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Single-Grain Lamellar Microdomain from a Diblock Copolymer

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In metals and semiconductors, the growth of single grain materials has spawned new applications for these ordered materials. This suggests that a method for forming a single grain block copolymer nanostructure will lead to not only new insights into the physics of these ordered materials but also new uses. An understanding of the methods of manipulating the orientation of block copolymer nanostructures in bulk sample is important as a means of both producing oriented materials of practical use and understanding the ordering process of these materials. In typical low molecular weight diblock copolymers grain sizes are often less than a few micrometers.[1,2] Growing single grain lamellar materials from block copolymers is not only an interesting challenge but also important for taking full advantage of these polymers, e.g., as optical materials.[3]

Shear is an established method of controlling orientation, as is the use of flow.[4,5] There have been some reports concerning the use of shear to form single grain materials of diblock copolymers.[6,7] We also recently found that the lamellar normals are aligned parallel to an applied temperature gradient (∇T) axis during the ordering process.[8] Furthermore, reports of the use of surfaces[9−11] and an electric field[12] to orient block copolymers have appeared. In this communication, we report the parameters necessary for the formation of a single, macroscopic, lamellar grain: molecular weight and composition of the block copolymer, magnitude of the ∇T, and speed of the moving ∇T.

We prepared a polystyrene-*block*-polyisoprene diblock copolymer with a polystyrene (PS) block number-average molecular weight M_n of 1.12×10^4, a polyisoprene (PI) block M_n of 1.46×10^4, and a polydispersity index M_w/M_n of less than 1.05 (by GPC) by living anionic polymerization with *sec*-butyllithium as an initiator and cyclohexane as a solvent. By small-angle X-ray scattering (SAXS) and TEM, this block copolymer was found to have a lamellar structure, which is consistent with the volume fraction polystyrene, f_{PS}, of 0.40.[13] Note that these parameters, in particular the molecular weight of the PS block, differ from that of the polymer described in our recent Communication on ∇T effects.[8]

SAXS was measured using a two-dimensional (2-D) imaging plate (IP) detector and a MAC Science X-ray generator with point focus optics[14] and a SAXS beam diameter at the sample surface of about 0.5 mm. The background intensity was not subtracted from the data shown here.

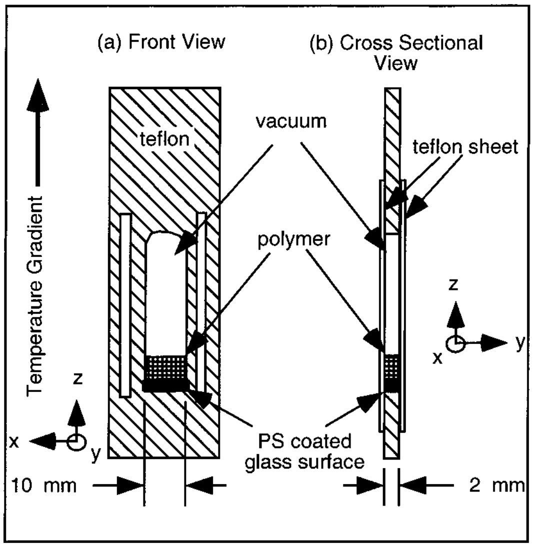

Figure 1. Schematic of the cell used to hold the polymer sample. The surfaces on either side are covered with thin sheets of Teflon. Key: (a) front view and (b) cross-sectional view of the temperature cell at the center.

Samples were prepared in a “zone heating device,” described in a recent communication,[8] described in detail in a recent patent application,[15] and will be discussed in detail elsewhere.[16] This arrangement produces a sharp, moving ∇T along the *z* axis. In this work, the ∇T was set to be about 70 °C/mm.

The diblock copolymer was mixed with a small amount of antioxidant (BHT) and cast from a 5% solution of polymer in toluene. Then, it was placed inside a 2 mm thick and 10 mm wide Teflon sample cell with a glass surface on one end (see Figure 1) and thin Teflon sheets on either side. Note that here the glass surface is aligned perpendicular to the temperature gradient (so that the ∇T and surface effects combine, unlike our previous work on ∇T effects[8]). The temperature gradient was slowly moved along the *z*-axis at 25 nm/s (2.16 mm/day), while the entire arrangement was kept under vacuum to prevent sample degradation, This is considerably slower than the speed reported in our recent communication on ∇T effects.[8] Before measurement by X-ray scattering, the polymer was vitrified in liquid nitrogen and the glass surface was carefully removed.

