Orientation of Lamellar Nanostructures in the Patterned Thin Films of a Diblock Copolymer

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Introduction. Diblock copolymers are composed of two different polymers that are spontaneously self-assembled into periodic nanostructures, of which the size and morphology can be easily controlled by the molecular weight and composition of copolymers.[1,2] When diblock copolymers are confined to physically or chemically defined patterns, the interfacial interaction and structural commensurability between the copolymer and the patterns strongly influence the assembly of copolymer chains. The confining of diblock copolymers in topographically or chemically patterned structures has frequently been employed to control the order and orientation of the nanostructures of the copolymers.[3–8] For example, Kramer and co-workers demonstrated the spherical nanodomains of diblock copolymers in long-range order by graphoepitaxy.[3] Thomas and co-workers also reported the well-ordered nanodomains of copolymers in topological patterns.[4] Lamellar nanodomains of diblock copolymers were also guided and oriented in large areas with chemically patterned substrates.[7] By confining diblock copolymers inside the cylindrical nanopores of anodized aluminum oxides, Russell and co-workers observed novel nanostructures such as helices and toroids that were not observed in bulk samples.[9,10] Since nanoimprint lithography is known to be an effective patterning method in nanometer scale,[11] Huck and co-workers recently demonstrated the ordered nanostructures of diblock copolymers when copolymers were patterned by nanoimprinting.[12]

In this communication, we demonstrated a critical role of the kinetic process in lamellar ordering in confined geometry by investigating the lamellar nanostructures of diblock copolymers in patterned thin films by the visualization based on transmission electron microscopy. Depending on the initial morphology of a diblock copolymer film, which was prepared without or with preannealing, the orientation of lamellae inside the pattern was either parallel or perpendicular to the substrate. The discrepancy in the lamellar orientation after patterning was ascribed to the kinetic effect during the lamellar development inside the pattern.

Experimental Section. Polystyrene-*block*-poly(4-vinylpyridine) (PS-PVP, $M_n^{PS} = 20\,000$ g/mol, $M_n^{PVP} = 19\,000$ g/mol, polydispersity index = 1.09) was purchased from Polymer Source Inc. Copolymers were dissolved in *N,N*-dimethylformamide to yield 10.0 wt % solution and were then spin-coated at 1000 rpm on polyimide substrates (Kapton, Dupont). The thickness of spin-coated films was about 860 nm. The copolymer film was molded with or without preannealing. The condition of preannealing was at 210 °C for 48 h in a vacuum oven.

A composite mold consisting of *soft* poly(dimethylsiloxane) (PDMS) as a supporting flat layer and *hard* PDMS as a topologically patterned layer was replicated from a silicon oxide master as previously described in the literature.[13] The line dimensions in the pattern were 750 nm in width and 950 nm in depth.

The patterning process is schematically depicted in Figure 1. The composite mold was placed on the top of a copolymer film with a light weight to ensure the good conformal contact. The sample was then annealed at 210 °C in a vacuum oven for 2, 4, 8, 10, and 20 days and then slowly cooled to room temperature. The mold was then removed from the copolymer film.

For cross-sectional transmission electron microscopy (TEM) analysis, the patterned PS−PVP film on top of a polyimide substrate was covered with epoxy and was cured at 60 °C for 12 h. Thin sections (about 80 nm thick) were obtained using an RMC MTX ultramicrotome with a diamond knife. Samples were exposed to I_2 vapor for 2 h to selectively stain the PVP block. TEM was performed on a Hitachi 7600 operating at 100 kV.

Small-angle X-ray scattering (SAXS) measurements of bulk block copolymer samples were performed on the 4C1 beamline using synchrotron X-ray radiation source at the Pohang Accelerator Laboratory, Korea.[14] The wavelength of the X-ray source was 1.608 Å.

