Orientationally Registered Crystals in Thin Film Crystalline/Amorphous Block Copolymers

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Introduction. An extremely difficult but technologically important problem is the positioning of two or more separate crystals of a material such that their unit cells are oriented in precisely the same direction yet are physically separated by distances of nanometers to millimeters. Establishing a simple route to accomplish this opens avenues to materials with unique optical properties for guiding and transmitting light, for multilayered storage devices, and for layered sensory devices. Channel cut crystal monochromators for X-rays use such structures to produce monochromatic radiation with exceptionally low divergence, in fact theoretically parallel radiation.[1] Crystallographic registry of the channel walls is ensured since the channel is cut from a single large crystal of silicon or germanium. Here, self-assembling, organic materials based on a poly(ethylene oxide) (PEO) containing crystalline/amorphous block copolymer are shown to have multiple, perfectly aligned crystalline layers separated from one another by 10−15 nm.

The morphologies of PEO-containing microphase-separated crystalline/amorphous block copolymers in both bulk[2−5] and thin film[6−8] have been investigated previously. In this study, we utilized a symmetric, diblock copolymer of poly(ethylene oxide) and poly(butadiene), denoted P(EO-*b*-BD), which has a total molecular weight of 11 000 g/mol (5000 g/mol PBD and 6000 g/mol PEO). PEO and PBD are highly immiscible, and in the bulk, P(EO-*b*-BD) self-assembles into an alternating lamellar morphology of amorphous PBD and crystalline PEO.

Experimental Section. Thin films of P(EO-*b*-BD), 40−150 nm in thickness, were spin-coated from toluene solutions onto silicon wafers for interference optical microscopy and silicon nitride membranes (100 nm thick) for electron diffraction studies. Samples were heated above the equilibrium melting temperature of PEO[9−11] and then rapidly cooled to various temperatures, 25 °C for instance, at which the PEO block crystallized.

The structures of the thin films were studied using an Olympus BX60F3 optical microscope. All the optical

