

Getting to the Bottom Morphology of Block Copolymer Thin Films^{*}

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Abstract We demonstrate a general approach for attaining the bottom morphology of block copolymer (BCP) thin films. In our former measurements on PS-*b*-PMMA films, surface morphology maps of the BCP films revealed distinct ordering regimes where the cylinders orient predominantly perpendicular or parallel to the interface and an ‘intermediate’ regime where these morphologies coexist. However, this earlier work did not explore the bottom morphology of BCP thin films. In this study, we investigated the block copolymer morphology near the solid substrate in the cast block copolymer film having a perpendicular cylinder morphology on the surface.

Keywords: Block copolymer; Thin film; Morphology.

INTRODUCTION

Periodically ordered nanostructures arising from the microphase separation of block copolymers (BCP) through self assembly are considered to be a viable fabrication platform for nanoscale patterning for next generation high density data storage and ultra-low density dielectric materials^[1, 2]. Of particular interest are block copolymers that form cylindrical nanodomains oriented perpendicular to the substrate on which the BCP films are cast. Understanding the factors that control the microstructure of polymer thin films on hard substrates is important for templating applications or applications as barrier membranes. Characterization of these materials requires an investigation of the surface morphology as well as the internal structures of these films. Since the film substrate interface often plays a significant role in directing the BCP morphology through selective surface interactions, the BCP in the vicinity of the solid substrate is of particular interest. Routine, high resolution measurement method of this substrate morphology is critically needed.

Traditional transmission electron microscopy (TEM) is a powerful tool for this type of structural determination, but this method is time consuming and technically difficult. Moreover, it is not always possible to perform cross-sectional dissection of these ultra thin films (microtoming) in a manner that retains film orientation with respect to supporting substrate. AFM is a powerful tool to image the surface morphology of the polymer-air interface under ambient atmosphere condition, but its application for structural analysis on the bottom of the films has been limited to date due to difficulties in sample preparation and the limited

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experimental methods available for such studies.

Fasolka *et al.*^[3, 4] demonstrated a robust method using poly(acrylic acid) (PAA) that opens the possibility for imaging by TEM the microphase-separated nanostructures of very thin BCP films. Russell *et al.*^[5] have likewise shown that images of the underside of BCP films are possible using hydrogen fluoride (HF) solving silicon substrate technique. Recently, we studied a series of flow coated cylinder forming block copolymer thin films showing a typical microphase separation with cylinders oriented perpendicularly to the surface near the air interface^[6, 7], where the perpendicular orientation of the cylinders on the air surface of thin films was confirmed by AFM and rotational SANS measurements. Rotational SANS also indicated a mixed morphology deeper within the film. The BCP morphology near solid substrate was not determined in that work, however, here we address this basic characterization problem by lifting off the film from the substrate and utilizing atomic force microscopy (AFM) to image the underside of BCP films. This new method of BCP characterization notably requires no staining procedure or microtoming. Moreover, this method of sample preparation is not limited to thin film and silicon substrate and can be readily applied to other polymeric films with different film thickness and on different substrates. We demonstrate the application of this method to the characterization of the BCP morphology near the solid substrate in cast BCP film forming a perpendicular cylinder morphology.

EXPERIMENTAL

Preparation of BCP Thin Films

PS-*b*-PMMA with a total relative molecular mass of 47.7 kg/mol, a polydispersity index of 1.07 and a mass fraction of PS of 0.74 and PS-*b*-PEO with a total relative molecular mass of 22.5 kg/mol, a polydispersity index of 1.08 and a mass fraction of PS of 0.71 were purchased from Polymer Source, Inc. The 25% by mass aqueous solution of 250 kg/mol poly(acrylic acid) (PAA, polydispersity index ≈ 2) were purchased from Polysciences Inc. PS-*b*-PMMA and PS-*b*-PEO films were prepared *via* spin coating and flow coating from a 4% by mass block copolymer solution in toluene onto the plasma treated Si wafer. The film thickness was characterized with UV-Visible interferometry (0.5 mm diameter with standard uncertainty of ± 1 nm at 500 nm film thickness). The samples were placed in a vacuum oven to anneal at different temperatures for 15 h. A typical procedure for generating a block copolymer film *via* flow coating is outlined as follows. The substrate is affixed to the translation stage. A knife blade is mounted on the tip-tilt-rotation stage. The blade is positioned at a fixed angle of 5° in our system and brought down into contact with the substrate. At this point, the blade tilt is adjusted to bring the blade level with the surface of the substrate. The blade is then elevated to a given height above the substrate (typically 200 μm), and a drop of polymer solution (typically 50 μL for a 25 mm wide blade) is syringed along the leading edge of the blade. Since the blade height is only a couple hundred μm , capillary forces wick and hold the solution under the blade. Once the solution is placed under the knife blade, the operational commands are sent to the translation stage to initiate the desired motion. As the stage moves, a liquid film remains behind. The liquid film then dries to a solid film whose thickness is determined by the solids concentration in the wet film.