Results and Discussion. We molded the lamella-forming PS−PVP block copolymers, of which the average period was 43 nm characterized by TEM as well as by SAXS (Supporting Information Figure S1). A thin film of the copolymer with average thickness of 860 nm was spin-coated on a polyimide

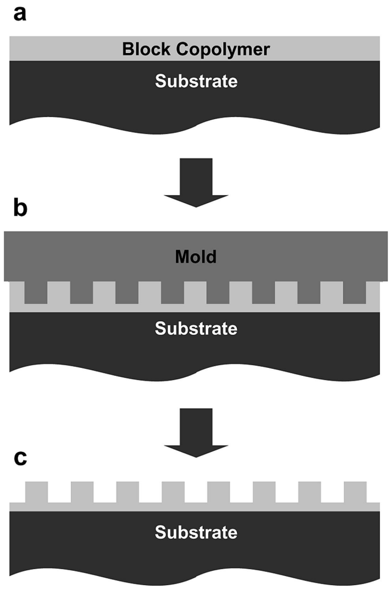

Figure 1. Schematic on the patterning process: (a) spin-coating of a PS−PVP film on a polyimide substrate; (b) patterning of the PS−PVP film with a hard PDMS mold; (c) removing of the mold from the patterned PS−PVP film. The copolymer film was molded with or without preannealing after spin-coating.

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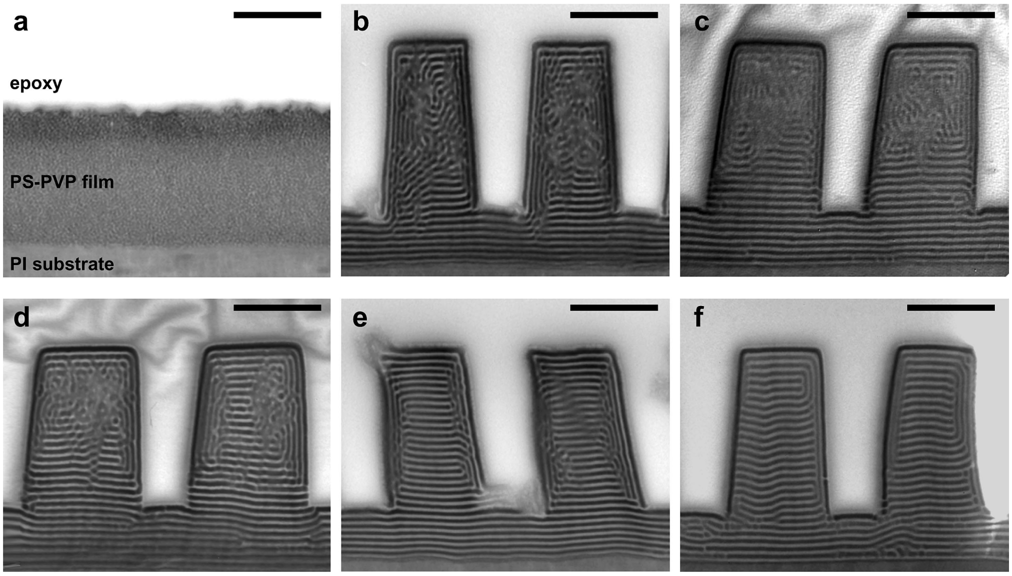

Figure 2. Cross-sectional TEM images of PS−-PVP films without preannealing: (a) as spin-coated; molded at 210 °C (b) for 2 days, (c) for 4 days, (d) for 8 days, (e) for 10 days, and (f) for 20 days. The scale bars are 500 nm.

substrate. The cross-sectional TEM image of Figure 2a shows the copolymer film on top of a polyimide substrate immediately after the spin-coating. A gray carbon layer also appeared on the top of the film, which was coated before epoxy embedding. The film was treated with iodine vapor, which can selectively stain the PVP block. It is noted that a distinct lamellar morphology was not clear in the PS−PVP film, implying the incomplete development of lamellae during the fast spin-coating process.

The spin-coated film shown in Figure 2a was patterned with the composite mold. The line pattern of the mold was well transferred to the copolymer film (Supporting Information Figure S2). Since the top width of the patterns in the mold was slightly smaller than the bottom width, the replicated patterns of the copolymers shown in the cross-sectional TEM images of Figures 2b−f were slightly tapered. The width and height of the patterns in the images were also slightly smaller than those of the original patterns in the mold due to the preparation procedure of TEM samples by epoxy embedding followed by microtoming. We note that the apparent difference in the dimension of patterns in Figures 2b−f was ascribed to the artifact derived from the microtoming process. Since the initial amount of the film on the substrate was more than enough to fill up the patterns of the mold, there exists a residual bottom layer of the copolymer underneath the portion of the block copolymer filled into the mold (Figures 2b−f). The thickness of the bottom layer was about 320 nm. The lamellae in the bottom layer were oriented parallel to the substrate due to the preferential interaction of the PVP block to the polyimide substrate and the PS block to the PDMS mold, which was supported by the observation of the dark PVP layer and the gray PS layer at the interfaces of the substrate and the mold, respectively. It is noted that the orientation of lamellae in the bottom layer was almost completed after 2 days of annealing (Figure 2b).

