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Notes

Kinetic Constraints on the Development of Surface Microstructure in SBS Thin Films

Ginam Kim and Matthew Libera*

Department of Materials Science and Engineering,
Stevens Institute of Technology, Hoboken, New Jersey 07030

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Studies of block copolymer surfaces have shown that the lower surface-energy constituent preferentially locates itself at the free surface. For example, Hashimoto and Hasegawa[1,2] used transmission electron microscopy (TEM) with microtomed cross-sections of bulk specimens to show that a surface layer of dark contrast due to OsO_4-stained polyisoprene forms in solvent-cast lamellar polystyrene−polyisoprene (PS−PI) diblock. Similar observations were made by Schwark et al.[3] for a PS-56 wt % polybutadiene (PB) diblock cast and vacuum annealed. Green et al.[4,5] used XPS and Russell et al.[6,7] used SIMS and neutron scattering on diblock PS−PMMA (poly(methyl methacrylate)) to show that, in the strong-segregation limit, the lower surface energy PS forms a continuous layer at a film's free surface.

Departures from the case where the lowest surface energy constituent is found at the free surface have been reported. Turturro et al.[8] used TEM to study solution-cast PS−PB diblock thin films. They showed a number of cases where both the lower and higher surface-energy block components were present at the surface. Chen et al.[9] found using FTIR and ESCA a surface layer enriched in PDMS in PS/PDMS (poly(dimethylsiloxane)/PS triblock after solvent evaporation in air. Green et al.[10] showed using XPS that under relatively fast solvent evaporation conditions the PS fraction in PS/PMMA symmetric diblock copolymers deviates from unity allowing some surface enrichment by the slightly higher surface-energy PMMA block. Thomas et al.[11] and Schmitt et al.[12] using XPS also found two-component surface layers in PS/PEO (poly(ethylene oxide) and BAPC (Bisphenol A polycarbonate)/PDMS block copolymer samples made by solvent evaporation in air.

The present research uses cross-sectional TEM combined with quantitative image analysis to study the surface morphology in solvent-cast SBS (polystyrene−polybutadiene-polystyrene) thin films. Departures from the thermodynamically preferred case involving a continuous PB surface layer are observed. Films cast under relatively fast solvent evaporation conditions have a demixed surface morphology where both PS and PB microdomains are present at the free surface. Post-cast annealing generates a continuous surface layer of dark contrast, but quantitative analysis indicates that this layer is partly enriched by PS.

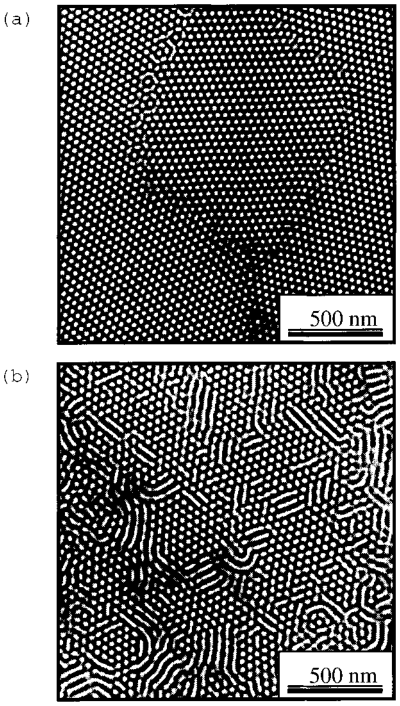

Figure 1. Plan-view bright-field TEM images of the (a) as-cast and (b) annealed OsO_4-stained SBS thin films.

Thin-film specimens (~100 nm thick) of SBS triblock copolymer (30 wt % PS, $M_w = 112\ 000$) were prepared by casting 0.1 wt % solutions in toluene onto polished NaCl single crystals. Casting was performed in a glass dish with a small hole in its foil cover. Toluene drops were place around the substrate to generate a toluene partial pressure. Films were produced after about 3 h. Each film was cut into squares and floated onto water. Squares approximately 1 mm × 1 mm were collected onto holey-carbon TEM grids. Specimens were annealed on their support grids at 140 °C for 18 h at 10^{-6} Torr. Films were stained by 20 min exposure to OsO_4 vapor. After plan-view study, a thin carbon layer was evaporated on each side of the stained film. The film and its Cu grid were then embedded in epoxy and cryomicrotomed at −130 °C. Plan-view and cross-sectional specimens were examined in a Philips CM30 Supertwin TEM and a Philips CM20 FEG TEM/STEM. Digital images were collected directly using a Gatan Multiscan camera (CM20) or by digitizing prints and quantitatively analyzed using the Digital Micrograph software system from Gatan.

