Reactive Ion Etching (RIE) Reveals Biphasic Self-Assembled Mesostructures in Block Copolymer Thin Films

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Primary CNF Tools Used: Oxford 81 Etcher

Abstract:

The surface morphology of thin films of a triblock terpolymer was first characterized by atomic force microscopy, which shows a different mesostructure from the one suggested by small-angle X-ray scattering. Reactive ion etching by CF_4 plasma of the polymer film was carried out at CNF to bring out the substructure beneath the surface, which turned out to be biphasic. The plasma etching, combined with microcopy and scattering techniques, offers a powerful tool for a comprehensive probe of the self-assembled mesostructure inside the block copolymer thin films.

Summary of Research:

The surface morphology of block copolymer thin films can be characterized by scanning electron microscopy (SEM) or atomic force microscopy (AFM). It is challenging, however, to gain a real-space picture of the underlying structures with microscopy techniques. In our experiment, thin films of the triblock terpolymer poly(isoprene)-*block*-poly-(styrene)-*block*-poly(N,N-dimethylaminoethyl methacrylate) (PI-*b*-PS-*b*-PDMAEMA, or ISA) were prepared by spin-coating a 5.0 wt% solution in tetrahydrofuran (THF) onto a silicon wafer. After solvent vapor annealing (SVA) in THF for 19 h, Figure 1a,b shows the top surface morphology, as imaged with AFM. Films displayed periodically ordered hexagonal patterns with distinct regions attributed to each of the three blocks: PI?PS core?shell cylinders in a majority PDMAEMA matrix. Figure 2c,d depicts this structure schematically, with PI cylinder cores represented in green, PS cylinder shells in blue, and the PDMAEMA matrix in light pink.

In addition to the surface morphological characterization by AFM, grazing-incidence small-angle X-ray scattering (GISAXS) was performed to better understand the subsurface structures. The observed scattering pattern (Figure 2) was consistent with a core?shell double gyroid structure with the (211) planes parallel to the substrate and compressed 52% along [211] axis, i.e., along the film normal. The associated lattice parameters were as follows: a = 90.7 nm and $b = c$ = 121.4 nm, with angles α = 98° and $\beta = \gamma$ = 113°. According to the lattice parameters, the distance between neighboring (211) planes is 25.5 nm. Compression of the film was likely a result of rapid drying that occurred immediately upon the removal of samples from the SVA environment.

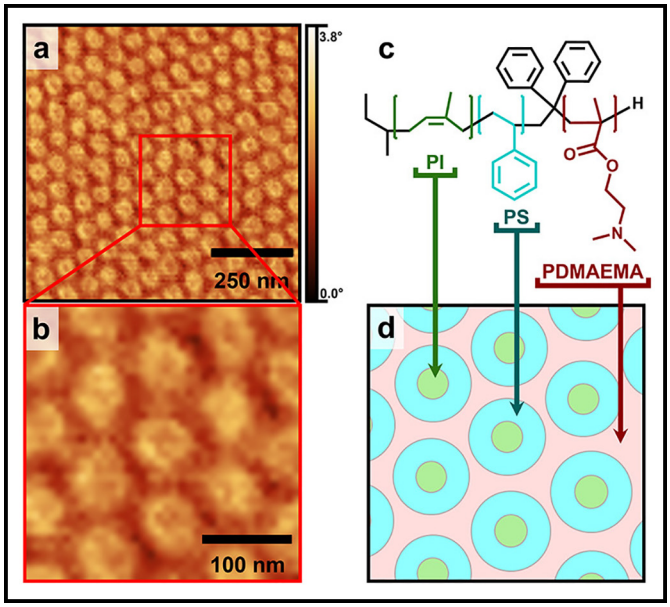

Figure 1: (a) AFM phase image of an ISA thin film. A magnified region marked with a red square in (a) is shown in (b), enabling identification of all three top surface blocks of the ISA structure depicted in (c). A schematic of the top surface morphology consistent with the AFM images is depicted in (d), showing PI cylinder cores (green), PS cylinder shells (blue), and the PDMAEMA matrix (light pink).

