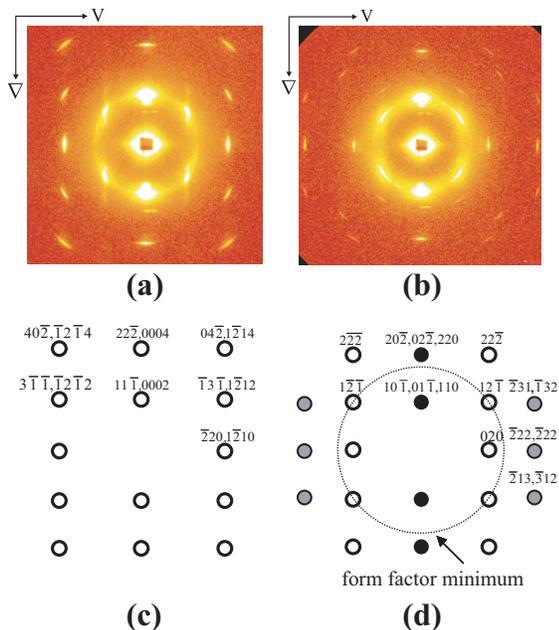


FIG. 2. SAXS patterns for SI(8-7) in DEP $\phi = 0.35$ in the vorticity direction (a) after shearing at 30°C (fcc/hcp) and (b) after heating to 40°C without shear. (c) and (d) represent the corresponding index of SAXS patterns for (a) and (b).

beam directions [Fig. 2(d)]. This also suggests that there are at least two different orientations of the bcc unit cells after transformation from fcc/hcp mixed crystal. Another important feature is that the intensity of the first-order peaks that come from the stacking of the layers does not change after the transformation. This implies that the closest packed planes remain parallel during the transformation.

Discussion

Both fcc-to-bcc and hcp-to-bcc transformations, shown in this system, have been well-established in many simple metals, such as Fe, Mg, and Zr. Their transformation mechanisms are known as the Bain distortion and the Burgers mechanism, respectively. Also, the orientation relationships (ORs) between the parent and the daughter phases have often been observed in these transformations. For example, when the closest-packed planes and the closest-packed directions remain parallel for the fcc and bcc structures ($\{111\}_{\text{fcc}} \parallel \{110\}_{\text{bcc}}$ and $\langle 110 \rangle_{\text{fcc}} \parallel \langle 111 \rangle_{\text{bcc}}$), it is known as the Kurdjumov-Sachs (K-S) OR. The most well-known ORs between the fcc and bcc structures are the K-S and Nishiyama-Wassermann (N-W) ORs. They differ from each other only by a small in-plane rotation of 5.26° , as shown in Fig. 3(b). The analogous ORs for the hcp and bcc structures are the Burgers and Pitsche-Schrader ORs, respectively.

Figure 3(a) represents the Bain distortion for the fcc-to-bcc transformation. This transformation occurs by

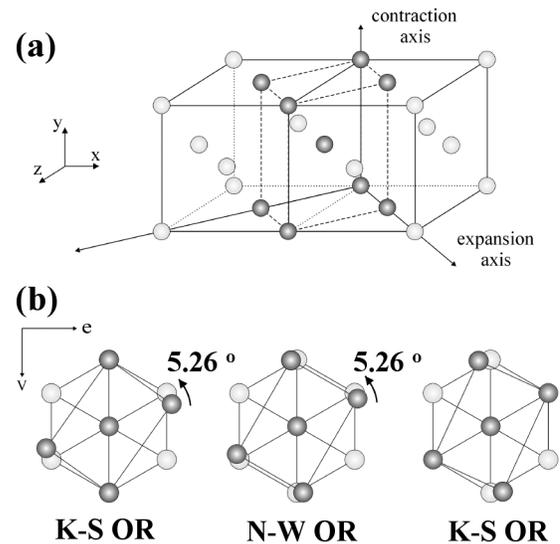


FIG. 3. (a) Illustration of the Bain distortion. Distorted bcc unit cell is imbedded (dark spheres) in two fcc unit cells. (b) Superposition of close-packed $\{111\}_{\text{fcc}}$ (light spheres) and $\{110\}_{\text{bcc}}$ planes (dark spheres), illustrating two K-S ORs and one N-W OR after compression along one contraction axis in (a).

