Communications to the Editor

The Effect of Temperature Gradient on the Microdomain Orientation of Diblock Copolymers Undergoing an Order−Disorder Transition

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Introduction. The self-assembly of block copolymers below the order−disorder transition (ODT) temperature results in interesting nanostructures. An understanding of the methods of manipulating the orientation of the nanostructures in bulk sample is important both as a means of producing oriented materials of practical use and understanding the ordering process of these materials. Shear is an established method of controlling orientation, as is the use of flow.[1,2] Recently, there have been many reports concerning the effects of shear on the orientation of diblock copolymers forming lamellar morphology.[3−19] In addition, electric fields[20] and surfaces[21−23] have been shown to cause alignment of block copolymer nanoscale patterns. However there are few (if any) experimental reports of using temperature gradient to align diblock copolymers. There are a few recent theoretical efforts concerning the effect of a temperature gradient, in the form of a propogating front, during the ordering process. A recent effort along these lines is Zhang et al.'s use of simulations to examine the effect of a shifting quench boundary on the orientation of lamella.[24] Previously, front propagation in a diblock copolymer system has been investigated numerically by Liu and Goldenfield.[25] Dynamics of front propagation were studied by Paquette.[26] Finally, Chen et al.[27] discussed front propagation rate selection. Since the effects of flow fields, surfaces, and electric fields have been shown to be important in aligning diblock copolymer, one naturally asks if the use of a temperature gradient is also important in orienting a diblock copolymer sample.

In this communication, we report on the use of an applied temperature gradient to orient the lamellar structure formed by a diblock copolymer. To show the effect of temperature gradient (∇T effect), we need to clearly identify the effect of the sample surfaces on the lamellar orientation. This was achieved by placing a glass surface at an approximately 45° angle with respect to the temperature gradient. In this way, the surface effect will be dramatically tilted compared to the ∇T effect, and each can be clearly identified and separated. For example if the lamellar normal is aligned parallel to the normal of the glass surface, the surface effect dominates, and if the lamellar normal is aligned parallel to the temperature gradient axis, then the ∇T effect dominates. We found that the surface effect is dominant close to the surface and weakens further away from the sample surface. Far from the sample surface, the ∇T effect is dominant.

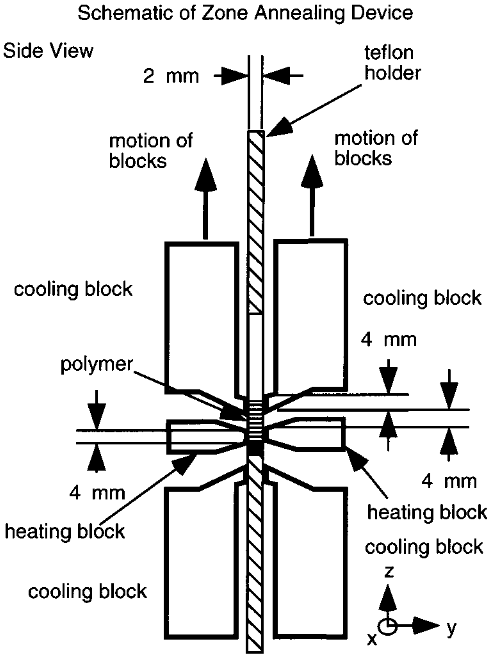

Figure 1. Schematic of zone heating device used for applying temperature gradient. The axes are designated as follows: Oz is parallel to the temperature gradient ∇T, Oy is parallel to the film normal, and Ox is parallel to the film surface and perpendicular to ∇T.

Experimental Methods. In this study, we used a polystyrene-*block*-polyisoprene diblock copolymer with a polystyrene (PS) block number average molecular weight M_n of 1.2×10^4 and a polyisoprene (PI) block M_n of 1.2×10^4. The polydispersity index M_w/M_n is less than 1.05 in both cases (by GPC). The block copolymer was prepared by living anionic polymerization with *sec*-butyllithium as an initiator and cyclohexane as a solvent. By X-ray scattering and TEM, this block copolymer has a lamellar structure, which is consistent with the nearly 50 wt/50 wt composition of the diblock copolymer.[28]

SAXS was measured using a two-dimensional imaging plate (IP) detector and a MAC science X-ray generator with point focus optics.[29] The data shown here, in contrast to usual practice, does not have the background intensity subtracted.

