Unexpected Hexagonally Perforated Layer Morphology of PS-*b*-PMMA Block Copolymer in Supported Thin Film

Insun Park, Soojin Park, Hae-Woong Park, and Taihyun Chang*

Department of Chemistry and Polymer Research Institute, Pohang University of Science and Technology, Pohang 790-784, Korea

Hoichang Yang and Chang Y. Ryu*

Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York 12180

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ABSTRACT: Block copolymer ordering in thin films on a preferentially wetting flat substrate is studied using a polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymer, which forms PMMA cylinders in bulk. Tapping-mode AFM and cross-sectional TEM were employed to characterize the thin film ordered structure of the PS-*b*-PMMA on a flat silicon surface with native oxide that is preferentially wetted by PMMA blocks. The PS-*b*-PMMA in thin film develops hexagonally perforated layer (HPL), which is different from its cylindrical bulk morphology. The HPL structure of PS-*b*-PMMA exhibits islands and holes at the surface, which persists up to the film thickness as high as $6L_0$. Surface-induced reorganization of the block copolymers on PMMA-preferring flat surface may be responsible for the formation of the layerlike nonbulk structure of HPL, which has been templated from the flat surface and propagated into a multilayered HPL films.

Introduction

Thin film ordered structures of block copolymers have been successfully used in the “bottom-up” nanofabrication to template their nanoscale self- and directed-assembly into nanoscale patterning on hard substrates.[1−3] While the bulk phase behavior of block copolymer has been well described in terms of two parameters, the composition and the degree of segregation between the blocks,[4] the thin film ordered structures and their orientations can be complicated due to the film thickness constraints and interfacial interactions.[5−7] There have been extensive studies on directing the block copolymer structure in thin films via manipulation of substrate topography[8−10] or surface energy modification using random copolymer brush[11,12] or cross-linked thin film layer,[13] and via kinetic controlling, such as the solvent evaporation rates.[14,15]

In thin films, the interfacial interaction may influence the thin film morphology to be different from the bulk, if the interfacial energy between the substrate (or air) and the individual block is different. If the surface is preferentially adsorbed by one block to minimize the interfacial energy while satisfying the commensurability of the block domain, the alignment and the shape of the domain structure in the vicinity of the interface may be different from the bulk. In a symmetric diblock copolymer (similar block lengths), because of the conformational planar interface of lamellae to the flat surface, the preferential attraction of one block to the substrate surface leads to the parallel orientation of lamellae without inducing a new morphology in thin films.[6] In the case of the asymmetric block copolymers forming cylinder or sphere domains, however, theoretical works suggest that the preferential wetting of one block in thin films may induce layerlike domain structures in a region close to the planar surface.[16−18] It is also predicted that the extent of the region where this layerlike character predominates depends on the extent of segregation of the two blocks.[16] Deviations from the bulk ordered structure, such as perforated lamellar and lamellar structures, have been experimentally observed in thin films of diblock copolymers, such as polystyrene-*b*-poly(2-vinyl pyridine) ($f_{\mathrm{P2VP}} \sim 0.25$)[19] and poly(ethylene−propylene)-*b*-poly(ethylethylene) ($f_{\mathrm{PEE}} = 0.23$),[20] and triblock copolymers, such as a polystyrene-*b*-polybutadiene-*b*-polystyrene (14k−73k−15k) on silicon substrate with native oxide.[17]

In this study, we investigate thin film morphology of a polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymer, which forms PMMA cylinders in bulk. We have applied a semi-prep HPLC separation technique to remove the homo-PS precursors and then eliminate the possible complication due to the surface migration of the homo-PS in thin films. We found that the HPL morphology of HPLC fractionated PS-*b*-PMMA exhibited the layer ordering can extend over $6L_0$. Such a long-range ordering of the HPL structure is unexpected from the current theoretical prediction and would be a result of the strong surface field.

Experimental Section

A PS-*b*-PMMA diblock copolymer was purchased from Polymer Source ($M_w = 66.4$ kg/mol, $\mathrm{wt}_{\mathrm{PMMA}} = 0.311$, $M_w/M_n = 1.02$). The block copolymer was fractionated to remove the homo-PS precursor by normal phase liquid chromatography (NPLC) with a bare-silica column (Nucleosil, 100 Å pore, 100 × 22 mm) and a mixture of isooctane/THF (35/65, v/v) as the mobile phase.[21] The details of the NPLC fractionation of the PS-*b*-PMMA sample were reported previously.[22,23] The homo-PS which amounts to about 10 wt % of the as-received block copolymer was removed from the sample. The molecular weight and the composition of the purified PS-*b*-PMMA were characterized by size exclusion chromatography (SEC) and ^{1}H NMR, respectively.[23] The molecular weight of the PS-*b*-PMMA is 66.5 kg/mol ($M_w/M_n = 1.01$), and the weight fraction of PMMA block is 0.345. The PMMA content is larger in the fractionated sample than the as-received sample due to the removal of homo-PS precursor.

