Sequential, Orthogonal Fields: A Path to Long-Range, 3-D Order in Block Copolymer Thin Films

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Received May 15, 2003; Revised Manuscript Received June 25, 2003

ABSTRACT: The use of two orthogonal, external fields is shown to control the orientation of lamellar microdomains in three dimensions in diblock copolymer thin films. An elongational flow field was applied to obtain an in-plane orientation of the microdomains of the copolymer melt, and an electric field, applied normal to the surface, was then used to further align the microdomains. Thin films of symmetric diblock copolymers of poly(styrene-*b*-methyl methacrylate) with long-range order and orientation of the lamellar microdomains were obtained as evidenced by small-angle X-ray scattering and transmission electron microscopy.

Introduction

The long-range orientation and ordering of microdomains in thin films of diblock copolymers are requisite for applications that require spatial definition of structures in three dimensions. Thin films of block copolymers with microdomains oriented normal to the surface are finding increasing uses as templates and scaffolds for functional nanoscopic materials.[1] Many methods have been developed, such as shear and elongational flow fields, electric fields, surface fields, and solvent flow, to achieve the desired microdomain orientation.[2−9] Shear and elongational flow fields that result in nearly single-crystal-like textures of the microdomains, as for example produced in roll-casting processes, have proven successful in achieving long-range ordering in bulk samples.[10,11] Copolymer films with lamellar and cylindrical microdomains, prepared by these methods, typically contain microdomains parallel to the shear or elongation direction, i.e., parallel to the surface of the sample. Many emerging applications for thin films of diblock copolymer require an orientation of the microdomains normal to the surface that cannot be achieved by the methods developed for bulk samples. In thin films, electric fields have been effectively used to achieve an orientation of the microdomains normal to the surface.[12,13] However, such fields are unidirectional, causing a high degree of orientation along the field line direction but lacking any preferred orientation in the plane normal to this direction. Consequently, a second field is required orthogonal to this field to achieve a morphology where the microdomain orientation can be controlled in three dimensions.

Winey et al. investigated the influence of the thermal history on the microdomain orientation in a lamellar diblock copolymer after shearing and showed that large grains grew from nuclei formed during the shearing process.[14] This observation points toward a route to achieve three-dimensional ordering in diblock copolymer thin films. Using a shear field to generate oriented nuclei, a second field applied normal to the shearing direction can be used to further orient the growing microphase-separated morphology and, thereby, produce a near single-crystal texture.

Here, a simple process is shown that combines an elongational flow field with an applied electric field where the three-dimensional control over the orientation of lamellar microdomains in thin films of poly(styrene-*b*-methyl methacrylate) diblock copolymers is achieved. Roll-pressing was done below the order−disorder transition (ODT) but above the glass transition temperatures of both blocks where oriented nuclei of the microdomains form. Subsequent annealing under an electric field applied normal to the film surface produced a lamellar microdomain morphology with a high degree of long-range order and orientation as evidenced by small-angle X-ray scattering and transmission electron microscopy.

Experimental Section

Symmetric polystyrene-*block*-poly(methyl methacrylate) diblock copolymers, PS-*b*-PMMA, were prepared by standard anionic polymerization methods, with M_n = 45 600 and a polydispersity M_w/M_n = 1.08. The equilibrium period of the lamellar microdomain morphology in the bulk is 18.7 nm, corresponding to the scattering vector q^* = 0.336 nm^{-1}, determined by small-angle X-ray scattering. Here $q = 4\pi/\lambda \sin\theta$, where λ is the wavelength of the X-rays and 2θ is the scattering angle. Copolymer films were prepared by roll-pressing, which is schematized in Figure 1a. A powder of the copolymer was sandwiched between two Kapton sheets and heated at 130 °C for 5 min before rolling. The rollers were heated at 170 °C and rotated at 5 mm s^{-1}. Clear, uniform films of the copolymers, ∼ 300 μm thick, were obtained after 4−6 passes through the rollers. Two or three additional rolling passes were done to reduce the film thickness to ∼30 μm. The length of the film increased approximately 8 times in the rolling direction while the width increased only slightly (typically less than a factor of 2). The final shape of the film is shown schematically in Figure 1b. The flow patterns in the film vary across the width of the film during rolling. Near the center of the film (position 1), the orientation is uniaxial, whereas near the edge of the film (positions 2 and 3), it is biaxial. Other, more complex orientations occur elsewhere across the film. The experiments shown here were performed using samples taken from the center of the film.

