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Perpendicular Orientation of Domains in Cylinder-Forming Block Copolymer Thick Films by Controlled Interfacial Interactions

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ABSTRACT: We report the induction of perpendicularly oriented cylindrical domains in PS-*b*-PMMA block copolymer (BCP) films thicker than 100 nm by thermally annealing on a substrate modified with a random copolymer. The effects of annealing temperature, composition of the substrate-modifying random copolymer, and BCP film thickness on the morphology of PMMA cylinder forming PS-*b*-PMMA were studied. For BCP films thicker than 100 nm, the fabrication of perpendicular PMMA cylinders is highly dependent on both the substrate-modifying random copolymer and the annealing temperature as these two parameters control the interactions of the BCP with the substrate and the free surface, respectively. We found the best perpendicular structures to be created by using a random copolymer brush with a styrene fraction (F_{St}) near 0.70 and an annealing temperature near 230 °C. Perpendicular cylinder structures were achieved in ~300 nm thick films using these conditions. When the BCP film was thicker than 300 nm, nucleation and growth of the microdomains proceeded independently from each interface. We present scanning electron microscope (SEM) and cross-sectional transmission electron microscope (TEM) images of these perpendicular structures and explain the results on the basis of previous simulation reports.

Introduction

The self-assembly of block copolymer (BCP) materials in thin films is useful for creating ordered nanostructures.[1−5] For certain applications of BCP thin films, controlling the shape, size, and orientation of microdomains is critical. In general, the shape and size of the microdomain can be controlled by varying the molecular weights and relative volume fractions of each block in the BCP. The orientation of the microdomains in thin films is mainly controlled by the interaction of each block with the substrate and the free surface through wetting energetics and polymer confinement effects resulting from the film thickness. Balancing the interfacial interactions of A-*b*-B block copolymers using A-*r*-B or A-*r*-B-*r*-C random copolymers, so-called surface neutralization, provides a simple route for the fabrication of perpendicularly oriented domain structures within ~50 nm thick films.[6−10] In previous studies, films of cylinder forming polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) have been successfully used as etch masks or nanotemplates.[11−15]

Thicker films (> 100 nm) are useful for a variety of applications including the fabrication of separation membranes,[16] nanorods,[15] and nanowires.[17] For thicker films of PS-*b*-PMMA it is a challenge, however, to produce perpendicular domains even on a neutral or nonpreferential surface. Although the surface energy difference ($\Delta\gamma_S$) between PS and PMMA at 170 °C is less than 1%,[18] this causes the segregation of PS at the free (or vacuum) interface and induces the parallel orientation of domains in thicker films.[6] Several different approaches have been explored to extend the perpendicular orientation of domains to thicker films on nonpreferential substrates such as applying an electric field,[19] adding homopolymer,[20] and placing surface active neutral random copolymers[21] or low molecular weight surfactants[22] at the free interface.

Alternatively, it is proposed that nonpreferential boundary condition can be achieved at the free interface by controlling the annealing temperature.[23] Mansky et al. demonstrated that segregation of PS at the free surface can be suppressed by increasing the temperature up to 250 °C. Subsequently, Sivaniah et al. fabricated perpendicularly oriented symmetric PS-*b*-PMMA with a 300−900 nm thick film on a rough surface by annealing at 230 °C.[24,25] Annealing PS-*b*-PMMA at these temperatures on a random copolymer modified surface, however, has not been demonstrated for both symmetric and asymmetric BCP above ~100 nm. Propagation of perpendicularly oriented microdomains from the substrate to the free surface requires finely tuned interfacial interactions of each block at both the free surface and substrate interface. The compositional ranges of random copolymers that induce perpendicular domain alignment (denoted as the perpendicular windows) in thin films (below 50 nm thickness) were recently reported by us[26] and others.[27] It was found that symmetric and asymmetric BCPs require different random copolymer compositions as an optimum nonpreferential layer. Therefore, the influence of annealing temperature on the orientation of BCP domains in thicker film should be addressed based on the knowledge of perpendicular window rather than a single neutral composition.

Here, we have studied the effect of annealing temperature, surface composition, and film thickness on the orientation of PMMA cylinders in films up to ~900 nm on cross-linked random copolymer layers. Nonpreferential boundary conditions were obtained simultaneously and independently at both the substrate and free surface interfaces by tuning the random copolymer composition and the annealing temperature.