Silicon wafers were treated with piranha solution (conc H_2SO_4/30% H_2O_2 = 3/1 (v/v)) for 1 h to form a clean silicon oxide surface

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* Corresponding authors. Taihyun Chang: Tel +82-54-279-2109; FAX +82-54-279-3399; e-mail tc@postech.edu. Chang Yeol Ryu: Tel 518-276-2060; FAX 518-276-4887; e-mail ryuc@rpi.edu.

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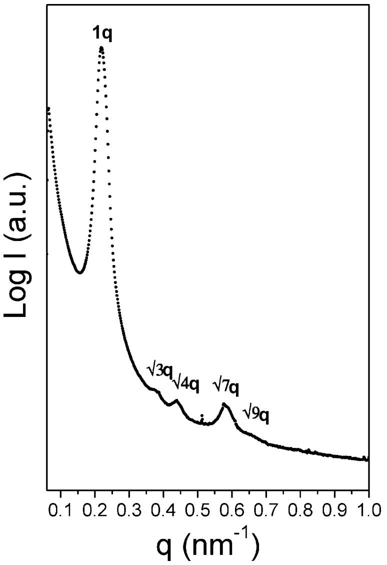

Figure 1. SAXS profile of PS-*b*-PMMA (wt$_{PMMA}$ = 0.345) in bulk annealed at 180 °C for 3 days.

and then extensively rinsed with deionized water. Toluene (Duksan, HPLC grade) solution of PS-*b*-PMMA (1−3 wt %) was spin-coated onto the silicon wafer at various spin speeds (2000−5000 rpm). The polymer films were annealed in a vacuum oven at 180 °C for 3 days.

For the characterization of bulk morphology, transmission SAXS measurement was carried out at room temperature using the synchrotron SAXS facility in Pohang Light Source, Korea.[24] The wavelength of the X-ray beam was 1.608 Å, and the energy resolution ($\Delta\lambda/\lambda$) was 1.5 × 10^{-2}. The 1 mm thick PS-*b*-PMMA sample was annealed at 180 °C for 3 days under vacuum and cooled to room temperature.

The surface morphology of the thin films was observed by a tapping mode AFM (Multimode Nanoscope IIIa, Digital Instrument/Veeco) under ambient conditions. In addition, the internal structure of PS-*b*-PMMA films was investigated by cross-sectional TEM. A PS-*b*-PMMA film on silicon substrate was first coated with a thin carbon layer and covered with an epoxy resin (Electron Microscopy Sciences, cat. #1232). After curing the epoxy resin at room temperature for 12 h, the epoxy-covered film was peeled off from the silicon substrate by immersing the sample in liquid nitrogen. A thin carbon layer was again deposited to the silicon substrate side of the detached film and then embedded with epoxy resin as before. Thin (∼50 nm) sections from the embedded film were obtained using a Reichert Ultra Microtome at room temperature with a diamond knife, and the PS domains in the sectioned films were selectively stained with RuO_4. TEM was performed on a Hitachi-7600 operating at 80 kV.

Results and Discussion

The SAXS profile of the bulk phase for the PS-*b*-PMMA is shown in Figure 1. The SAXS profile exhibits multiple-order scattering maxima at the positions of $1{:}\sqrt{3}{:}\sqrt{4}{:}\sqrt{7}{:}\sqrt{9}$... relative to that of the first-order peak, indicating that the PS-*b*-PMMA forms an ordered structure of the hexagonally packed cylinders in bulk. The domain spacing of the cylinder phase is 28.7 nm.

The surface morphologies of thin films of the PS-*b*-PMMA at different thickness were investigated and shown in Figure 2. The film thickness was measured by AFM after scratching the film.[25] In contrast to the cylinder morphology of the sample in bulk, the thin film samples exhibit a different morphology of a quite regular pattern of numerous dots. As shown in Figure 2B, Fourier transform of the dot pattern in the marked area shows that the dots are disposed in a nearly perfect hexagonal array.