After roll-pressing, the film was placed between two aluminized Kapton electrodes (each 25.4 μm thick) and annealed at 170 °C for 14 h under an applied electric field of ∼20 V μm^{-1}. Small-angle X-ray scattering (SAXS) was performed with nickel-filtered copper Kα radiation from a Rigaku rotating anode, operated at 8 kW. A gas-filled area detector (Siemens Hi-Star) was used. Scattering patterns were obtained with the

10.1021/ma0346409 CCC: $25.00
Published on Web 08/29/2003

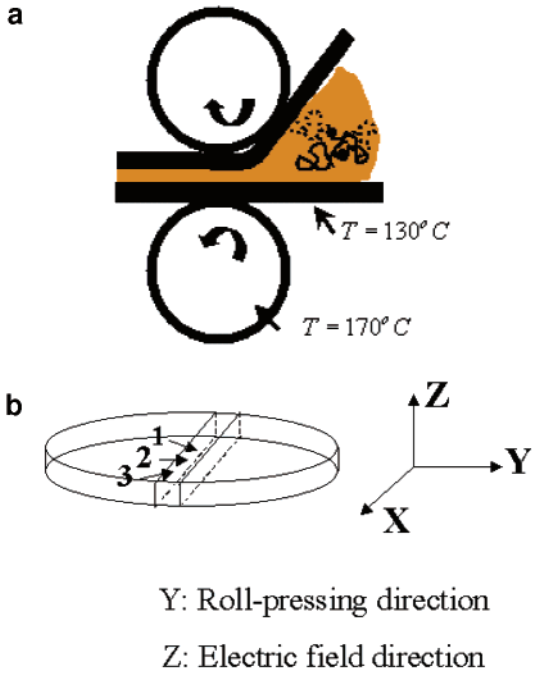

Figure 1. (a) Schematic drawing of the roll-pressing and (b) the typical shape of copolymer thin films after roll-pressing.

beam incident normal to the sample surface with a counting time of 30 min. For transmission electron microscopy, a thin layer of carbon (10−20 nm) was evaporated onto the surface to prevent the epoxy from diffusing into the copolymer films. The film was then embedded in epoxy and cured at 60 °C for 12 h. The samples were microtomed with a diamond knife at room temperature and retrieved with a copper grid from the water surface. The thin sections were exposed to ruthenium tetraoxide for 35 min to enhance the contrast. The images were taken with a JEOL 100CX TEM at an acceleration voltage of 100 kV.

Results and Discussion

Figure 2a shows the transmission SAXS pattern from the center of the sample after roll-pressing. A diffuse reflection is observed with peak position at $q^* = 0.342$ nm^{-1} and half-peak width of 0.102 nm^{-1}. The breadth of the reflection indicates that microphase separation is not complete during the roll-pressing, and a nonequilibrium morphology is frozen-in when the film is quenched to room temperature upon exiting the rollers. Transmission electron microscopy (TEM) showed an ill-defined, microphase-separated morphology (not shown here). The intensity of the SAXS along the ring of scatterings, i.e., the azimuthal angular dependence of the scattering, showed weak broad equatorial peaks, indicating that the oriented nuclei have formed during the roll-pressing.

Figure 3 shows the SAXS pattern of the roll-pressed, thin film after annealing at 170 °C under an applied electric field (∼20 V/μm). Two sharp equatorial reflections, with peak position at $q^* = 0.336$ nm^{-1} and half-peak width of 0.052 nm^{-1}, are seen, indicating a high degree of orientation of the lamellae normal to the surface and along the direction of flow. This is in contrast to thin films annealed only with an applied electric field; i.e., without a roll-pressing, elongational flow field, an isotropic ring of scattering is seen due to the random orientation of grains of the lamellae oriented normal to the surface.