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Experimental Section

Materials. Asymmetric PS-*b*-PMMA was purchased from Polymer Source Inc. (Dorval, Quebec, Canada) and used without further purification (PS 46 kg/mol, PMMA 21 kg/mol, PDI 1.09; cylinder row-to-row distance, d_0, measured from top view SEM image is ~32 ± 1 nm). Different compositions of **PG4** copolymers (Figure 1) were synthesized by nitroxide-mediated living free radical polymerization (NMP) following similar procedures. A representative procedure is detailed here: For one sample of **PG4-70**, a mixture of NMP unimer initiator (0.02 g, 0.061 mmol), St (2.69 g, 25.8 mmol), MMA (0.96 g, 9.6 mmol), and GMA (0.2 g, 1.47 mmol) was degassed by three freeze/thaw cycles and sealed under nitrogen. The polymerization mixture was reacted at 120 °C for 36 h.

Substrate Modification and BCP Film Preparation. Solutions of **PG4** in toluene (0.3% w/w) were spin-coated at 4000 rpm onto silicon wafers and then baked under vacuum at 160 °C for 3 h for the thermal cross-linking of the epoxide.[10] The substrates were sonicated in toluene (at 60 °C) to remove random copolymer that was not cross-linked and rinsed with fresh toluene to yield ~10 nm thick **PG4** layers. Different thicknesses of BCP were deposited onto **PG4**-modified wafers by changing the solution concentrations from 1 to 10 wt %. Block copolymer films were annealed at 190 °C (3 days) or at 230 °C (1 day) under vacuum. For some samples, the PMMA was removed prior to imaging using UV exposure and acetic acid washing.

Characterization. Top-down scanning electron microscope (SEM) images of the block copolymer microdomains were acquired with a LEO-1550 VP field-emission instrument using an accelerating voltage of 1 kV. Annealed BCP thick films were etched by O_2 plasma (power = 50 W, pressure = 10 mT, and O_2 flow rate = 10 sccm) with a vertical etch rate 50 nm/min for PS. Cross-sectional samples for transmission electron microscopy (TEM) were prepared by coating the top surface with gold to protect the BCP film followed by embedding in epoxy. After removing the substrate, the bottom surface was coated with gold followed by embedding in epoxy. The embedded samples were then microtomed at room temperature. The sections transferred to TEM grids and viewed with a bright field Philips CM 120 TEM at 80 kV accelerating voltage (Medical School Electron Microscopy Facility, University of Wisconsin—Madison).

Results and Discussion

Previously, we reported a cross-linkable random copolymer composed of styrene (St), methyl methacrylate (MMA), and glycidyl methyl methacrylate (GMA) for the formation of a substrate independent neutral layer.[10,26] In the current work, we synthesized a series of similar random copolymers (Figure 1) with a fixed amount of GMA monomers (4 mol %) and varied the styrene fraction (F_{St}) from 0.50 to 0.85. These copolymers are referred to as **PG4**.

Since the size and position of the perpendicular window also depend on the thickness of the BCP film,[27] we first defined the perpendicular window of **PG4** for PMMA cylinder forming PS-*b*-PMMA with a 45 nm thick film and found that **PG4** having 0.61−0.77 mole fraction of styrene was effective for achieving perpendicular PMMA cylinders. (See Supporting Information Figure S1 for SEM images.) The effect of composition of **PG4** on the assembled structure in thicker BCP films was examined by testing three different compositions, F_{St} = 0.70, 0.61, and 0.50, labeled as **PG4-70, PG4-61**, and **PG4-50** respectively. These compositions were chosen to be approximately in the middle (**PG4-70**), near the edge but still within (**PG4-61**), and outside (**PG4-50**) of the perpendicular window determined for the 45 nm thick BCP film. On **PG4**-modified substrates different thicknesses (45−175 nm) of BCP films were deposited and annealed at 190 °C for 3 days to attain the equilibrium morphology prior to imaging.