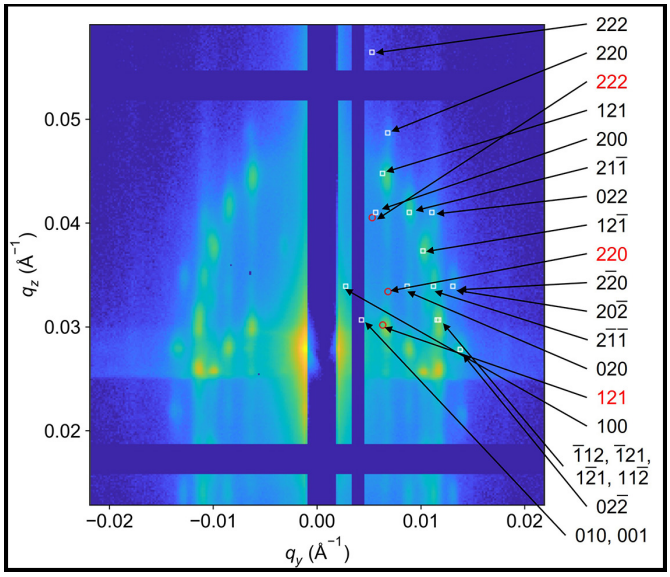

Figure 2: GISAXS patterns of an ISA thin film showing indexed peaks matching a double gyroid structure with the (211) plane parallel to the surface and compressed along the film normal. White squares and red circles correspond to expected peak positions through the reflection and transmission channels, respectively, in GISAXS.

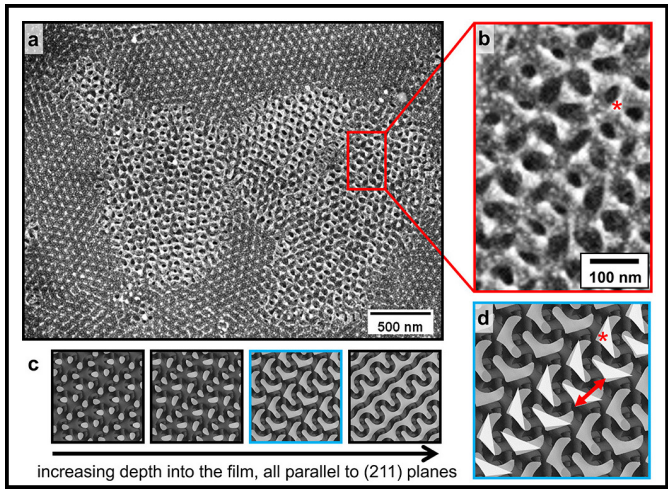

Figure 3: (a) SEM image with a selected area at higher magnification in the (b) red box of an ISA thin film surface after etching with CF_4 plasma for 7 s and (c) simulated (211) plane morphologies of the co-continuous double gyroid along the [211] axis at different depths. Comparing (d) a specific slice, outlined in blue, from the simulation stack to the area enlarged in (c) reveals clear similarities. Red asterisks in (b) and (d) indicate PI-rich locations that appear brighter in SEM due to preferential staining of the PI block with RuO_4. The red double arrow in (d) indicates the spacing between neighboring repetitive features in the (211) plane.

The GISAXS results suggest a different morphology from that revealed by AFM on the surface, but a straightforward comparison is difficult due to the scattering pattern in the reciprocal space. To reconcile these structural differences, it was of interest to investigate the change in structure when moving away from the top surface layer, i.e., deeper into the film. To visualize this transition, the thin films were etched with CF4 plasma and stained with RuO_4 for ~ 15 min to increase contrast in the subsequent SEM images. Figure 3a shows an SEM image of a film etched for 7 s. While there are still regions displaying hexagonal order, the image of the etched film now also clearly reveals areas that resemble a co-continuous structure. Regions with hexagonal lattice structure had a center-to-center cylinder distance of 71.2 ± 1.6 nm. The spacing between the neighboring repetitive features in the (211) plane (see red double arrow in Figure 3d) was 117.0 ± 4.1 nm, similar to the 112.7 nm spacing calculated from GISAXS data. Figure 3b shows an enlarged SEM image area that displays features consistent with a co-continuous structure. By comparing this pattern to simulated (211) planes of the double gyroid along the [211] axis at different depths (Figure 3c), a bent-triangular structure alternating from one side to another is clearly recognizable (see the blue box in Figure 3c). With the PI block stained more heavily as compared to PS, the corner marked with a red asterisk indicates a PI-rich location. These areas appear brighter in the SEM image from greater electron scattering and can be assigned to a similar structure in the simulation (compare Figure 3b,d). Therefore, reactive ion etching enables real-space microscopy characterization of underlying structures in self-assembled block copolymer thin films, which could differ from the surface.

References:

[1] Lee, W. Y., Chapman, D. V., Yu, F., Tait, W. R., Thedford, R. P., Freychet, G., Zhernenkov, M., Estroff, L. A., and Wiesner, U. B. (2022), Triblock Terpolymer Thin Film Nanocomposites Enabling Two-Color Optical Super-Resolution Microscopy. Macromolecules, 55(21), 9452-9464.