Inside the patterns, however, the orientation was not complete after 2 days of annealing when Figures 2b−f were compared. The wetting layer of the gray PS block on the PDMS mold surface was visible, which in turn induced the orientation of a few additional layers of the PVP and PS blocks parallel to the mold surface. Beyond these wetting layers in the patterns, however, the lamellae were not oriented to any specific direction after the 2 days of annealing (Figure 2b). At the dividing region between the pattern and the bottom residual block copolymer layer, the parallel lamellae with respect to the substrate continuously propagated from the bottom residual layer but were not fully developed into the middle of the patterns after the 2 days of annealing (Figure 2b). As annealing proceeded further, more parallel lamellae were induced in the middle of the patterns (Figures 2c,d). Beyond 10 days of annealing in the presence of the mold, most of the lamellae in the middle of the patterns were oriented parallel to the substrate, except a few bilayers close to the mold surface (Figures 2e,f). The parallel orientation to the substrate in the pattern implies that propagation of the ordering from the parallel lamellar domain in the bottom layer could be dominant over induction of the ordering from the surface of the PDMS mold. It is believed that the apparent difference in the lamellar thickness between the parallel lamellae and the layers close to the mold was ascribed to the artifact derived from the microtoming process because we confirmed that the lamellae difference was not consistent when the microtoming direction was altered.

To investigate the effect of predevelopment of lamellae in thin film on the ordering within the pattern, a spin-coated copolymer film was preannealed prior to molding. In the cross-sectional TEM image of the preannealed film of Figure 3a, the wetting layers of the dark PVP block and the gray PS block oriented parallel to the substrate were observed at the interface of the substrate as well as at the surface of the film. Several periods of the lamellae parallel to the interface and surface were developed due to the preferential wetting on both interfaces. In the central region of the film, however, the lamellae were not fully oriented parallel to the substrate because the film might be too thick to achieve the complete parallel orientation of the lamellae originating from both interfaces. The lamellar orientation in a thin film comparable to the bottom layer (Supporting Information Figure S3) was superior to that in a thick film (Figure 3a). However, the lamellar ordering in a thin film was not much dependent on the top interface.

The preannealed film shown in Figure 3a was again subject to patterning with the composite mold. Figures 3b−f show the internal morphologies after 2−20 days of molding. The apparent difference in the dimension of patterns in Figures 3b−f was again due to the artifact derived from the microtoming process. Similar to the previous case without the preannealing of the