Atomic Force Microscope (AFM)

AFM images were obtained in both height and phase modes with an Asylum MFP-3D scanning force microscope in the tapping mode. The tapping mode cantilevers with spring constant ≈ 50 N/m, resonance frequency range from 100 kHz to 200 kHz and the drive frequency with the offset of -5% were used. Both height and phase images were recorded simultaneously during scanning. The minor phase (PMMA cylinders) and major phase (PS matrix) correspond to darker and lighter regions in the AFM image, respectively. To obtain the real space images of AFM to avoid the artifacts, the samples with the same annealing conditions were scanned in multiple positions in order to get more images with $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$.

RESULTS AND DISCUSSION

The poly(styrene-block-methyl methacrylate) (PS-*b*-PMMA) and poly(styrene)-*b*-poly(ethylene oxide) (PS-*b*-

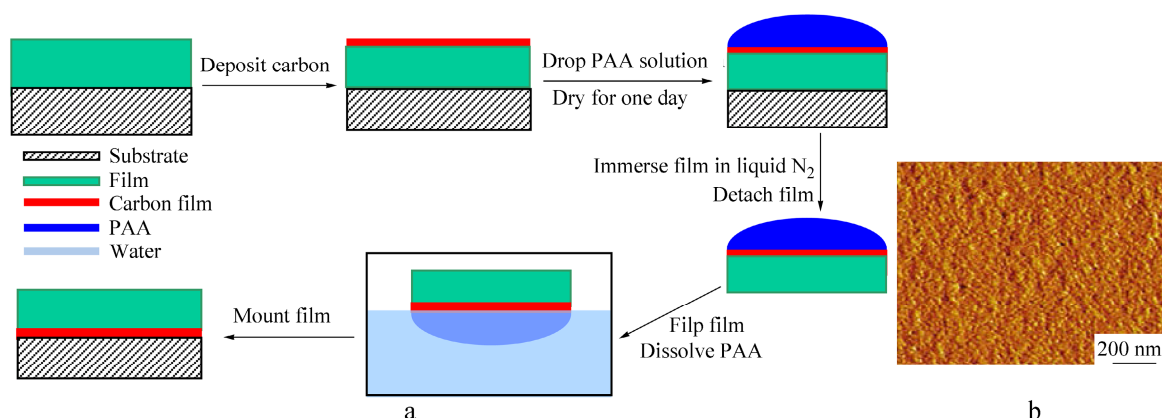


Fig. 1 Schematic figure showing a procedure for preparing the film substrate interface of the original film to be presented in a top view geometry (a); The AFM phase image of the bottom layer of as-cast BCP film (b)

