Communications to the Editor

Dynamically Sheared Body-Centered-Cubic Ordered Diblock Copolymer Melt

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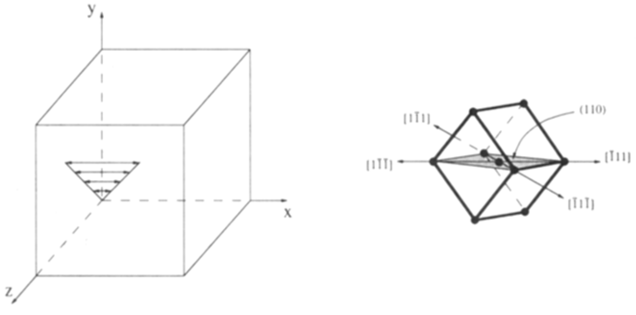
Application of a symmetry breaking field (e.g., electric, hydrodynamic, surface) to an ordered block copolymer can lead to macroscopic microstructure orientation.[1–6] Hydrodynamic fields have proven particularly effective when dealing with lamellar or cylindrical morphologies as first demonstrated by Keller et al.[1] using extensional flows that lead to highly aligned hexagonally packed cylinders in styrene–butadiene–styrene (SBS) triblock copolymer melts. Subsequently, Hadziioannou et al.[2] obtained comparable results with styrene–isoprene diblock and triblock copolymers using a reciprocating shear deformation that also produced a highly oriented lamellar material.[3] More recently, we have applied the dynamic shearing technique to the investigation of model polyolefin diblock copolymer melts near the order–disorder transition (ODT),[7–10] demonstrating that lamellae orientation and T_{ODT} are also dependent on the shear rate.[9,10] In all these cases the driving force for microstructural alignment can be attributed to a tendency to eliminate interfacial material oriented transverse to the flow direction: shear causes cylinders and lamellae to orient with interfacial normal vectors directed perpendicular to the flow direction. We are unaware of any reports that deal with the influence of hydrodynamic fields on the body-centered-cubic (bcc) spherical microstructure in block copolymer melts.

Unlike lamellar and cylindrical domains, individual spherical domains are not affected by a symmetry breaking field. Nevertheless, there are numerous examples when ordered collections of spherical particles respond anisotropically to an applied force. For example, simple atomic crystals yield, under sufficiently large shearing forces, through the movement of dislocations on specific slip systems that vary between different crystal structures.[11] Colloidal crystals, a much softer form of matter, also deform along preferred crystallographic directions, although the yielding mechanism is believed to be more collective than in the case of atomic solids.[12–15] Block copolymers are intermediate in microstructural scale to these two extremes, with interdomain spacings between about 50 and 500 Å (in comparison to roughly 5 Å and 0.1–1.0 μm for atomic and colloidal systems, respectively). This paper reports our initial findings concerning the response of a bcc ordered diblock copolymer melt to a reciprocating shear deformation.

A model poly(ethylenepropylene)–poly(ethylethylene) (PEP–PEE) diblock copolymer containing 83% by volume PEP with $M_N = 1.7 \times 10^5$ and $M_W/M_N \cong 1.05$ was prepared by anionic polymerization of isoprene and butadiene followed by heterogeneous catalytic saturation as described in an earlier publication.[16] In order to obtain neutron scattering contrast deuterium gas was used in the saturation step. We have found that sufficient deuterium exchange occurs during the deuteration of *cis*-1,4-polyisoprene (and very little with 1,2-polybutadiene) that adequate neutron contrast can be achieved in these materials without the use of deuterated monomers. Rheological and small-angle neutron scattering experiments established that the order–disorder transition for this material occurs at $T_{ODT} = 105 \pm 5$ °C. Below this temperature a bcc ordered spherical microstructure exists.[17] A complete description of these results will be presented in a later publication; similar experiments have been reported earlier.[7,8,18]



a.) coordinate system b.) bcc unit cell orientation

Figure 1. (a) Laboratory coordinate system for dynamic shearing and SANS experiments. SANS patterns were obtained from a dynamically sheared specimen by orienting the neutron beam along the *x* (shear direction), *y* (shear gradient direction), and *z* axis. (b) Cell orientations for the twinned bcc crystal structure obtained upon shearing. The (110) slip plane and ⟨$\bar{1}$11⟩ slip directions are coincident with the *x*–*z* plane and *x* direction, respectively.