On **PG4-70**, perpendicular cylinder structures formed on the top surface in 45−109 nm thick films as seen in the top-down SEM images in Figure 2. Increasing the film thickness to 175 nm, however, caused the appearance of line structures between the spots. These lines we interpret as parallel cylinders and we refer to them as defects. On **PG4-61**, a 45 nm thick BCP film showed minor defects and the number of defects increased with the

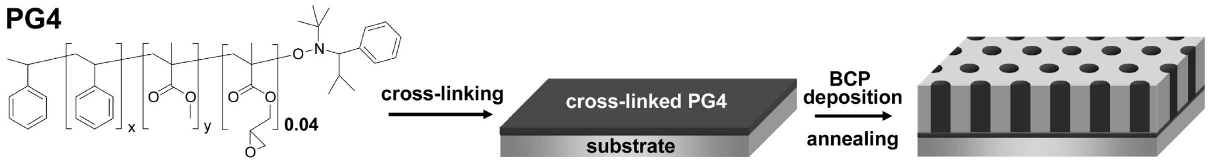

Figure 1. Schematic illustration of cross-linked layer formation to induce perpendicular PMMA cylinders.

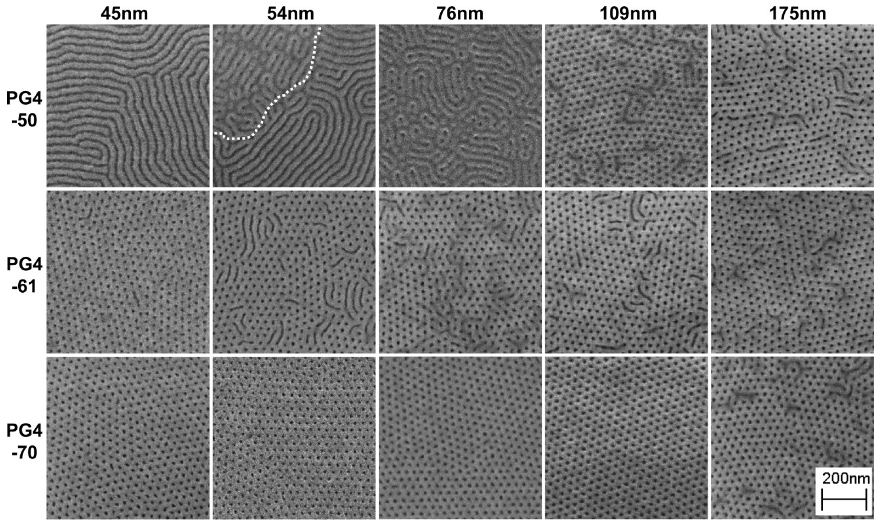

Figure 2. Top view SEM images of assembled BCP films of five different thicknesses on **PG4**-modified substrates (annealed at 190 °C).

thickness. For **PG4-50**, either parallel cylinders or terrace structures were formed in BCP films with thicknesses between 45 and 76 nm. The SEM image for the 54 nm film was taken at a terraced structure boundary (the dashed white lines showing the boundary). Interestingly, in thicker BCP films on **PG4-50**, perpendicular cylinders are seen on the top surface, even though they are not of perfect quality. The same experiment was done with a bare Si substrate and gave similar results as **PG4-50** (see Supporting Information Figure S2). The quality of perpendicular cylinders as seen from these top-down SEM images for 175 nm thick BCP films is comparable regardless of the composition of the substrate modifying layer, indicating that, at this thickness, the structures near the free surface are not influenced significantly by the substrate.

To investigate the likelihood that the perpendicular cylinders seen on the top surface of BCPs on **PG4**-modified substrates propagate through the entire thickness of the film, we cross-linked the PS domains of the 109 nm thick BCP film with UV radiation and partially peeled the film from the substrate. This allowed direct observation of the domain orientation in the bottom layer of the BCP film. From the SEM images (Figure 3a) it is clear that the bottom layer of BCP on the **PG4-50** substrate primarily consisted of parallel cylinders and on **PG4-70** consisted of perpendicular cylinders. (See Supporting Information Figure S3 for lower magnification of SEM images.) The nonuniformity of the rows of spots in the bottom image of **PG4-70** is likely due to mechanical deformation of the cross-linked PS matrix during the film peeling process. Additional evidence for the propagation of the perpendicular cylinders through the thickness of the BCP film on the **PG4-70**-modified substrate comes from the SEM images (Figure 3b) of the film etched 30 and 60 nm below the top surface. Even on **PG4-70**, however, increasing the BCP thickness to 175 nm resulted in the appearance of some parallel cylinders on the top surface when annealed at 190 °C, indicating that this annealing temperature is most likely insufficient to provide a perfectly nonpreferential free surface.