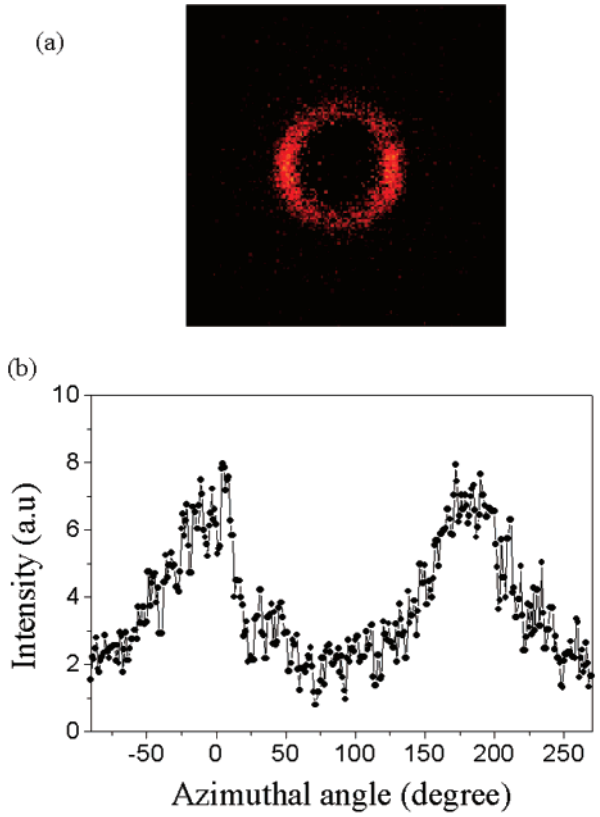

Figure 2. (a) SAXS pattern of a copolymer thin film after roll-pressing. (b) Integrated peak intensity as a function of azimuthal angle Ω.

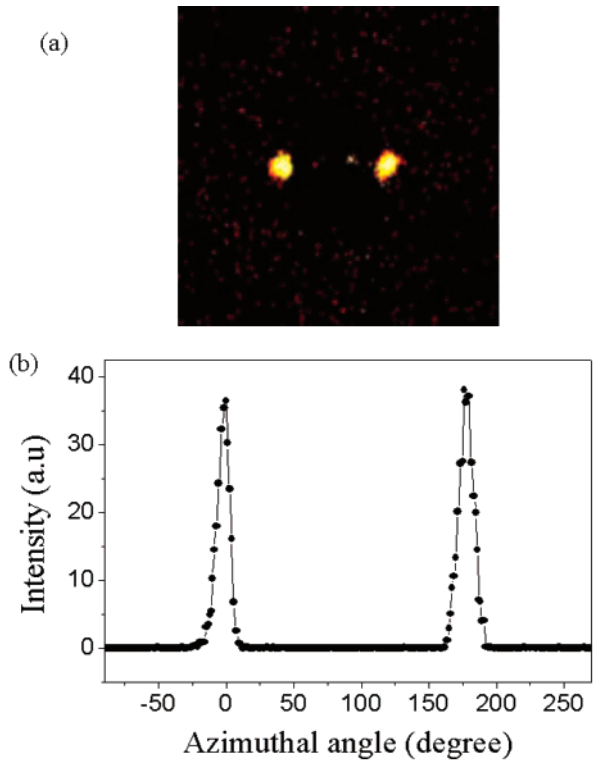

Figure 3. (a) SAXS pattern of copolymer thin films after roll-pressing and applying a subsequent electric field normal to the film surface. (b) Integrated peak intensity as a function of azimuthal angle Ω.