A sheared specimen was prepared using the dynamic shearing device described in several recent publications.[7–10] The material was heated under vacuum above T_{ODT}, cooled, and squeezed between 5 × 5 cm Teflon-covered brass plates to a thickness 1 mm. Using a 100% strain amplitude and a frequency of $\omega = 0.02$ rad/s, the specimen was subjected to a reciprocating shear deformation for 12 h at 90 °C followed by 1 h at 80 °C and 4 h at 70 °C; the absolute shear rate was $|\dot{\gamma}| = 0.01$ s^{-1}. After this procedure three neutron scattering specimens were prepared at room temperature by cutting the sheared material into 1-mm-thick strips and mounting them between quartz windows so as to provide neutron beam access to the three orthogonal directions indicated in Figure 1a.

Small-angle neutron scattering (SANS) experiments were conducted at room temperature on the NIST/Exxon/University of Minnesota 30-m instrument at the National Institute of Standards and Technology located in Gaithersburg, MD, using $\lambda = 6.0$ Å wavelength neutrons ($\Delta\lambda/\lambda = 0.14$) and pinhole collimation. Scattering patterns were recorded on an area detector and corrected for background scattering. SANS data are reported in arbitrary intensity units.

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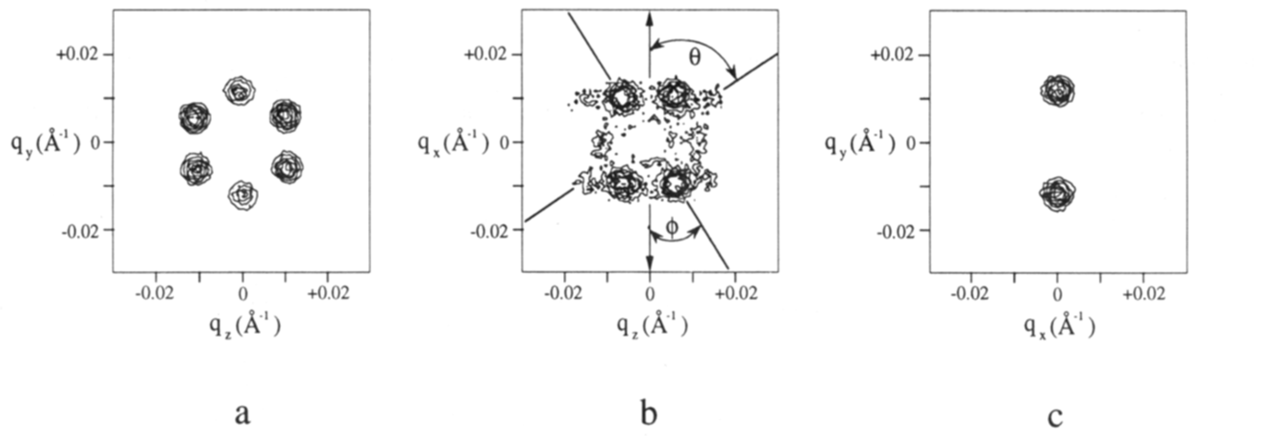