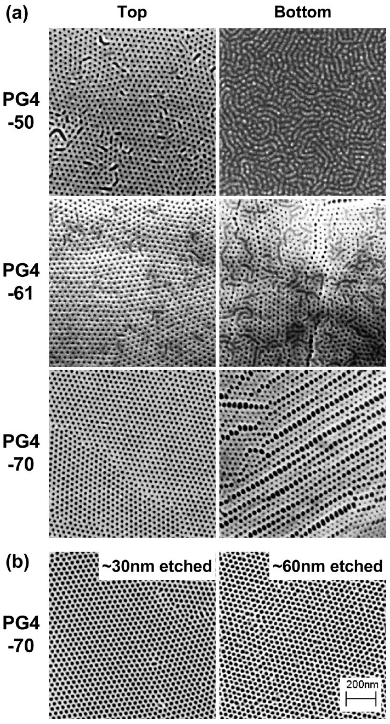

Figure 3. SEM images of (a) top and bottom layer of 109 nm thick PS-*b*-PMMA on **PG4** and (b) top view SEM image of etched BCP film on **PG4-70** (initial film thickness was 109 nm). All BCP films annealed at 190 °C.

We subsequently increased the annealing temperature to 230 °C, and as seen in Figure 4, this markedly improved the quality of the assembled structures in a 175 nm thick film on **PG4-70**. With the 230 °C annealing, BCPs on **PG4-50** and **PG4-61** still showed defects on the top surface of the 175 nm thick film. Unlike annealing at 190 °C, however, defect structures occurred primarily at the grain boundary. The orientation of the cylinders on **PG4-61**, when annealed at 230 °C, was either parallel or perpendicular depending on the film thickness. Increasing the annealing temperature increases the mobility of polymer chain and reduces the annealing time in addition to making the surface energy of the two blocks nearly equal. Equilibrated structures can be obtained in a few minutes above 220 °C, compared to an hour when annealed at 190 °C.[29] The fact that all of our samples were annealed for 3 days at 190 °C and 1 day at 230 °C, however, suggests that all samples can be considered thermodynamic equilibrium structures.

By comparing the results at two different annealing temperatures, it is clear that to induce the perpendicular orientation of cylinders in a thicker film such as the 175 nm thick film, 230 °C annealing is required. The higher annealing temperature clearly affects the free surface of the film, increasing the quality of the perpendicular structures. At the same time it is also apparent that high temperature alone is not sufficient to induce the perpendicular orientation of cylinders near the **PG4**-modified substrate. The optimum **PG4** composition in conjunction with the proper annealing temperature is necessary to induce the perpendicular orientation of cylinders consistently for a range of film thickness.

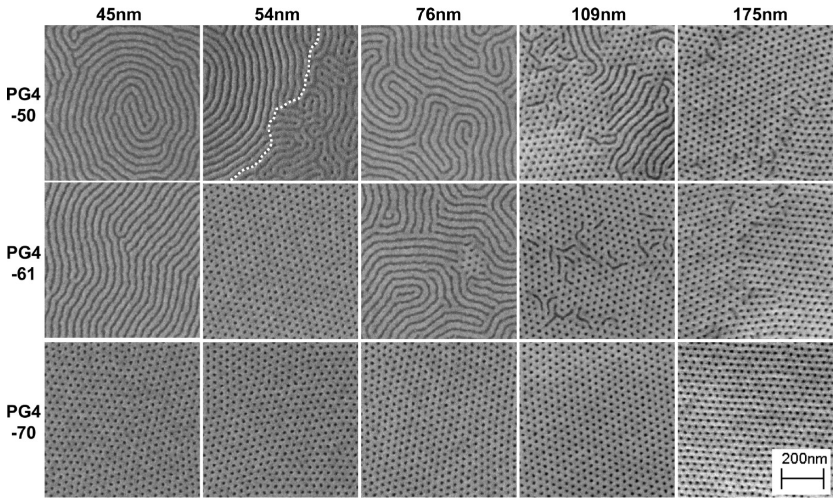

Figure 4. Top view SEM images of assembled BCP films of five different thicknesses on **PG4**-modified substrates (annealed at 230 °C).