To quantify the degree of the alignment, the order parameter or orientation function, f, was calculated, where

$$f = \frac{3\langle \cos^2 \Omega \rangle - 1}{2}$$

and

$$\langle \cos^2 \Omega \rangle = \frac{\int_0^{\pi} d\Omega \, (I_q(\Omega) \cos^2 \Omega \sin \Omega)}{\int_0^{\pi} d\Omega \, (I_q(\Omega) \sin \Omega)}$$

where Ω is the azimuthal angle defined from the orientation direction ($\Omega = 0$) and $I_q(\Omega)$ is the intensity at a given Ω integrated over its full width in q. f has limits of $-1/2$ and 1, corresponding to orientation of lamellae normal to and parallel to the flow direction and 0 corresponds to a random orientation. From the data in Figure 3b, $f = 0.9$; i.e., the lamellae are almost fully oriented in the flow direction. Thus, three-dimensional control over the microdomain orientation was achieved with the lamellar planes oriented parallel to the flow direction and normal to the surface.

SAXS data show that a global orientation of microdomains in the diblock copolymer thin film has been achieved. On a more local level, TEM was used as a probe. Figure 4 shows the cross-sectional TEM images of the copolymer film viewed into the flow direction, i.e., the *XZ* plane in Figure 1b. Figure 4a is a typical TEM image at both surfaces of the thin film where a mixed orientation can be seen. At both surfaces, the lamellae orient parallel to the surface of the electrodes. This arises from a preferential wetting of PMMA on the electrodes as discussed previously.[15] In the center of the film, the lamellae are oriented perpendicular to the substrate (parallel to the electric field direction). The four-spot Fourier transform (FFT) pattern of this micrograph, resulting from the mixture orientation, is shown in the inset. Figure 4b shows a typical TEM cross-sectional image for rest of the film along the *Z* direction. Over very large areas, the orientation and order are defect-free. Only one grain was found within the field of view. This result is quite remarkable in comparison to previous results using only an electric field where many grains are found.[16] The Fourier transform (FFT) of this micrograph is shown in the inset. Two sharp spots are observed in the pattern, showing the presence of only one large grain of lamellae, with a uniform separation distance between the lamellae, oriented normal to the surface and in the flow direction. The uniformity of the spacing in the micrograph also reflects the perfection in orientation, since different orientations of the lamellae would result in different widths of the lamellae in the TEM image. To characterize the extent of the ordering, TEM images were taken every ~3 μm along the *X* and *Z* directions of the sample. The FFT of each of these TEM images is shown in Figure 5. Again, the interlamellar spacing is constant across the film, and no deviation of the orientation along *Z* was observed. In the *X* direction, the ordering extends over hundreds of microns. Only a small fraction of the FFT's is shown here. Though the order and orientation extend very large distances, defects still exist with typical defects shown in Figure 6. Shown in the inset is the FFT transform of the micrograph. However, from the SAXS measurements, it is apparent that the number of defects is very small.

SAXS and TEM results confirm that 3-dimensional control over lamellar microdomain orientation can be achieved by using two orthogonal fields, namely an elongational flow and an electric field, applied sequentially. The copolymer thin film was biased first by an elongational flow field that produced oriented nuclei during the roll-pressing at a temperature below the ODT. Complete ordering of the copolymer in an applied external electric field yielded a lamellar microdomain morphology where there was a three-dimensional control over the orientation.