PEO) microphase-separated films were prepared on a silicon wafer. Figure 1(a) illustrates the procedure for preparing the film substrate interface of the original film for measurements by AFM after a film delamination and flipping procedure. The block polymer thin films are cast on silicon wafers and annealed. After that, the films are coated with vapor-deposited carbon under vacuum. The introduction of evaporated carbon layer promoted the adhesion between poly(acrylic acid) (PAA) and BCP film and seemed to ease PAA/specimen film removal^[3]. Then, the PAA solution was deposited onto the specimen film by hand using a pipet and left to dry for one day at the room temperature until it was stiff. The PAA solution deposited on the specimen formed a dome with diameter of 3 mm to 4 mm (approximately 3 mg PAA solution). The PAA solution was poured on to the center region of specimen film (the PAA solution would flow off the edge of the substrate if deposited on the region of specimen film near the edge of the substrate.). In our study, the drying of PAA solution is extremely slow. We used a petri dish to cover the sample during the drying of PAA solution that would maintain a low evaporate rate. The rapid evaporation of the water in PAA solution could lead to the unwanted cracking and cavitations. The relatively large size of the intact PAA/specimen can be obtained during the slow evaporation of water in PAA solution. The stiff PAA/specimen film on the substrate was immersed in the liquid nitrogen for approximately 2 sec. Since the difference in thermal expansion coefficients between the substrate and polymer film is dramatic, the abrupt different contractions caused by the rapid cooling under the liquid nitrogen lead to the PAA/specimen layer to detach easily from the substrate. The PAA then was dissolved in water by placing the specimen/PAA complex on a pool of deionized water with the PAA side down. The floating specimen film was mounted on a silicon wafer for AFM and dried under ambient condition (see Fig. 1a). Without stirring the deionized water, the specimen film floating on the surface of water was relatively stable. We did not observe the specimen film was turned upside down during dissolving PAA and retrieving the specimen film on the substrate. The AFM images of the top layer were captured prior to coating carbon layer onto the specimen film and the AFM images of the bottom layer were obtained after dissolving the stiff PAA layer in a bath of deionized water and retrieving the specimen film onto the substrate. Here, the layer of evaporated carbon was used to protect the specimen film through later steps including the immersion of films into the liquid nitrogen and dissolution of PAA on a pool of deionized water. After dissolving the stiff PAA layer, the specimen carrying the carbon layer was floating on the surface of deionized water. The carbon layer protecting the specimen film directly contacted with water and the bottom layer of specimen film (now at the polymer-air interface) was not immersed in the deionized water. The only concern was the influence of water vapor on the morphology of bottom layer during the sample preparation. In our study, the dissolution of the stiff PAA was carried out in an open system and the pressure of water vapor was relatively low as compared to a close system, *e.g.*, in a desiccator or glass box. In order to investigate the influence of the water vapor on the morphology of the bottom layer of specimen, we detached the as-cast BCP film using the same sample preparation process. The AFM image (see Fig. 1b) shows a

featureless structure of the bottom layer near the substrate. It indicates that no significant evolution of the morphology of bottom layer is observed during the sample preparation and the influence of the water vapor on the morphology of the bottom layer is not obvious.

First we gave an overview of our morphological observations on ordered BCP films and our interpretation of these patterns that the residual solvent and solvent annealing can perturb the BCP ordering. We examined these films by AFM to characterize the interface of these films. Figures 2 and 3 show that the top (air interface) and bottom (substrate interface) images of PS-*b*-PMMA films annealed at 182 °C for 6 h and PS-*b*-PEO cylinder-forming block copolymer thin films after annealing in the mixture of water and toluene saturated vapor in enclosed chamber for 45 h. The cylindrical PEO domains are present on both the top and the bottom of the film, as shown in Figs. 2(a) and 2(b). The ring patterns in 2D fast Fourier transform (FFT) image and FFT intensity peaks in 1D Power Spectra images provide the evidence of the repeat period of the block copolymer. The repeat distance of PS-*b*-PEO microdomains (*d*-spacing) obtained by taking a fast-Fourier-transform of the AFM image of a BCP surface pattern is 35 nm. The thickness of the 120 nm thin film is approximately 3 times of the bulk equilibrium period. Annealing the film in the presence of the mixture of water-toluene saturated vapor, that leads to a PS-*b*-PEO film forming an array of nanoscopic, vertically oriented cylindrical domains of PEO. The preferential interactions of PEO block with the substrate and the lower surface energy PS block ($\gamma_{\text{PS}} = 33 \text{ mN/m} < \gamma_{\text{PEO}} = 43 \text{ mN/m}$) would promote an orientation of the cylindrical microdomains parallel to the surface at equilibrium. The non-equilibrium structure of perpendicularly oriented cylinders is caused by the solvent annealing procedure^[5, 8]. Due to the presence of toluene and water, which are selectively good solvents for PS block and PEO block, respectively, the interfacial interactions are strongly modified. Any preferential affinity of the blocks to the substrate and air interface tending to align the copolymer chains parallel to the substrate or air surface is markedly reduced and, consequently an orientation of the cylinder morphology normal to both surfaces is formed. In the PS-*b*-PEO system, the ‘breath figure’ effect caused by the solvent annealing would induce the ordering of BCP with a perpendicular cylinder orientation at the polymer-air interface. ‘Breath figure’ describes the formation of structures caused by condensed water vapor on a cold surface^[9]. The water is good solvent for PEO block. The water condensation onto the hydrophilic domain leads to PEO cylinder oriented