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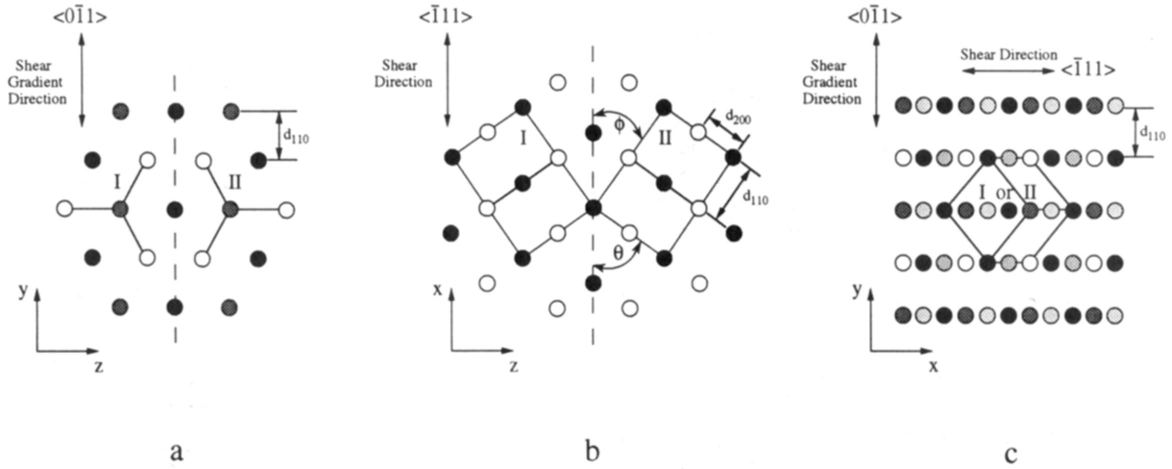
Figure 2. Small-angle neutron scattering patterns obtained from a dynamically sheared PEP–PEE diblock copolymer melt (f_{PEP} = 0.83), with the neutron beam directed along (a) the *x* (shear) direction, (b) the *y* (shear gradient) direction, and (c) the *z* direction (see Figure 1). The main diffraction spots represent instrument resolution limited (110) reflections that result from a twinned bcc crystal structure. Weak (200) reflections are also evident in b.



a b c

Figure 3. Crystallographic projections of the twinned bcc structure depicted in Figure 1, based on the three specimen orientations used in obtaining the SANS experiments shown in Figure 2. Dashed lines represent twinning boundaries. In each projection the differently shaded circles correspond to one stacking sequence of planes of spheres with normals parallel to the beam direction. Degenerate unit cell orientations I and II are indicated by the solid lines. Twinned unit cells are obtained by a 180° rotation around the *x* axis.

Three 2-dimensional SANS patterns, corresponding to the $\mathbf{q}_y$–$\mathbf{q}_z$, $\mathbf{q}_x$–$\mathbf{q}_z$, and $\mathbf{q}_y$–$\mathbf{q}_x$ scattering planes (see Figure 1a), are presented in Figure 2. All three scattering patterns are characterized by instrument resolution limited primary diffraction spots at $|\mathbf{q}| = q^* = 0.012$ Å^{-1}; weak second-order reflections at $2^{1/2}q^*$ are also evident in $\mathbf{q}_x$–$\mathbf{q}_z$. These results can be associated with a perfectly twinned bcc crystal structure, as illustrated in Figure 1b, where the double-ended arrows correspond to the two equivalent reciprocating shearing directions, $[\bar{1}11] \leftrightarrow [1\bar{1}\bar{1}]$ and $[\bar{1}1\bar{1}] \leftrightarrow [1\bar{1}1]$, that lie in a (110) plane. (We attribute the lack of higher order reflections to the close proximity to T_{ODT} and broad mosaicity. As demonstrated with the lamellar microstructure in a previous publication,[6] the composition profile becomes nearly sinusoidal as $T \rightarrow T_{\mathrm{ODT}}$ with a concomitant loss of higher order reflections.)

In order to firmly establish the relationship between this twinned structure and the observed scattering patterns, we have provided crystallographic projections in Figure 3 for the two unit cell orientations indicated in Figure 1b. The *x* (i.e., shear) direction corresponds to the family of $\langle\bar{1}11\rangle$ directions, each producing an equivalent hexagonal pattern of (110) reflections as found in the $\mathbf{q}_y$–$\mathbf{q}_z$ scattering plane. With the neutron beam incident along the *z* axis, the $\langle 11\bar{2}\rangle$ family of directions is accessed. These generate equivalent pairs of (110) reflections that are seen in $\mathbf{q}_y$–$\mathbf{q}_x$. The *y* (i.e., shear gradient) direction, which is coincident with the $\langle 110\rangle$ directions, provides the crucial evidence for a twinned bcc structure. Each of the two unit cell orientations produces a pair of (110) reflections forming an angle of $\phi = 35.3°$ with the shear axis (i.e., a $\langle\bar{1}11\rangle$ direction). In a single crystal only two reflections would be observed. Because the two unit cell orientations are degenerate with respect to the shear deformation, equal populations of both are produced, leading to the four (110) reflections observed in the $\mathbf{q}_x$–$\mathbf{q}_z$ scattering plane. Weak (200) reflections, located at $2^{1/2}q^*$ and at an angle of $\theta = 54.7°$ with respect to the shear direction, are also evident in the $\mathbf{q}_x$–$\mathbf{q}_z$ scattering plane. This compliment of scattering patterns cannot be obtained from face-centered-cubic (fcc), simple cubic, or hexagonal close-packed (hcp) crystal structures. (The primary cubic structure is excluded since the powder pattern from a polycrystalline specimen does not exhibit (*h*00) reflections.)