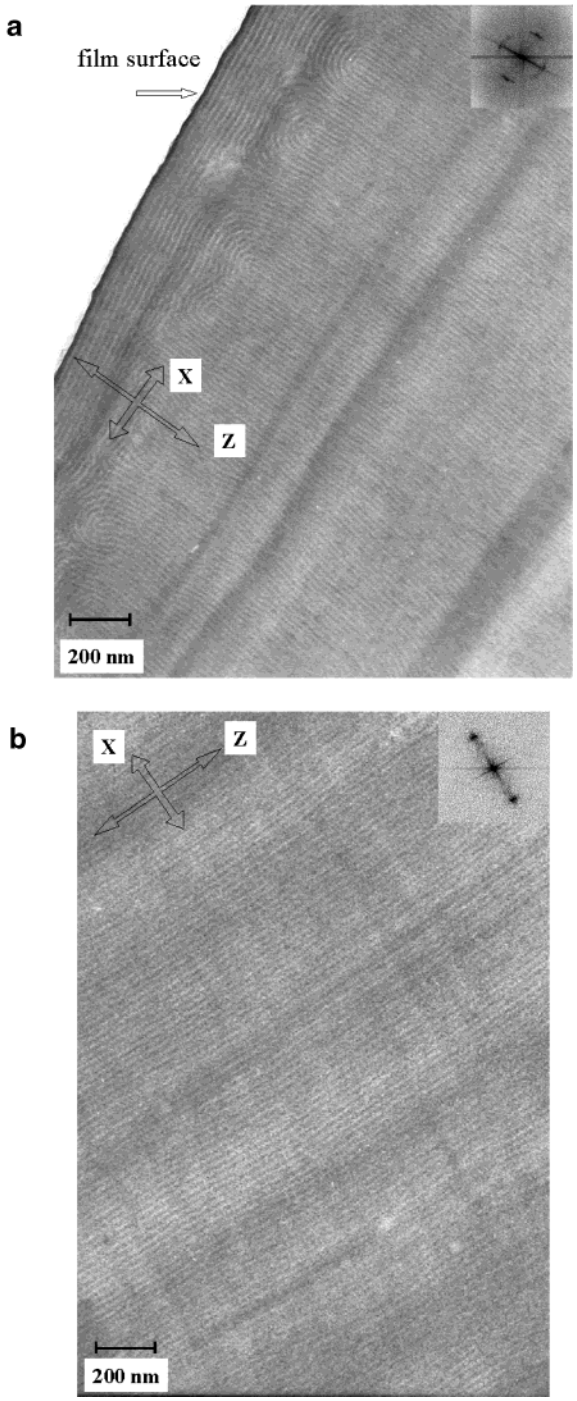

Figure 4. TEM cross-sectional images of (a) the copolymer/substrate interface and (b) the interior of the film.

Several important parameters affected the degree of orientation and ordering in these samples. The influence of the electric field strength on the microdomain alignment along the applied electric field direction has been studied, and there is a critical electric field strength

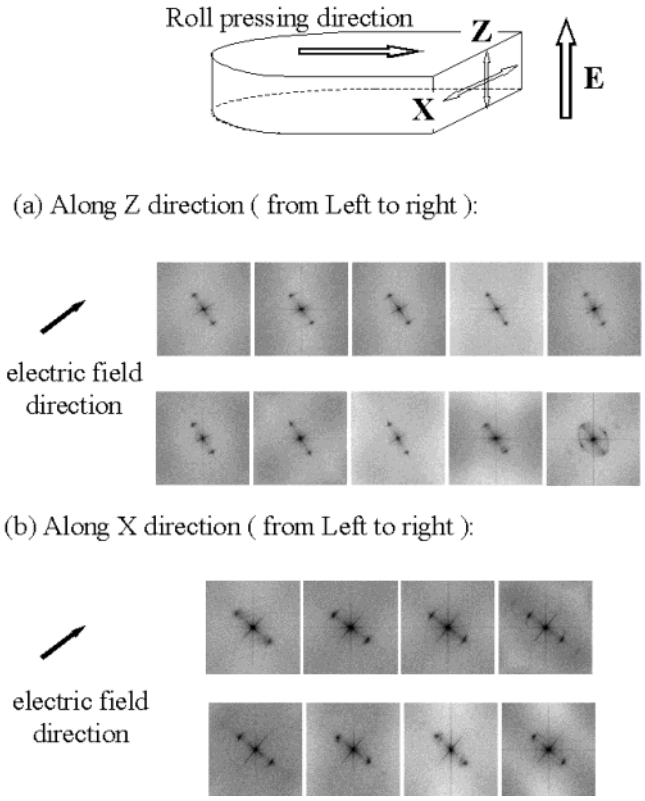

Figure 5. FFT patterns of TEM images at different positions of the film. The TEM images were taken every ~3 μm (a) normal to the film surface (along the *Z* direction in Figure 4a), the image on the left side was taken right after Figure 4a, and subsequent images were taken toward the other side of the film. The last image on the right of the *z*-axis sequence (top) exhibits a four-point pattern due to the mixed orientation of the lamellar microdomains at the film edge. (b) The first image was taken in the center of the film, and subsequent images were taken normal to the flow direction (along the *X* direction in Figure 4a). The grain size is too large to show it fully, and only a small portion is shown.