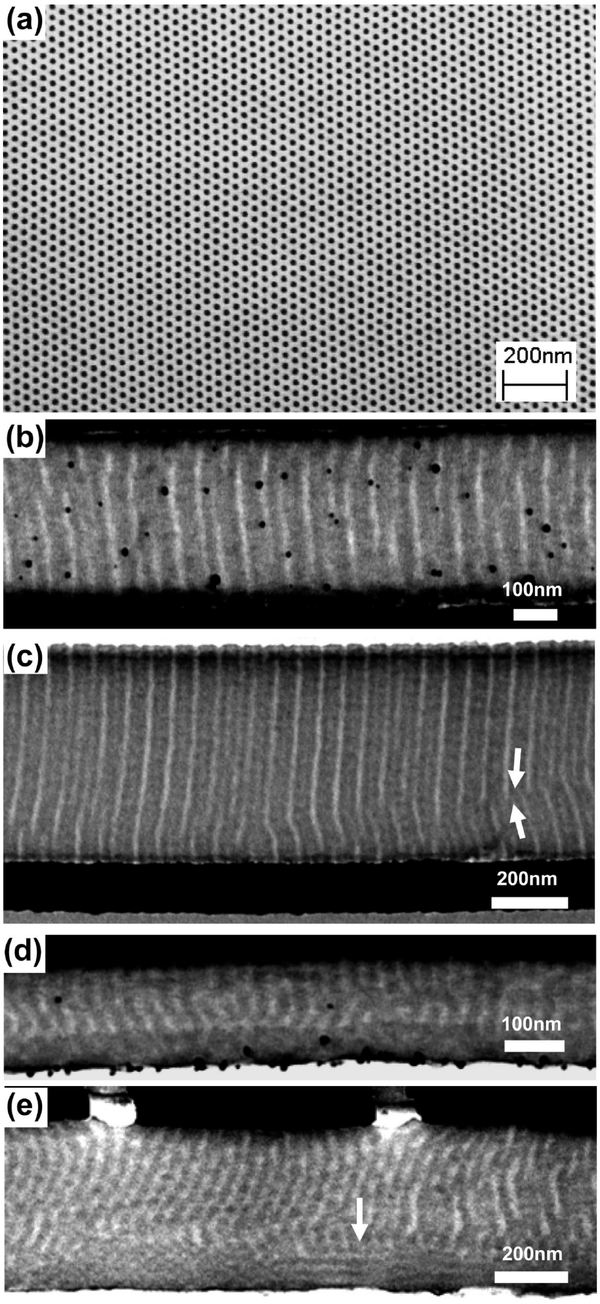

Figure 5. (a) Top view SEM image of a ∼300 nm thick film on **PG4-70**. Cross-sectional TEM image of films on **PG4-70** with thicknesses of (b) ∼300 nm and (c) ∼500 nm and cross-sectional TEM images of films on **PG4-50** with thicknesses of (d) ∼250 nm and (e) ∼500 nm. All samples were annealed at 230 °C. In the TEM images, the top surface corresponds to the BCP/free surface interface.

On the basis of these findings, we can readily optimize our process to generate perpendicular cylinders in thicker films. When the BCP film thickness was increased to ∼300 nm and annealed at 230 °C on **PG4-70** (Figure 5a), perpendicular domains were observed on the top surface. The cross-sectional TEM images (Figure 5b) show that the perpendicular cylinders propagate through the entire 300 nm thick film. We further show in Figure 5c that on **PG4-70** with 230 °C annealing we can create perpendicular cylinders in ∼500 nm thick film. For comparison, 250 and 500 nm thick BCP on a **PG4-50**-modified substrate, annealed at 230 °C, produced the same quality of perpendicular alignment on the top surface as **PG4-70** (data not shown); however, the perpendicular cylinders do not propagate through the film as shown in Figure 5d,e. Previously Son et al.[22] and Zhang et al.[28] reported similar results showing that perpendicular orientation originating from the free surface did not propagate to the bottom layer of the BCP on a bare Si substrate.

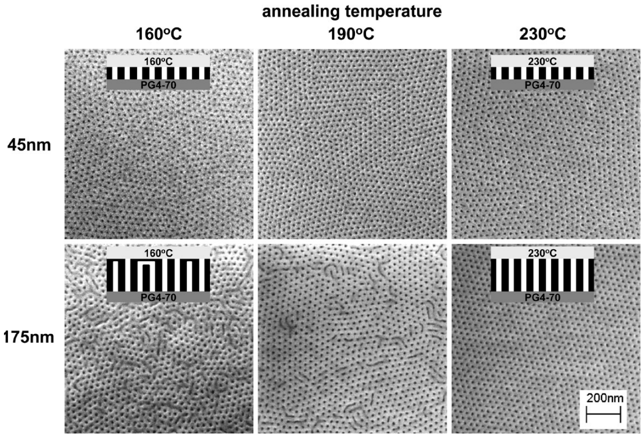

Figure 6. Top view SEM images of assembled BCP films of two different thicknesses on **PG4-70** annealed at different temperatures.