The PS coated glass block depicted in Figure 1 was prepared according to the procedure described by Philipse and Vrij.[17] Quartz glass blocks were first reacted with 3-methacryloxypropyltrimethoxysilane (TPM), a silane coupling agent in a mixture of ammonia/water (25% ammonia) and ethanol, rinsed with ethanol, and then dried. The treated glass blocks were then placed in a styrene/toluene solution, and the styrene was polymerized with AIBN as an initiator. During polymerization, some of the growing polymer chains reacted with the C−C double bond in the TPM layer attached to the silica surface. Therefore, a PS layer was formed on the glass surface. Note that we used bare quartz blocks (not coated with PS) in our previous work.[8]

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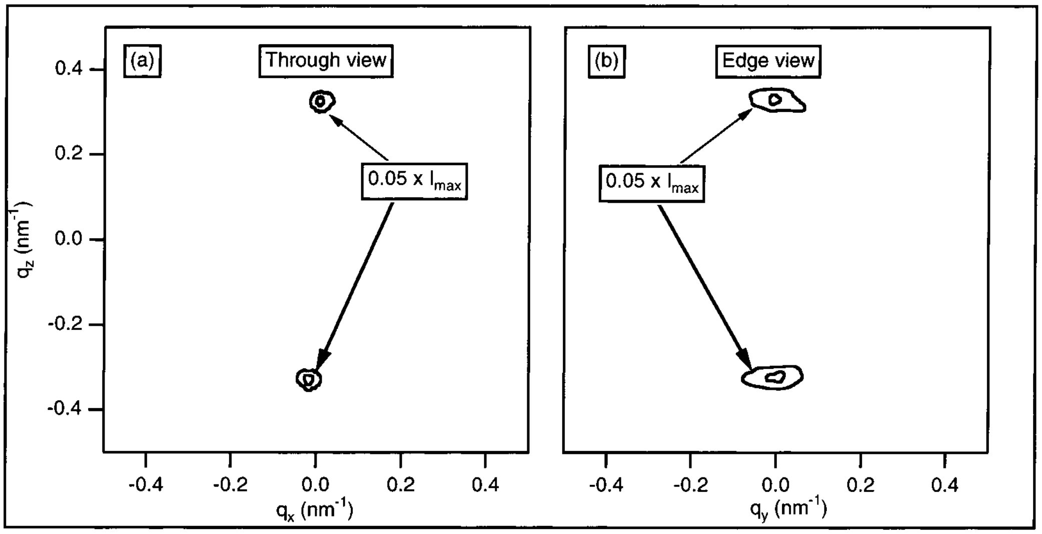

Figure 2. Two-dimensional (2-D) X-ray scattering pattern of the first-order scattering peak from single grain lamella taken with the incident beam (a) along the *y* axis and (b) along the *x* axis. Contour lines are drawn at 0.5 and 0.05 times the maximum scattered intensity for each 2-D scattering pattern. The contour lines reflecting 0.05 times the maximum scattered intensity are indicated on the figures.

Transmission electron microscopy (TEM) was performed with a JEOL JEM 2000 FXZ electron microscope at 200 kV. Ultrathin sections were cut with a Reichert-Nissei FCS cryo-ultramicrotome at −90 °C, below the glass transition temperature of PI ($T_g = -68$ °C), and exposed to OsO_4 vapor to selectively stain the PI block of the block copolymer.

Figure 2a shows the two-dimensional (2-D) SAXS pattern from the single grain material with the incident X-ray beam parallel to the *y*-axis. Contours are drawn at 0.5 and 0.05 times the peak scattered intensity, I_{max}, for each pattern. In this case, the beam center is about 0.5 mm away from the glass surface along the *z* direction and in the middle of the sample along the *x* direction. The scattering peaks are sharp and pointlike, with nearly the same shape and width as the incident beam. This is in contrast to typical scattering from multigrain block copolymers where the 2-D SAXS pattern from the first-order peak is a ring or an arc (in the case of an oriented sample). Therefore, there seems to be no scattering from grains with different orientations. The scattering corresponds to the ideal scattering from a single lamellar grain with very small lattice distortions and with its lamellar normal perpendicular to the glass surface and parallel to the applied ∇T axis. By measurement of the scattering at various distances from the glass surface, we observe that this single grain persists over a distance of at least 1.0 mm away from the glass surface (*z*-axis direction), 6 mm along the glass surface (*x*-axis direction), and nearly 2 mm thick (*y*-axis direction).[16]

To confirm the orientation of the lamella and ensure that there is no scattering from other grains with their lamellar normals parallel to the *y* axis (therefore not observed in Figure 2a), we rotated the sample 90° about the *z* axis so that the X-ray beam was parallel to the *x* axis. The 2-D SAXS scattering pattern after this rotation is shown in Figure 2b. We define this orientation as the edge view. In this scattering pattern, there is no scattering in the direction of q_y, which confirms that this sample is made of a single grain of lamella with the lamella normals parallel to the *z* axis and the ∇T axis and perpendicular to the glass surface.[18,19] Note that this orientation gives the lamellae edges oriented perpendicular to the film surface.