Figure 1 shows plan-view images of as-cast[1a] and post-cast annealed[1b] specimens. The as-cast microstructure consists of PS cylinders on a hexagonal array in a continuous PB matrix as expected from the phase diagram.[13−15] The cylinders are oriented perpendicular to the film plane. The annealed microstructure shows a mixed morphology with regions of vertical cylinders and regions in the process of transforming to the more stable in-plane cylinder morphology.[16]

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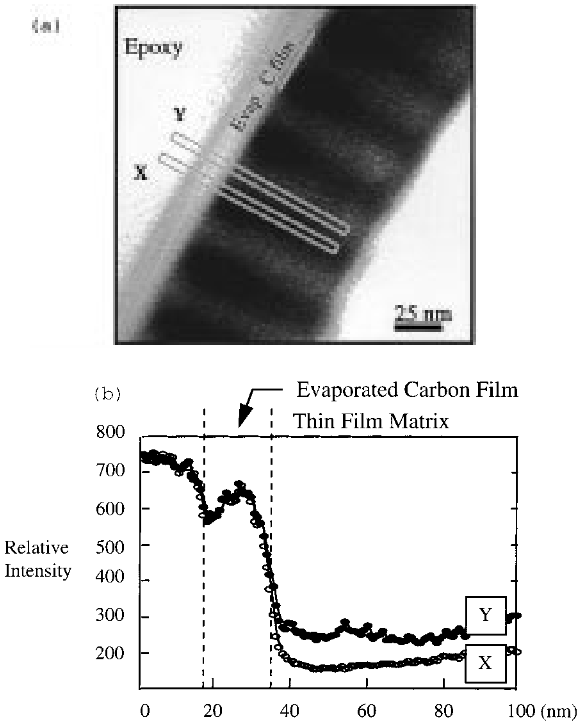

Figure 2. (a) Cross-sectional image of as-cast vertical cylinder morphology with (b) line profiles (X and Y) showing that a pure PB layer does not exist at the free surface.

Figure 2a shows a cross-sectional image of an as-cast film. X and Y in Figure 2b are line profiles plotting image intensity in arbitrary units as a function of position. These profiles were taken from the regions indicated by the rectangular boxes and were averaged over a 10-pixel width to reduce noise due to nanoscale fluctuations in the Os distribution. Profile X shows a region of uniform dark contrast through the bulk of the specimen. The average intensity there is 182. There is a steep rise in the intensity at the free surface. The maximum intensity corresponds to the evaporated carbon film. Profile Y again shows a region of uniform contrast in the bulk. The average intensity value there is 262. There is again a steep rise in contrast at the surface. Profile Y is everywhere greater than profile X. This result shows that the surface of the as-cast film has a demixed structure with both PS-rich and PB-rich surface microdomains. If there was a continuous PB layer, profile Y would dip at least to the level of profile X at the surface (at ~40 nm in Figure 2).

Figure 3 shows a similar image and profiles characterizing a post-cast-annealed specimen. The image samples a film region with vertical PS cylinders avoiding areas with the mixed transition morphology.[1b] Figure 3a shows a continuous layer of dark contrast at the free surface. The fact that no such layer is present at the bottom surface is most likely due to the contact between the film and the holey-carbon support during annealing. The intensity profiles in Figure 3b through the PB matrix (X) and the PS cylinder (Y) confirm that the surface layer is PB-rich. The scan across the PS cylinder in the film interior has an average intensity of 180. At the surface the intensity decreases to 108 prior to rising again at the evaporated carbon layer. The fact that the intensity of the PS profile at the surface does not reach a minimum value at least as low as that seen at the surface of the PB profile (~70) indicates that the surface layer is not pure but has some amount of dissolved PS. If there was no PB-rich surface layer at all, the PS intensity profile would not dip at the surface but would instead rise monotonically as in Figure 2b.