The optimum **PG4** composition ($F_{St} = 0.70$) and the higher annealing temperature (230 °C) used in our study together account for the induction of perpendicular cylinders in thick films. On the basis of the current data in the literature, the surface energy difference ($\Delta\gamma_S$) of PS and PMMA cannot be explicitly calculated for our system, since it depends not only on temperature but also on the molecular weight of the polymer blocks. Mansky et al. studied the segregation of the dPS block at the free surface in a ∼170 nm thick film of P(dS-*b*-MMA) ($M_w = 32\,000$, styrene volume fraction = 65%) as a function of temperature by measuring neutron reflectivity.[23] They found that the degree of segregation of dPS at the free surface can be reduced by increasing temperature and goes to zero above 225 °C. Our results with the 175 nm thick films showing better ordering of structures at higher temperatures provide some evidence that at 230 °C $\Delta\gamma_S$ indeed becomes smaller than at a lower temperature (Figure 6). Thus, at higher temperature there is less of a thermodynamic driving force for the domains to assemble parallel to the free surface than at lower temperatures. On the other hand, as shown in Figure 6, the annealing temperature has less effect on the domain orientation of 45 nm thick film at the free surface, indicating that in films less than 50 nm thick substrate composition is the main parameter that controls the domain orientation.

Recently Ryu et al. reported that the thickness window that allows perpendicular orientation can be widened by slightly increasing the volume fraction of PS in the BCP.[41] They showed that perpendicular cylinders can be achieved up to 45 nm thick on an optimized neutral layer by annealing at 170 °C. This is comparable to our films annealed at 160 °C. As shown in Figures 2 and 4, increasing the annealing temperature above 160 °C dramatically increases the thickness window for **PG4-70** up to 109 nm at 190 °C and above 175 nm at 230 °C. (See Supporting Information Figure S4 for 160 °C annealing results.)

Considering the random copolymer composition, most reports in the literature have used the hydroxy-terminated PS-*r*-PMMA with a composition of $F_{St} = 0.58-0.60$ to generate perpendicular BCP structures. We know from recent reports by us and others,[26,27] however, that this composition is near the edge of the perpendicular window for PMMA cylinder-forming BCP films with a thickness of ∼d_0. In our study, **PG4-61** represents this composition.

It is interesting to note that as we increased the BCP film thickness, the bottom layer of the BCP film showed more parallel cylinders on **PG4-61** with 190 °C annealing (see Figures 3a and 7a). This indicates that as we increased the distance between the

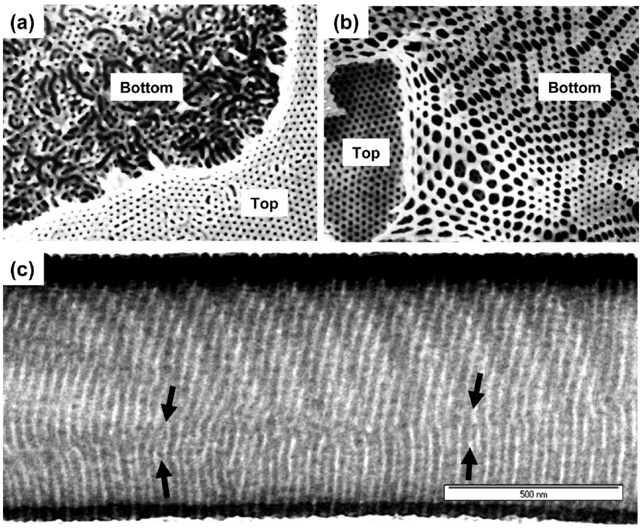

Figure 7. (a) SEM image of top and bottom layer of 175 nm thick film annealed at 190 °C on **PG4-61** and (b) on **PG4-70**. (c) TEM image of ~900 nm thick film on **PG4-70** annealed at 230 °C.