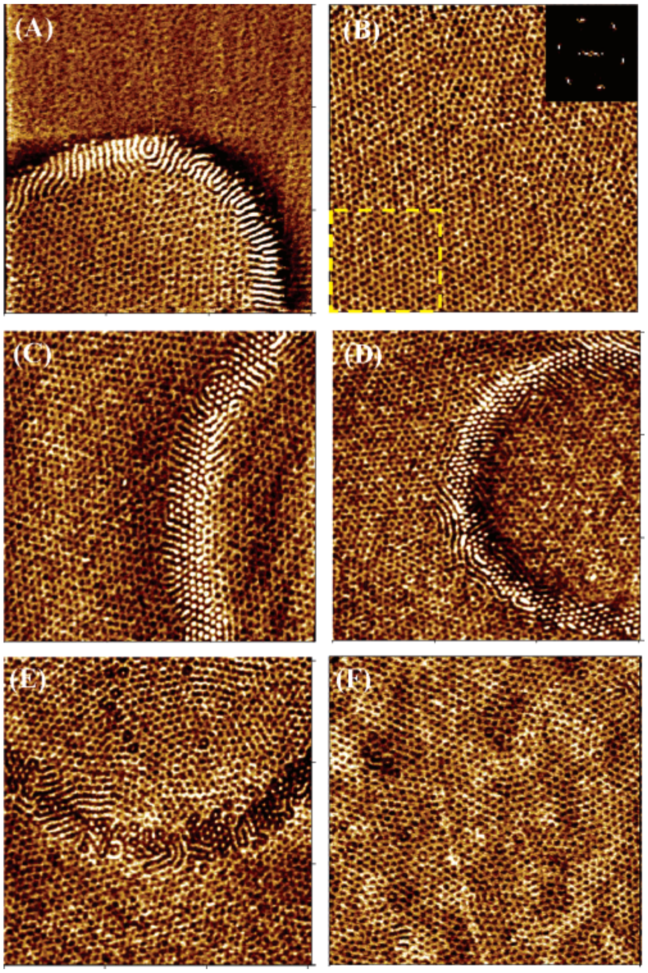

Figure 2. AFM phase-images (1.5 × 1.5 μm) of PS-*b*-PMMA (wt$_{PMMA}$ = 0.345) films showing the island or hole structure depending on film thickness: (A) island, $^{1}/_{2}L_0 < L < {}^{3}/_{2}L_0$; (B) flat surface, $L \sim {}^{3}/_{2}L_0$; (C) island, $^{3}/_{2}L_0 < L < {}^{5}/_{2}L_0$; (D) hole, $^{3}/_{2}L_0 < L < {}^{5}/_{2}L_0$; (E) island, $^{5}/_{2}L_0 < L < {}^{7}/_{2}L_0$; (F) $L \sim 6L_0$. L_0 (∼30 nm) is the thickness of one repeating layer.

Considering the weight fraction of PMMA in the sample (wt$_{PMMA}$ = 0.345), the dotted pattern can represent either perpendicularly oriented cylindrical morphology of PMMA cylinders or hexagonally perforated layer (HPL) morphology with a PMMA layer sandwiched by PS layers and perforated by hexagonally packed PS short struts.

The AFM phase images of the thin films at different thickness also exhibit well-developed island and hole structures as presented in Figure 2A−F. The island and hole structures result from the commensurability in a layered structure. Surface energy differences between the blocks leads to the orientation of lamellae or cylinders parallel to the film surface.[26,27] Since the polar PMMA layer wets the polar substrate surface preferentially and the PS layer tends to be exposed to the air due to its lower surface energy,[11,28] only the films of a half-integral multiple of the repeating layers are able to exhibit a smooth surface without islands or holes. This island and hole structure of the thin film is a convincing piece of evidence against the perpendicularly oriented cylinder morphology since the perpendicularly oriented cylinder morphology is not bound to such commensurability.

The dotted pattern is only observed by hard tapping and prevails in all the film surfaces regardless of the thickness except for the ground area of the island structure in Figure 2A. These observations support that the dot pattern represent the PMMA layer perforated by small PS domains beneath the PS top layer.