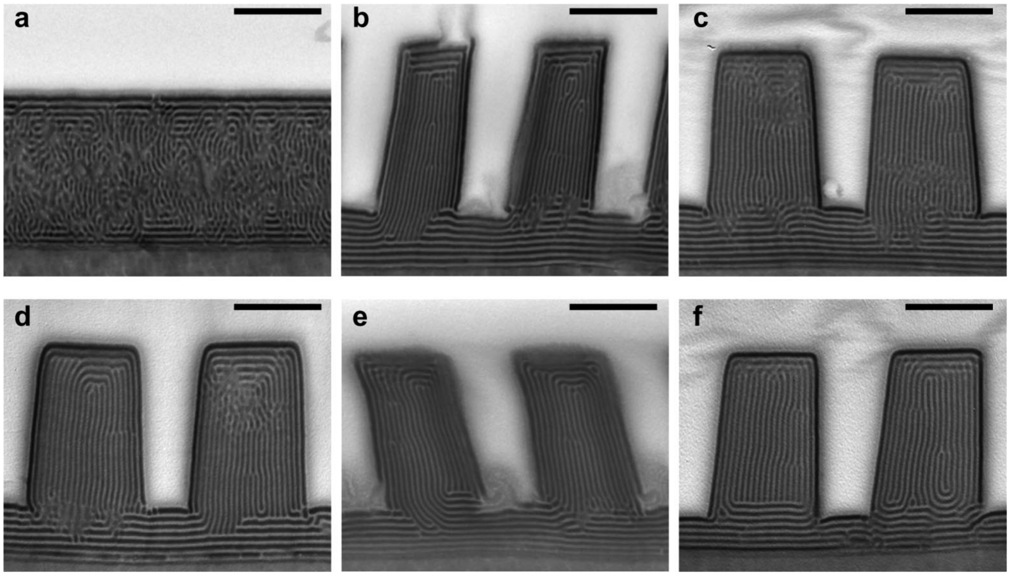

Figure 3. Cross-sectional TEM images of PS−PVP films with preannealing: (a) preannealed after spin-coating; molded at 210 °C (b) for 2 days, (c) for 4 days, (d) for 8 days, (e) for 10 days, and (f) for 20 days. The scale bars are 500 nm.

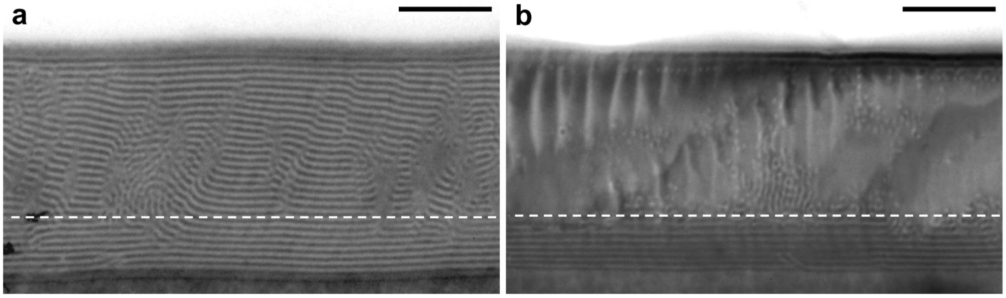

Figure 4. Cross-sectional TEM images of PS−PVP films in the direction parallel to the long axis of the pattern: (a) without preannealing; (b) with preannealing. Both films were molded at 210 °C for 10 days. The scale bars are 500 nm. The patterned portion and the bottom residual layer were divided by white dashed lines.

film, there exists a bottom residual layer of the copolymer underneath the patterned portion of the film, for which the lamellae were oriented parallel to the substrate. The wetting layer of the gray PS block along the mold surface was also visible in the images. Inside the pattern, however, we observed the completely different orientation of lamellae when compared with the previous case without preannealing. As shown in Figures 3b−f, the lamellae inside the patterns were oriented perpendicular to the substrate, in sharp contrast to the parallel lamellae in the patterns shown in Figures 2b−f. In Figure 3, the perpendicularly oriented lamellae inside the pattern molded for 2 days and 20 days of annealing were not much different, whereas the complete parallel lamellae inside the pattern were only observed after the 10 days of molding in the case without the preannealing (Figure 2). We also note that the perpendicularly oriented lamellae in the pattern shown in Figures 3b−f were perpendicular to the substrate and, at the same time, parallel to the long axis of the pattern. It is, however, also possible to have perpendicularly oriented lamellae with respect to both the substrate and the long axis of the pattern, which was rarely observed in our experiments.

In order to prove that the orientation of lamellae inside the pattern shown in Figures 2 and 3 was developed entirely along the long axis of the pattern, we obtained the cross-sectional images in the direction parallel to the long axis of the pattern. The cross-sectional TEM images in parts a and b of Figure 4 show the lamellae patterned for 10 days without preannealing and with preannealing, respectively. The patterned portion and the bottom residual layer were divided by white dashed lines in the images. Without preannealing, the lamellae inside the pattern as well as at the bottom residual layer (Figure 4a) were oriented parallel to the substrate consistently along the long axis of the pattern, although the lamellae in some region of the pattern were not perfectly oriented parallel to the substrate. With preannealing (Figure 4b), the lamellae at the bottom residual layer were oriented parallel to the substrate and several parallel lamellar layers at the top of the patterned portion, which were believed to be derived from the surface of the mold, were also observed. Inside the pattern, however, the perpendicular lamellae were in parallel with the sectioning plane so that the alternating lamellar structure was not identified. From the cross-sectional images of Figure 4, we confirmed that the orientation of lamellae inside the patterns shown in Figures 2 and 3 was consistently formed along the long axis of the patterns.