free surface and the **PG4-61** layer, the ability of **PG4-61** to induce perpendicular structures near the substrate decreased. On the other hand, the BCP on **PG4-70** (see Figures 3a and 7b) showed the same quality of perpendicular cylinders at the bottom of the BCP regardless of the film thickness. It is known that the propagation of the surface field is limited to a few periods from the interface before it dissipates.[30] In thin enough films, the effect of both interfaces can be additive, and the final microdomain structures is the result of the interaction of the BCP with the two interfaces. Thus, the equilibrated structure in the thin film reflects the particular characteristics of both boundary conditions. As the thickness of BCP film increased, however, the two surface fields become disconnected from each other and nucleate the microdomain orientation independently, based on the magnitude and nature of interaction with each block of the BCP.[31,32]

For thicker films, each surface must be optimized independently to produce perpendicular structures, which is what we see with **PG4-70**. For thinner films the cylinders merge into connected, through-film structures, and for thicker films they merge to form grain boundaries. In very thick films this boundary where the two propagation fronts merge can be observed (arrows in Figures 5c and 7c). Similar results can be observed when two surfaces direct different microdomain orientations as shown in Figure 5d,e. In all cases the free surface nucleates a thicker layer of single domains (larger grain).

Since the surface field decays rapidly over a few hundred nanometers, it appears that increasing the BCP film thickness above a certain thickness turns the center of the BCP film into a bulklike state where BCP orientation is independent of the two interfaces.[30] In our experiment with 300−900 nm thick films, while cylinders with completely randomized orientation were not observed, disconnections or Y-shape cylinder junction can be observed in some areas specifically where the two fronts merge (as seen in the ~900 nm thick film, Figure 7c).

While 230 °C annealing on **PG4-70** produced perpendicularly orientated cylinders over a range of thicknesses, the orientation of cylinders on **PG4-61** was thickness dependent. Previous theoretical and simulation investigations showed that for certain boundary conditions the equilibrium morphology of symmetric and asymmetric BCPs can form either parallel or perpendicular domains in thin films, depending on the film thickness of the BCP and the interactions of the surfaces with the film.[33−38] From simulations it is known that to induce the perpendicular orientation of cylinders in BCP films over a range of thicknesses confined between two identical surfaces, slight preferential wetting of the surfaces for the majority block is required.[38] The energetic preference of the surface for the majority block is balanced by the entropic preference of the surface for the minority block, resulting in the surfaces acting as nonpreferential layers for both blocks.[37−39] According to Wang et al.,[38] when the BCP is placed between two energetically neutral surfaces, the domains orient parallel or perpendicular to the substrate depending on the BCP thickness.

The boundary conditions of the work by Wang et al. do not exactly match our experimental conditions since in our case (i) the BCP film is unconfined, allowing the formation of terrace structures, and (ii) the two interfaces are not identical. Nonetheless, our results show some similarities with the simulations in terms of thickness dependence of the BCP orientation. The results from films on **PG4-70** reveal perpendicular structures at all thicknesses, similar to the substrates with slight preference to the majority block in the simulations. The domains in films on **PG4-61** when annealed at 230 °C change orientation depending on film thickness. When the initial BCP thickness is close to commensurable thickness with natural period of BCP such as 45 nm (~$1.4d_0$) or 76 nm (~$2.4d_0$), parallel orientation of cylinders was induced. On the other hand, with a 54 nm (~$1.7d_0$) thick film, perpendicular orientation of cylinders was achieved. Similar results were reported earlier for symmetric BCP films confined between nearly nonpreferential substrates where perpendicular lamellae occured when the film thickness was not commensurate with the equilibrium period of the BCP.[40] In thicker films such as at 109 and 175 nm, we do not see this trend since confinement of the film has less of an effect in thicker films. The microdomain orientations of the top and bottom of the BCP layers are independent of each other in thicker films and are determined by the wetting conditions of the closest surface.

Conclusion

In conclusion, we have shown that the fabrication of perpendicular PMMA cylinders in thick BCP films is highly dependent on both the substrate-modifying random copolymer and the annealing temperature as these two parameters control the interactions of the BCP with the substrate and the free surface, respectively. By choosing the optimal composition of the random copolymer for the PMMA cylinder-forming PS-*b*-PMMA and the proper annealing temperature, we can achieve what appears to be a nonpreferential top and bottom surface. Especially for thicker films, both the high annealing temperature and an optimum composition of substrate modifying random copolymer are essential for inducing perpendicular domains through the thickness of the film. The ability to create these cylinders in films thicker than 100 nm opens up possible applications in membranes and photovoltaics and may have additional benefits when extended to functional block copolymer systems.

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Supporting Information Available: Additional SEM images of assembled BCP films. This material is available free of charge via the Internet at http://pubs.acs.org.

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