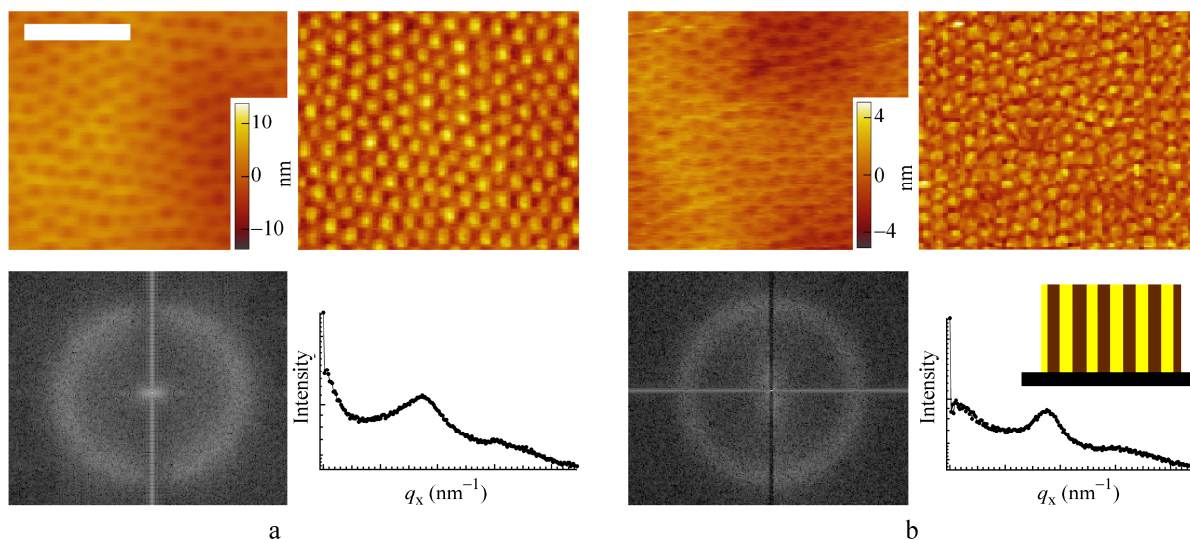


Fig. 2 AFM top layer (a) and bottom layer (b) images of a spin cast 120 nm PS-*b*-PEO film after solvent vapor annealing in the mixture of water and toluene for 45 h

The scale bar in (a) corresponds to 200 nm and is applied to (b). Both height image (left upper) and phase image (right upper) are shown. The fast Fourier transform (FFT) of the phase image and 1D Power Spectra from FFT Image by taking a circular average of the intensity of 2D FFT image are shown to the left bottom and right bottom, respectively.

perpendicularly to the polymer-air interface. The ‘neutral’ boundary condition at this interface caused by the solvent vapor and/or the ‘breath figure’ effect during the solvent annealing would induce the ordering of BCP with a perpendicular cylinder orientation at the polymer-air interface and propagate into the film. The perpendicular cylinders in the PS-*b*-PEO film were observed on the bottom layer of specimen film near the substrate. We suggested that the perpendicular cylinders induced at the polymer-air interface propagated through the whole film. Upon taking the samples out from the chamber filled with the mixture of toluene and water vapors, the toluene concentration decreases much faster than water due to the faster evaporation rate of toluene. The glass transition temperature of the PS matrix rapidly increases above room temperature, locking in the non-equilibrium oriented morphology.