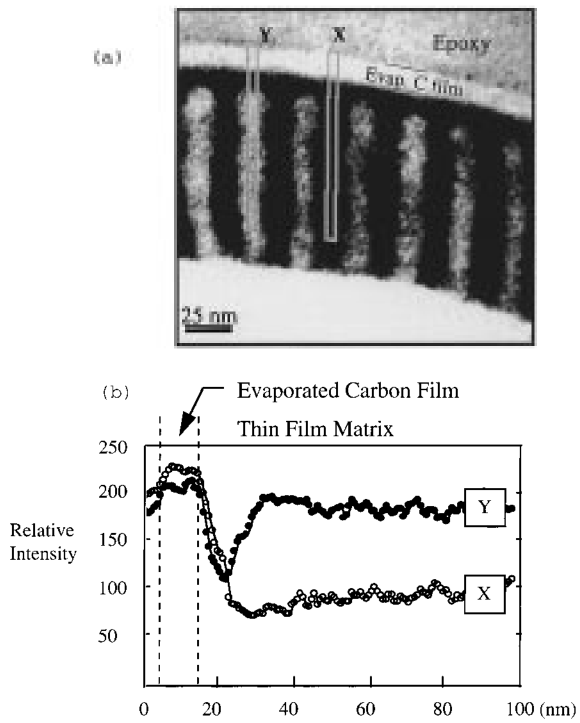

Figure 3. (a) Cross-sectional image of annealed vertical cylinder morphology with (b) line profiles (X and Y) showing a PB-rich surface layer.

The observed deviations from a continuous surface layer of the lower surface-energy PB constituent can be understood in terms of kinetic constraints during film formation. The as-cast film has a demixed surface structure with both PB-rich and PS-rich surface microdomains. The fact that a continuous PB-rich layer is formed upon annealing indicates that this particular solvent evaporation process provides insufficient time with high polymer mobility for adequate microstructural rearrangement to achieve a thermodynamic equilibrium. In addition, the annealed specimen has a PS enrichment in the surface layer above the PS cylinders relative to surface regions above the PB matrix suggesting that the system has still not achieved equilibrium. The obvious kinetic constraints on development of the surface microstructure can in part be attributed to molecular weight considerations. The molecular weight of the PB block is substantially above the PB homopolymer entanglement length. Furthermore, PS blocks exist at both ends of the SBS molecules leading to bridges between PS cylinders and loops back to a given cylinder which further constrain the overall molecular mobility. The ability to form demixed surface structures has implications for adhesive and emerging templating applications. The observations suggest potentially fruitful experiments comparing diblock and triblock architectures of varying molecular weight and composition to identify kinetic windows into generating mesoscale surface structures.

References and Notes

(1) Hasegawa, H.; Hashimoto, T. *Polymer* **1992**, 475.
(2) Hasegawa, H.; Hashimoto, T. *Macromolecules* **1985**, *18*, 589.

(3) Schwark, D.; Vezie, D.; Reffner, J.; Thomas, E. L.; Annis, B. *J. Mater. Sci. Lett.* **1992**, *11*, 352.
(4) Green, P. F.; Christenson, T. M.; Russell, T. P.; Jerome, R. *J. Chem. Phys.* **1990**, 92, 1478.
(5) Green, P. F.; Christenson, T. F.; Russell, T. P. *Macromolecules* **1991**, *24*, 252.
(6) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *Phys. Rev. Lett.* **1989**, 62, 1852.
(7) Russell, T. P.; Coulon, G.; Deline, V. R.; Miller, D. C. *Macromolecules* **1989**, *22*, 4600.
(8) Turturro, A.; Gattiglia, E.; Vacca, P.; Viola, G. *Polymer* **1995**, 36, 3987.
(9) Chen, X.; Gardella, Jr., J. A.; Kumler, P. *Macromolecules* **1992**, *25*, 6621.
(10) Green, P. F.; Christenson, T. F.; Russell, T. F.; Jerome, R. *Macromolecules* **1989**, *22*, 2189.
(11) Thomas, H. R.; O'Malley, J. *Macromolecules* **1979**, *12*, 323.
(12) Schmitt, R. L.; Gardella, J. A., Jr.,; Magill, J. H.; Salvati, L., Jr.,; Chin, R. L. *Macromolecules* **1985**, *18*, 2675.
(13) Richards, R. W. in *Multicomponent Polymer Systems*; Miles, I. S.; Rostami, S., Eds.; John Wiley: New York, 1992; pp 103−147.
(14) Thomas, E. L.; Lescanec, R. L. In *Self-Order and Form in Polymeric Materials*; Keller, A., Warner, M., Windle, A. H., Eds.; Chapman and Hall: London, 1995; pp 147−164.
(15) Schulz, M.; Bates, F. S. In *Physical Properties of Polymers Handbook*; Mark, J. E., Ed.; AIP Press: New York, 1996; p 427.
(16) Kim, G.; Libera, M. *Macromolecules*, in press.
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