required to achieve the alignment.[7,17] A similar situation is found with the elongational flow field where a high degree of in-plane ordering is achieved only when the strain rate is high. The ordering parameter decreases with decreasing strain rate. The high degree of in-plane orientation shown was obtained with a strain rate ~8. Lower degrees of orientation were obtained using lower strain rates. However, a simple shear flow generates the in-plane orientation. Thus, three-dimensional ordering could only be achieved when both field strengths are sufficiently high. These results shown here were acquired from the samples in the center where there is a high degree of uniaxial stretching. Other locations in the sample that are subjected to different flow fields do not exhibit such order and orientation. Different SAXS patterns were found that show a direct correlation between the flow direction and the in-plane microdomain orientation. Consequently, the in-plane orientation of the microdomains can be tailored by varying the flow pattern.

The experiments shown here have been done with copolymer films that were ~20−50 μm thick. For many applications, films with thickness ≤1 μm are desirable. Fundamentally, the mechanism behind the method reported here should be applicable for such thin films also. Slight modifications in producing an elongational flow field are necessary, since such thin films would be

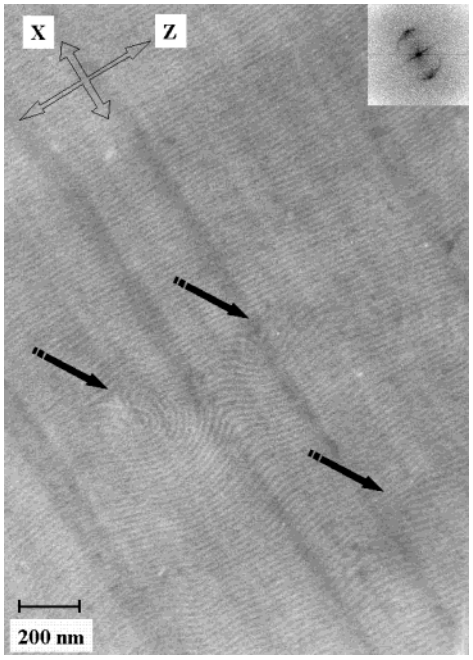

Figure 6. Cross-sectional TEM image of typical defects. While there were few defects, the defects shown were observed the most frequently.

supported on a rigid substrate. This can be solved by use of novel shearing techniques as, for example, that recently developed by Chaikin and co-workers to achieve long-range ordering in thin block copolymer films with spherical or cylindrical microdomains or by use of highly oriented flow fields in solution, as recently discussed by Kimura et al.[18,9] In either case, oriented nuclei in thin films can be generated that can then be used to initiate the growth of microdomains under an applied electric field.

Conclusions

It has been shown that the orientation of lamellar microdomains in P(S-*b*-MMA) can be controlled in three dimensions by use of two orthogonal external fields. An elongational flow field was applied to a copolymer melt to control the in-plane orientation, and a subsequent external electric field was applied to control orientation normal to the film surface. Excellent, long-range order and orientation of the lamellar microdomains were observed by SAXS and TEM.

Acknowledgment. The authors thank H. H. Winter and E. L. Thomas for helpful discussions and insights. Funding by the National Science Foundation-supported Material Research Science and Engineering Center (MRSEC) at University of Massachusetts, Amherst (DMR-0213695), the Department of Energy, Office of Energy Sciences (DE-FG02- 96ER45612) and the Keck foundation is gratefully acknowledged.

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MA0346409