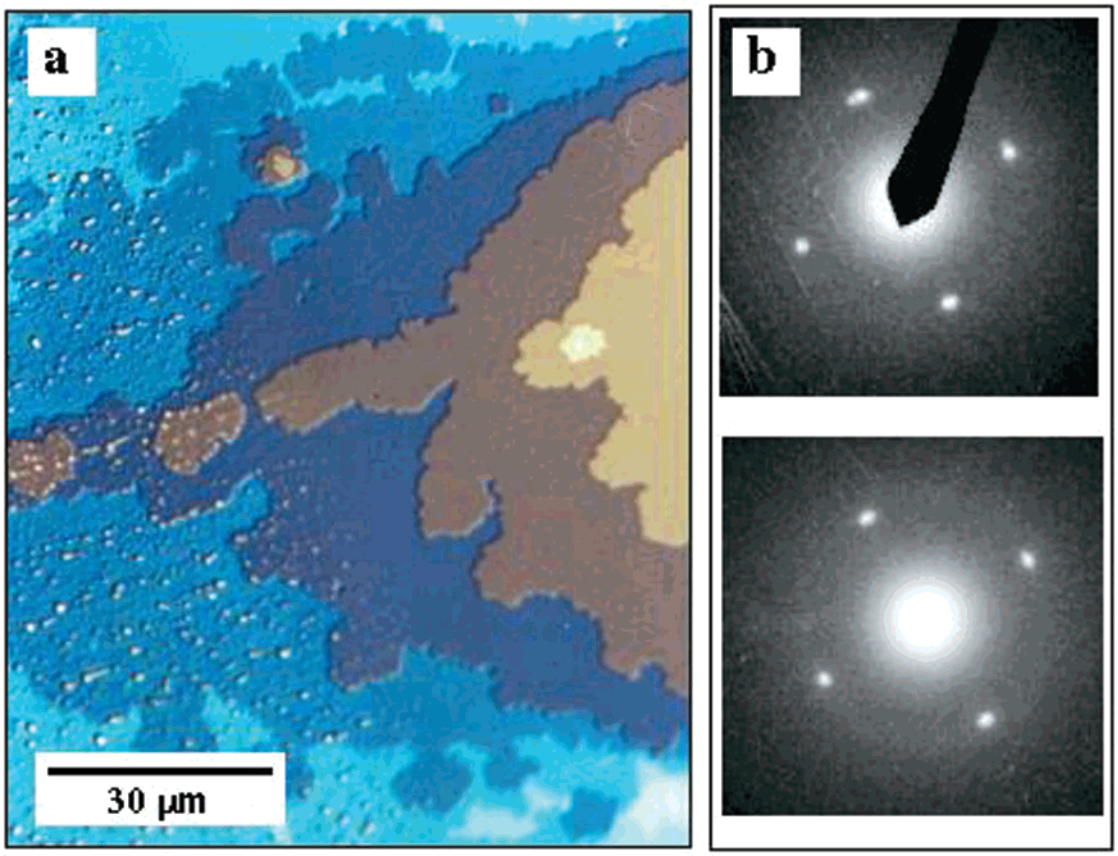

Figure 1. (a) Interference optical micrograph of a P(EO-*b*-BD) thin film showing the sharp changes in the interference colors due to the ordering of the copolymer parallel to the surface. A crystallization front is shown propagating from the left across the film. The texture arises from cracks within the crystalline layers due to the volume contraction upon crystallization. (b) Diffraction images on the right were taken at several points on the sample, passing through multiple layers. Only a four-point pattern is observed.

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images were obtained under reflection conditions to obtain interference colors from a white-light source. Normarski conditions were used to enhance the contrast of the terraced surface of the copolymer thin films.[12] Silicon nitride (Si_3N_4) membranes (100 nm thick) with a window size of 0.46 mm × 0.46 mm were obtained from Structure Probe Inc. The silicon nitride membranes permit a direct transmission electron microscope (TEM) observation of and diffraction from thin films.[13] TEM and electron diffraction experiments were performed on a JEOL 2000 FX-II transmission electron microscope. The diffraction camera length was calibrated by using an internal gold standard.

Results and Discussion. Above T_m, interference optical microscopy shows distinct color contours across the entire surface of the sample indicative of a microphase-separated morphology with lamellar layers oriented parallel to the wafer.[12] Consequently, in the melt, the thin films consist of alternating layers of PEO and PBD with half layers of PBD at both the air and substrate interfaces, as determined by X-ray photoelectron microscopy, contact angle, and optical microscopy measurements.

Upon crystallization at 25 °C, there is only a slight change in the interference colors with retention of the layered structure as shown in Figure 1. In multilayered films, distinct growth fronts with equal growth rates are seen, indicating that the growth of the PEO crystals proceeds independently in each layer. Atomic force microscopy on samples crystallized at 25 °C shows that the step change between each layer is 20 nm, which is very similar to the layer thickness of the uncrystallized block copolymer in the melt. Crystallization at temperatures greater than 25 °C results in increased layer thicknesses; however, the multilayered structure with layers parallel to the substrate is still retained.

The electron diffraction patterns shown in Figure 1 were obtained from two different positions of a thin, multilayered film on a silicon nitride membrane. The four spots correspond to the (120) reflection, indicating that the PEO unit cell and chain axis are oriented normal to the layers.[14] In all cases, regardless of the number of layers through which the beam penetrated, only four spots were observed. This can only occur if the PEO crystals in adjacent layers are in orientational registry even though the crystals are separated by 10 nm of amorphous PBD. This behavior can only occur if the PEO crystals in adjacent layers originate from the same nucleus, and there is an interconnection between layers. The strong immiscibility of PEO and PBD restricts layer interconnection to defect structures such as edge and screw dislocations. Screw dislocations have been observed in fully amorphous, microphase-separated, lamellar block copolymers.[15] Their helicoid structure, similar to that of a multilevel parking garage, provides a continuous path for crystal growth connecting parallel PEO layers. When a propagating PEO crystallite in a single layer encounters such a screw dislocation, it spreads to adjacent layers to produce a multilayered structure which originated from a single nucleus and thus has one crystallographic orientation.

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