compressing along one $\langle 100 \rangle$ direction and expanding along two $\langle 110 \rangle$ directions. Since the contraction axis can be any of three orthogonal axes, there is a threefold degeneracy in this case. This enables the bcc phase to still hold the threefold symmetry in the gradient direction after transformation. However, this simple Bain distortion cannot explain the smearing of the bcc peaks in the gradient direction, and it does not allow any reflections in the vorticity direction (none of the planes in the bcc unit cells can be oriented parallel to the vorticity direction). Wentzcovitch and Krakauer described a modified Bain distortion in terms of the layer shift so that the closest-packed planes remain parallel during the transformation, and K-S and N-W ORs are possible. As illustrated in Fig. 3(b), compressing along one axis results in three orientations of the bcc unit cells (two K-S ORs and one N-W OR). Since there is a threefold degeneracy, a total of nine bcc unit cells (six K-S and three N-W ORs) are produced after transformation. Three orientations in one contraction axis are featured as a group of three spots in the gradient direction [Fig. 1(d)]. In the vorticity direction, only two K-S ORs and one N-W OR give rise to the scattering Fig. 2(d)], and the other six ORs contribute to the layer stacking (the 110, 220, etc. reflections).

The Burgers mechanism is described in Fig. 4. The bcc structure is derived from the hcp structure by slippage of alternating $\{0002\}$ planes along a $\langle 10\bar{1}0 \rangle$ direction, followed by a slight compression along the $\{10\bar{1}0\}$ planes and expansion along the $\{12\bar{1}0\}$ planes. There is also a threefold degeneracy in moving alternating $\{0002\}$ planes, and each movement of the sphere along the $\langle 10\bar{1}0 \rangle$ direction can lead to three ORs

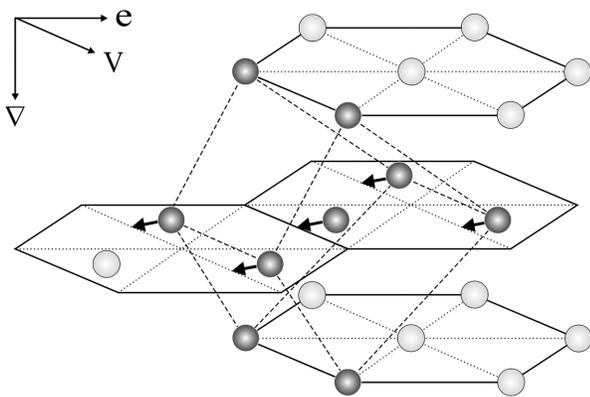


FIG. 4. Mechanism of the hcp-to-bcc transformation (Burgers mechanism). Distorted bcc unit cell is imbedded in the hcp structure. Arrows indicate the movement of spheres.

(i.e., two Burgers and one Pitsche-Schrader OR, which are analogous to the K-S and N-W ORs). As a result, the hcp-to-bcc transformation results in the same nine orientations of the bcc unit cells as does the fcc-to-bcc transformation.

The resemblance of modified Bain distortion and Burgers mechanism is significant and can be summarized as follows: (1) both transformations can be described in terms of slipping of the close-packed layers; (2) there is a threefold degeneracy; and (3) the same nine orientations of the bcc unit cells are produced. The difference is that in the modified Bain distortion, all the close-packed layers slip in the same direction, whereas in the Burgers mechanism, two consecutive layers move in opposite directions.

These mechanisms and the resulting ORs between close-packed and bcc structures are consistent with the analogous martensitic transformations in simple metals. This striking similarity between the block copolymers and the atomic systems illustrates an appealing universality of these transitions among the various systems.

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