Samples were prepared in a "zone heating device." This device consists of a pair of central heating blocks,

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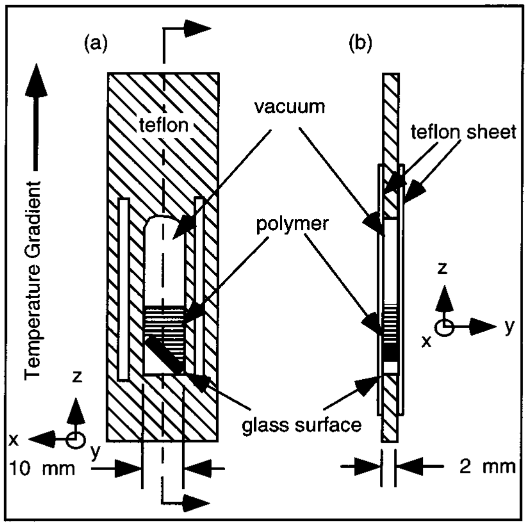

Figure 2. Schematic of cell used to hold polymer sample. The surfaces on either side are exposed to thin sheets of Teflon. Key: (a) front view of the temperature cell and (b) cross-sectional view of the temperature cell at the center.

surrounded by two pairs of cooling blocks. The centers of each pair of heating blocks and cooling blocks are aligned to form a sandwich, with the polymer film sample in the center (Figure 1). The heating blocks were set at 210 °C, above the order−disorder transition (ODT) temperature of the diblock copolymer, and the cooling blocks to 5 °C, well below the ODT temperature of the diblock copolymer (see Figure 1). This arrangement produces a sharp temperature gradient along the *z*-axis, on the order of about 30 °C/mm. The device is described in a recent patent application[30] and will be discussed in detail elsewhere.[31]

The diblock copolymer was mixed with a small amount of antioxidant (BHT) and cast from a 5% solution of polymer in toluene and then placed inside a Teflon sample cell of 2 mm thickness and 10 mm width with a glass surface on one end (see Figure 2). Thin Teflon sheets were placed on either side of the sample cell. The heating blocks were moved along the *z*-axis at 400 nm/s, while the entire arrangement was kept under vacuum to prevent sample degradation. Before SAXS measurement, the polymer was frozen in liquid nitrogen and the glass surface was carefully removed.

Results and Discussion. In preliminary experiments, we measured the lamellar orientation in a diblock copolymer film about 1 mm away from the glass surface with its normal along the *z*-axis; i.e., the glass surface has an orientation different from that shown in Figure 2, and found that over a wide range of crosshead speeds, the sample has preferred orientation with the lamellar normals perpendicular to the glass surface and parallel to the ∇T axis, suggesting a ∇T effect. However, the glass surface is also expected to induce alignment of the lamella with their lamella normals perpendicular to the glass, in the same direction as the ∇T axis. Therefore, we could not completely rule out the effect of the glass surface on the observed lamellar orientation.

To check this question, we prepared a sample in which the glass was tilted at approximately a 45° angle with respect to the temperature gradient axis (*z*-axis), as drawn in Figure 2. We then subjected the sample to the moving temperature gradient along the *z*-axis described above. Figure 3 shows a series of 2-D scattering patterns taken as the X-ray beam, irradiated along the *y*-axis, is moved away from the glass surface along the *z*-axis. The glass surface leads to the tilted orientation of the patterns seen in parts a and b of Figure 3. In this case, the X-ray scattering measurements showed that, close to the glass surface, the effect of the glass surface prevailed, as seen by the pair of strong scattering peaks at an angle of about 45° with respect to the *z*-axis. In fact, in Figure 3a, the X-ray beam partially missed the polymer. For beam positions further away from the glass surface, parts b and c of Figure 3, we observe that the peak position of the SAXS pattern rotates around the *y*-axis (film normal) to become aligned nearly parallel to the temperature gradient axis, i.e., nearly parallel to vertical in this figure (i.e., the *z*-axis).[31,32]