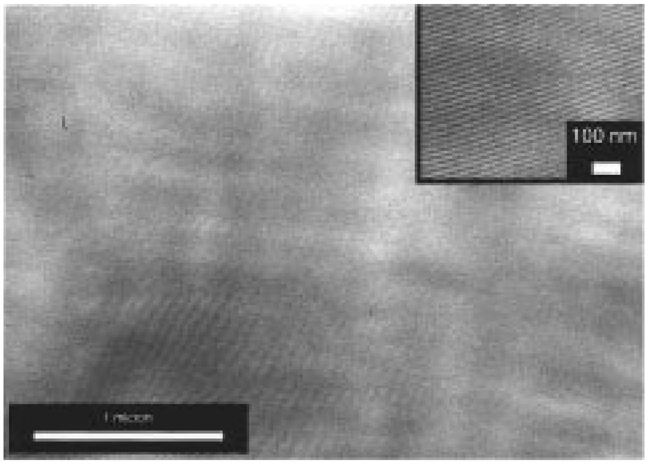

Figure 3. Representative TEM image of a single lamellar grain prepared by the zone heating process.

We also examined the sample by transmission electron microscopy to obtain a real space image of the grain structure. A typical micrograph is shown in Figure 3. Over large distances, much larger than the picture shown here, uniform lamellar sheets are observed. In this case, we do not observe grain boundaries, indicating that the scattering patterns observed correspond to a single grain rather than many smaller grains with similar orientations. Therefore, microscopy confirms the interpretation of the SAXS data; this sample is a large, single grain with lamellar microdomain structure with very small lattice distortions. While it may appear that the orientation distribution as observed by TEM is broader than that observed by SAXS, we believe this is an artifact of the microtoming process since the SAXS measurement "sees" orientation over a much larger volume of sample than a TEM measurement.

The polystyrene-coated glass surface provides a location for surface-induced ordering into the lamellar grain with the lamellar normals parallel to the *z* axis as the polymer is brought close to but slightly above the bulk ODT temperature as shown in earlier reports.[9−11]

Recent measurements revealed that the polystyrene coating is not essential for creating single grain materials.[16] Due to the slow speed of the moving ∇T and the large magnitude of ∇T, grain growth starting from the surface and along the z direction is favored over nucleation of new grains in the bulk during the transition from disorder to order.[20] That is, the block copolymer orders by adding new lamella to the already formed lamellae. In this way, a single large grain is able to grow. The conditions described here are important to the formation of a single lamellar grain.[16] For example using the conditions described in our previous Communication (a rate of 400 nm/sec, a different M_n and f_{PS}, and a ∇T of 30 °C/mm) leads to grain sizes of about 0.5 mm or less along the z axis. We have recently shown that a ∇T also acts to orient block copolymers during the ordering process with their lamella normals parallel to the z axis (the ∇T axis).[8] Therefore, we believe the single grain structure is a result of the *cooperative* effects of temperature-gradient-induced orientation and the surface-induced ordering in the diblock copolymer.[22] The ability to make nearly perfectly oriented block copolymers allows one to make “super-tailor-made” materials and extend their anisotropy from mesoscopic to macroscopic length scales.

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(18) The observed peaks in the edge view are somewhat broader than the through view due to the effect of the walls perpendicular to the x axis. The X-ray beam passed through one of these walls during measurement.

(19) We used the azimuthal angle dependence of the first-order scattering peak and the assumption of uniaxial orientation to estimate the second-order orientation factor, f (defined by the relation $f = (3/2)(\langle \cos^2\beta \rangle - 1)$ where β is the angle formed between the lamellar normal and the z axis and $\langle\ \rangle$ denotes the average over all lamellar stacks). f was evaluated to be 0.93 for this sample. These results will be discussed in detail in ref 16.

(20) The ordered PS lamellae developed for this block copolymer is expected to have T_g of ca. 60 °C, though it generally depends on the ordering condition.[21] The ordering under the slow moving ∇T effect for this specimen having an ODT temperature of 172 °C is expected to occur at temperatures much higher than T_g, so that vitrification may not significantly affect formation of the single lamellar grain.

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(22) Under the ordering condition employed in this work, both the surface boundary effect and the ∇T effect orient the lamellae in the same way, so that it is difficult for us to separate the two contributions. The separation was discussed in our previous work[11] where the surface boundary effect and the ∇T effect were deliberately misaligned. We found that far from the surface the ∇T effect outweighs the surface boundary effect under the conditions employed in that work. There is a fast growth direction of lamella in the nucleation and growth process in the bulk as elucidated in previous work.[21,23–25] The growth is faster along the lamellar normal than along the interface. The ordering process under applied fields is generally different from that under no applied fileds, elucidation of which deserves future work.

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