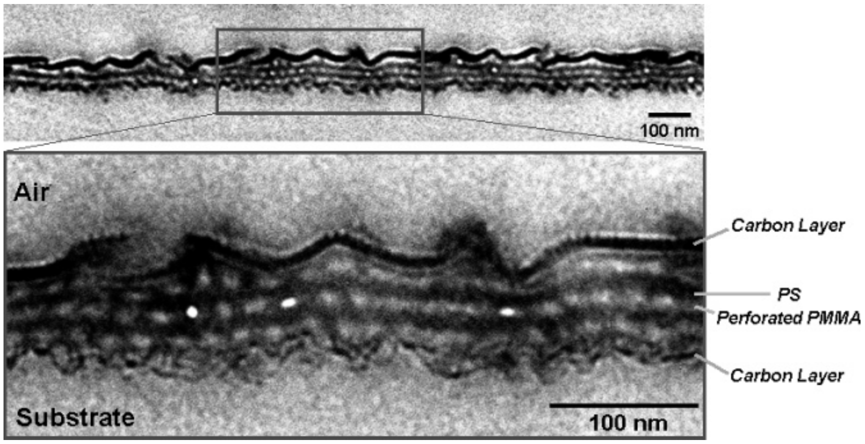

Figure 3. Cross-sectional TEM images of PS-*b*-PMMA ($wt_{PMMA} = 0.345$) film stained with RuO_4.

The ground area in Figure 2A is the $^1/_2L_0$ thick film while the island is L_0 thick. The $^1/_2L_0$ thick film represents the PS brush area where the PS-*b*-PMMA chains are bound to the substrate via the adsorption of PMMA blocks to the oxidized silica surface. The dot patterns persist up to the film thickness as high as $6L_0$, as shown in Figure 2F. The observed surface morphologies at various film thicknesses unambiguously confirm that the morphology in thin film showing the dotted surface structure corresponds to the HPL phase. However, the fact that the HPL structure is observed at the surface does not necessarily implies that a HPL is also formed inside of the thin film of multiple layers. Therefore, we investigated the internal structure of the film by using cross-sectional TEM.

Figure 3 shows the cross-sectional TEM images of the PS-*b*-PMMA film, which exhibits the hexagonally arrayed PS dots on the surface. The darker part of the image corresponds to the PS blocks selectively stained with RuO_4 and the brighter part represents the PMMA domain. The TEM image clearly shows that the PMMA layers are perforated by PS domains, which unequivocally confirms that the PS-*b*-PMMA thin film has HPL structure inside of the thin film, not just the surface layer.

Noncylindrical phases like HPL or lamellar in thin film have been found from the block copolymers showing cylinder bulk phase.[29−31] The phase transitions could be explained by the depletion of the *major* block due to the preferential affinity of the major block to the interface.[32,33] The depletion of the major block enriches the content of the minor block in the middle layer and leads to a more symmetric morphology relative to the cylinder such as the lamellar or the perforated layers. In this system, however, the phase change is not due to the depletion of the major block since the PMMA block (showing the high affinity to the substrate surface) is the minor block. The preferential wetting of the PMMA block onto the substrate must have reduced the content of the minor block (PMMA) in the middle layer, which would have led to a more asymmetric morphology. This is opposite to the current observation.

Furthermore, the thin film systems showing the phase change due to the depletion effect in the previous reports was thinner than $2L_0$.[29−31] In this study, the HPL structure is maintained over multiple layers ($>6L_0$), indicating the long-range effect of the surface field overcoming the equilibrium structure in bulk. Turner et al. predicted the transition from the surface field driven lamellar layer to the bulk cylindrical phase in a thick film.[16] The intermediate structure like modulated lamellae was depicted, but the HPL structure was not predicted since the in-plane density variation could not be taken into account. The HPL structure found in this system demonstrates that the interaction between PMMA chains and silicon oxide surface can be sufficiently large to induce the phase transition of the cylinder phase into the layered structure over several layers. And the planar character of the boundary surfaces lead to the stabilization of the HPL phase.

Such a multilayer HPL structure in block copolymer thin film deviating from the bulk morphology has not been observed to our knowledge. In the previous works, only the single brush layer at the interface was found, and the structure on top of the surface layer is more or less the same as the bulk structure.[19,20,34] One of the possible reasons why the PS-*b*-PMMA used in this study shows the multilayer HPL phase would be the high volume fraction of the minor component of this block copolymer ($f_{PMMA} = 0.335$) relative to the polymers used in the other studies found in the literature ($f_{minor} < 0.30$).[19,20,34] It remains to be confirmed whether the higher volume fraction of the minor component in the block copolymer used in this study indeed allows the enhanced stability of the multilayer HPL structure.

In summary, we obtained a pure PS-*b*-PMMA diblock copolymer by HPLC fractionation method. While hexagonally packed cylindrical structure is favored in bulk, the PS-*b*-PMMA in thin film exhibits HPL structure over multiple layers. The morphology change from cylinder to HPL in this system cannot be explained by the depletion of the PMMA blocks due to the preferential wetting of the silicon oxide surface but likely reflects the strong surface effect on the block copolymer morphology in thin film. The change in the phase diagram and the stability of the HPL phase in thin film would be interesting subjects to be investigated further.

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