We rotated the sample 90° around the *z*-axis in order to examine the scattering in the "edge view" with the incident beam along the *x*-axis. One of these results is shown in Figure 3d, which corresponds to the same point in the sample as Figure 3c, except for the change in orientation of the sample with respect to the X-ray beam. Once again we observe lamellae with their normals nearly parallel to the *z*-axis (i.e., the ∇T axis).

Here, we should point out that the case of cooling a block copolymer from a temperature above the ODT to a temperature below the ODT without a temperature gradient is well-known. The geometry of the film described here is similar to that used in our X-ray studies of block copolymers. Our group, as well as others, has found that an ordered lamellar block co-

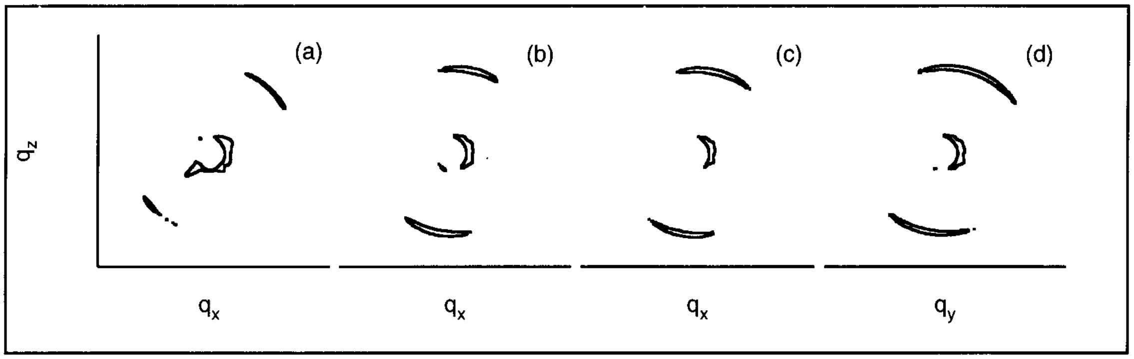

Figure 3. Two-dimensional (2-D) X-ray scattering pattern taken with the incident beam along the *y*-axis for case where the glass surface is at a 45° angle with respect to the temperature gradient axis as shown in Figure 2. The contour level in each plot is set to $0.75I_m$ where I_m is the maximum intensity of the first order scattering peak. Key: (a) The beam center is approximately at the glass surface. (b) The beam center is 1 mm from the glass surface along the *z*-axis. (c) The beam center is 2 mm from the glass surface along the *z*-axis and (d) is the same point as (c), but with the sample rotated 90° around the *z*-axis; i.e., the 2-D pattern was taken with the incident beam along the *x*-axis.

polymer prepared without a temperature gradient consists of space-filling polygrains with their lamellar normals randomly oriented and hence giving rise to SAXS patterns which are circularly symmetric with respect to the incident X-ray beam. Such behavior is observed for the particular block copolymer observed here as well. Therefore, the effects observed here can only be due to the applied temperature gradient.

These results show the ∇T effect on the orientation of a diblock copolymer. Furthermore, they separate the ∇T effect from the effect of the glass surface. Thus, we clearly show that temperature gradients during the ordering process play an important role in aligning diblock copolymer samples with the lamellar normals preferentially oriented along the z-axis and the lamellar edges standing normal to the sample surface, i.e., the Oxz plane.

The use of a temperature gradient as another technique for orienting diblock copolymers adds to our ability to make "tailor-made" materials and extend their anisotropy from microscopic to macroscopic levels.

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(32) With the ∇T effect alone, we expect the SAXS intensity maximum would be oriented parallel to q_z. A slight clockwise rotation in the pattern with respect to the z-axis in Figure 3c is probably due to flow effects during sample cooling.

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