These results bear a striking resemblance to those obtained by Ackerson and Clark[15] for a sheared colloidal suspension and appear to be related to plastic deformation in bcc atomic crystals.[11] Yielding and plastic deformation in metals is well-known to occur through the movement of dislocations along certain slip systems, $\{hkl\}\langle hkl\rangle$ where $\{hkl\}$ and $\langle hkl\rangle$ are families of planes and directions, respectively. For bcc metals such as sodium, chromium, and iron, the principal slip system is $\{110\}\langle\bar{1}11\rangle$; i.e., slip occurs most readily by moving dislocations in a $\langle\bar{1}11\rangle$

direction on a $\{110\}$ slip plane. This is precisely the deformation orientation we find for the bcc block copolymer melt.

During plastic deformation, polycrystalline metals develop texture through a combination of elongation and rotation of grains. The presence of surrounding grains greatly influences the way in which a particular grain deforms. For this reason, the deformation mechanism of a polycrystalline metal is more complex than that of a single-crystal deforming under the same load. It is not clear whether the same is true for the bcc block copolymer melt. This material is not a stiff solid, but rather a viscoelastic one. As a result, bcc block copolymer melt grain boundaries may not be as robust as those found in metals due to the added possibility of viscous flow in the former. As a result, the role grain boundaries play in the orientation of bcc block copolymer melts may be of much less importance than that observed in metals. This issue will be addressed more thoroughly in the future with the aid of electron microscopy.

Another system in which grain boundaries probably play a limited role is colloidal crystals. They can also be brought into a state of long-range order through the application of a shearing deformation. Under certain conditions the same twinned bcc structure that we observe has been reported.[15] However, the response of such soft materials to shear deformation appears to depend on shear rate,[13] particle volume fraction,[14,15] the nature of the interparticle interactions, and proximity to the disordering temperature.[12] Evidence of such variability in block copolymers can be found in a recent report by Mortensen et al.[19] They showed that application of a steady Couette flow produced a bcc single crystal in an aqueous solution of PEO–PPO–PEO triblock copolymer near T_{ODT} (this system orders with increasing temperature). However, the shear direction is reported to be coincident with a $\langle 11\bar{2} \rangle$ direction, and the $\langle 111 \rangle$ direction parallel to the shear gradient. This orientation is rotated relative to the one reported here. We have discovered a dramatic sensitivity to shear rate (and temperature) in the orientation of bcc polyolefin diblock copolymers, and these findings will be described in a subsequent report. Here we note that the present results were obtained in the high shear rate limit, $\dot{\gamma} \rightarrow \tau^{-1}$ where τ is the conventional terminal (i.e., reptation) time.

In summary, we have shown that bcc diblock copolymer melts can be induced to form twinned crystals with long-range order through the application of a reciprocating shear deformation. This result closely resembles those found with certain sheared colloidal suspensions,[15] suggesting that ordered block copolymer melts containing spherical microstructures may represent ideal substrates for the investigation of the deformation behavior of soft "flowing" crystals. These materials offer certain advantages including a controllable order–disorder transition temperature (through the variation of molecular weight), tractable rheological properties, and a relatively high degree of cohesiveness; i.e., sheared samples can be removed from the shear device and sectioned without destroying the long-range order. In future publications we will explore the roles of shear rate and temperature on the ordering behavior of this class of soft material.

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