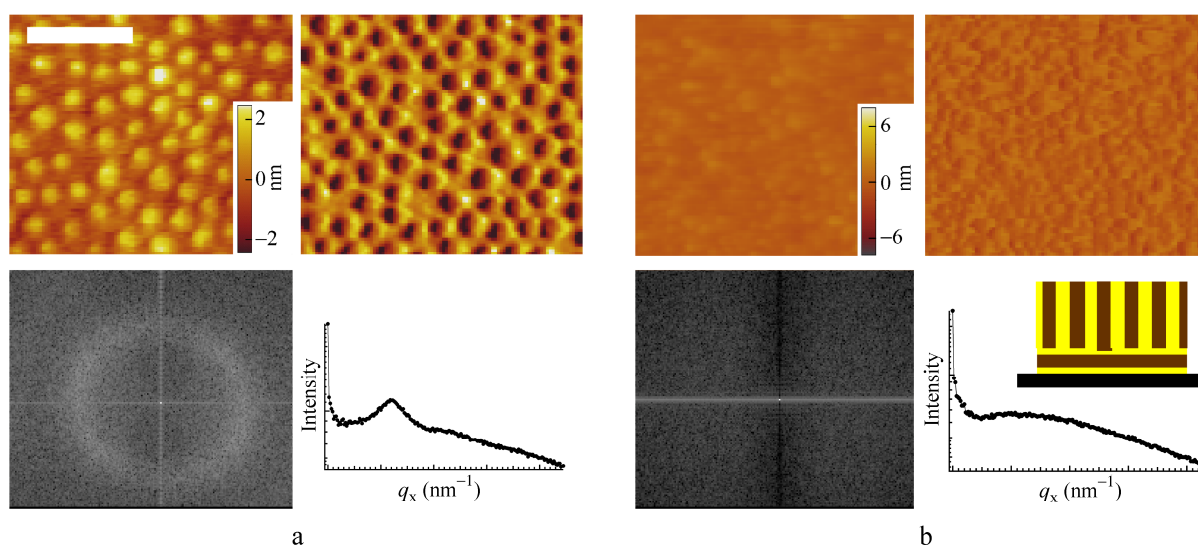


Fig. 3 AFM top layer (a) and bottom layer (b) images of a 250 nm flow cast PS-*b*-PMMA film after annealing in a vacuum oven at 182 °C for 6 h

The scale bar in (a) corresponds to 200 nm and is applied to (b). Both height image (left upper) and phase image (right upper) are shown. The fast Fourier transform (FFT) of the phase image and 1D Power Spectra from FFT image by taking a circular average of the intensity of 2D FFT image are shown to the left bottom and right bottom, respectively.

We also examine PS-PMMA block copolymer films by our methods. Heating a PS-*b*-PMMA film flow coated^[10] from a 4% block copolymer solution in toluene to 182 °C for 6 h, well above the glass-transition temperature of PS and PMMA, produces a film with perpendicularly oriented cylinders on the top (Fig. 3a) and featureless wetting layer on the bottom (Fig. 3b). The selective interaction of one of the copolymer blocks (PMMA) for the plasma treated silicon wafer substrate^[11, 12] because of the lower wetting energy of PMMA^[13–15] is expected to lead to the formation of PMMA wetting layer near this boundary. However, our previous study^[6] shows that an appreciable amount of the casting solvent (toluene) is retained in PS-*b*-PMMA BCP films, leading to robust tendency for the cylinders to orient normal to the substrate near the polymer-air interface of the film since the polymer-air boundary is more susceptible to perturbation by the residual solvent due to weakly selective for PS near the polymer-air interface. The question is then how far the cylinders propagate into the film from the polymer-air interface and, in particular, we are concerned whether the cylinders span the film as a whole. To answer these questions we have examined the bottom interface of the BCP film. The AFM images (see Fig. 3) show that the perpendicular cylinder layer is formed on the polymer-air interface, and near the solid substrate, the perpendicular cylinder orientation is not observed. These observations are consistent with our previous work^[6] that the cylinders oriented normal to the polymer-air was induced at the polymer-air interface and propagated into the film based on atomic force microscopy, neutron reflectivity (NR), and rotational small

angle neutron scattering (RSANS). Toluene is a good solvent for both PS and PMMA and the segregation of toluene at the polymer-air interface is then expected to weaken the already weak preference for polystyrene to segregate to the polymer-air interface in the films^[16]. The resulting 'neutral' boundary condition at this interface would then lead to a robust tendency for the PMMA cylinders to orient normal to the polymer-air interface. The cylinders near the substrate were oriented parallel to substrate due to relatively strong affinity of PMMA to the substrate (the interaction between the polymer and substrate dominated the ordering of BCP.)

CONCLUSIONS

We have succeeded in developing imaging the bottom morphology of model BCP films of interest in electronic application under ambient atmosphere by AFM, through a simple sample preparation procedure. The bottom AFM imaging demonstrated in this study provides a simple analytical technique to visualize the detailed interface structures of well ordered microphase-separated nanostructures that are related to the film structure at the top air surface. While the substrate interfaces of high quality microphase separated films provide the clear images of the nanostructure, the technique can be readily applied to other polymeric films with different film thickness and on different substrates. Additionally, these methods are expected to be invaluable in quantitative interpretation of structural data in 3D for polymer thin films obtained by scattering methods such as GISAXS and rotational SANS.

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