The dependence of the lamellar orientation inside the patterns on the initial morphology of the film which was prepared with or without preannealing implies that the lamellar orientation inside the patterns after molding can be rationalized by the kinetic process during the lamellar ordering. When the size of the pattern, viscosity, and surface energy of the copolymer used were considered, the time required for the copolymer to fill up the patterns was estimated to be in the order of a few minutes based on the governing equation given in the reference.[15,16] Experimentally, we also observed the complete filling of the patterns with the copolymer in about 7 min. Without preannealing of the film, it is reasonable to think that the lamellar orientation within the patterns could be induced after the patterns were filled with the copolymer due to the relatively short period of the filling time. The orientation of lamellae inside the patterns could be significantly influenced by the interfacial effect originating from the substrate. As a result, the parallel orientation of lamellae inside the patterns was achieved (Figure 2), presumably due to the ordering from the bottom layer dominant over the lamellae ordering from the surface of the mold.

In the case of the preannealed copolymer film, however, the lamellar domains are ripened in both thickness and length and also randomly oriented before patterning, except the region near the substrate and the surface of the film where the lamellar domains are oriented parallel to those interfaces. Since the molding temperature was above the glass transition temperatures of both blocks (i.e., PS and PVP) and yet much lower than the order−disorder transition temperature of the block copolymer,[17,18] it is believed that the lamellae domains were intact during the molding into the patterns, and their domain orientation could be strongly affected by the flow field to fill the patterns. The shear direction to fill up the patterns was almost parallel to the side walls of the patterns or perpendicular to the substrate. Thus, the lamellar tactoids were easily oriented parallel to the shear direction during the patterning, leading to the perpendicular orientation of lamellae inside the pattern as shown in Figure 3. It has been reported that the orientation of lamellae parallel to the shear direction was obtained even if the shear rate was not high.[19,20] Because of the shear-induced orientation at the early stage of molding into the patterns, the perpendicular orientation of lamellae is almost complete even after 2 days of molding (Figure 3b). Then, the perpendicular lamellae (Figure 3) as well as the parallel lamellae (Figure 2) inside the patterns did not change their orientation after prolonged annealing, presumably due to high energy costs required to change the orientation of lamellar domain inside the nanometer-sized channel. Thus, parallel and perpendicularly oriented lamellae or at least one of them (Figures 2f and 3f) can be kinetically trapped within the channel and in a local equilibrium state.

The orientation of lamellae in the channel could be affected by many factors including the diffusivity of copolymers, the domain size and morphology, the defect density, the interfacial energies among each block of copolymers, the mold, and the substrate. If the block copolymer inside the pattern were annealed above the order−disorder transition temperature, the lamellae formed inside the patterns upon cooling would result in the same orientation regardless of the initial morphology of the film. Since the order−disorder transition temperature of the PS−PVP copolymer in present case is known to be way above the thermal decomposition temperature,[17] the ultimate test for the global equilibrium for domain orientation is not experimentally possible with the block copolymer used. In addition, we note that a relative ratio of the height to the width of the channel could affect the equilibrium orientation of lamellae in the pattern because the number of defects such as L- or T-shaped lamellae which are necessarily formed along the side walls of the pattern should be minimized in an equilibrium state.

Conclusions. The orientation of lamellae inside the patterns during nanoimprinting was parallel or perpendicular to the substrate, depending on whether the initial block copolymer film before patterning was preannealed or not. Without preannealing, the parallel orientation of lamellae inside the patterns was obtained mainly due to the propagation of parallel lamellae from the bottom layer. In contrast, when the ripened (i.e., thick and long) lamellar domains within the film were developed by preannealing before molding, the lamellae inside the mold were oriented perpendicular to the substrate due to the shear-induced alignment of lamellae at the early stage of mold filling. Parallel and perpendicular lamellar structures or at least one of them cannot be in the global equilibrium state and can be considered in a kinetically trapped state within the channel.

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Supporting Information Available: TEM image and SAXS profile of the PS−PVP copolymer used in present study, a FE-SEM image of the patterned film of the PS−PVP copolymer, and TEM images of lamellae of the PS−PVP copolymer in thin films. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) $t = 2\eta z^2/R\gamma \cos\theta$, where t is the time required for polymers to fill up the mold (~6 min), η is the viscosity of polymers (~10^6 Pa·s), z is the height of the pattern (950 nm), R is approximately half of the width of the pattern (750 nm), γ is the surface tension of polymers (~40 mN/m), and θ is the contact angle of polymers on the mold (~70°).
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