Target Patterns Induced by Fixed Nanoparticles in Block Copolymer Films

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ABSTRACT It is well-known that thin films of cylinder-forming block copolymers (BCP) can exhibit a transition from a perpendicular to a parallel cylinder orientation with respect to the supporting solid substrate upon varying film thickness. We show that wave-like oscillations between these morphologies can be induced through the introduction of nanoparticles (NP) into flow-coated and annealed BCP films where the particles span the film thickness and are *fixed* by irreversible adsorption to the supporting substrate. We hypothesize that these novel "target" patterns arise from residual stresses that build up in the film while undergoing thermal treatment and film formation, and we support this hypothesis by showing the suppression of this type of pattern formation in films that are first thermally annealed near their glass transition T_g to relax residual stress. Similar undulating height patterns are also observed in heated *homopolymer* films with nanoparticles, consistent with our thermally induced stress hypothesis of the target pattern formation in BCP films and pointing to the general nature of wave-like thermally induced height variations in heated heterogeneous polymer films. Similar wave patterns should be induced by lithographically etched substrate patterns arising in device fabrication using BCP materials, which makes the phenomena of technological interest. These target patterns also potentially provide valuable information about the presence of residual stresses in cast films that arise during their processing.

KEYWORDS: target pattern · nanoparticles · block copolymer

The surface structure and alignment of nanodomains in block copolymers are being exhaustively studied in bulk,[1−4] solution,[5] and thin films[6−13] because of the many applications envisioned from the use of these nanoscale patterns. Various strategies such as external electric fields,[1,3,5,7,8] selective copolymer−substrate interactions,[10−13] shear fields,[2] solvent-vapor treatment,[9] geometrical confinement,[6] and temperature gradients[4] have resulted in improved alignment of block copolymer domains. However, the effect of introducing large particles in comparison with the characteristic BCP microphase separation dimension on the orientation of block copolymer morphology in thin films has not been previously emphasized as a means of controlling the BCP ordering and as a means of obtaining *in situ* information (elastic constants, residual stresses) about BCP films of interest from a nanofabrication standpoint. The problem of relatively large (comparable to the film thickness) nanoparticles in block copolymer films is also of interest in relation to understanding the nature of defects that arise from the inevitable introduction of dust particles or lithographically fabricated inclusions in thin block copolymer films during their fabrication for various technological applications.

In contrast to BCP films, the influence of immobile "filler" particles having a size comparable to the film thickness has been investigated both computationally and experimentally for phase separating polymer blend films.[14,15] Simulations, based on a generalization of the Cahn−Hilliard−Cook theory,[14] show that a selective affinity of one of the polymers for the filler surface leads to the development of *concentration waves* about the filler particles at an early stage of phase separation in near critical composition blends. Simulations further showed that the symmetry of the particle-induced composition waves reflects the symmetry of the filler particles and interference effects between their composition wave sources. These interference effects can stabilize or destabilize the phase separation morphology, depending on particle spacing and the preferential polymer−particle interaction, which enriches one or the other polymer component near the surface of the particles.[16] It is also established that polymer blends in thin films exhibit surface-directed polymer composition waves in the direction normal to the plane of the films,[16] and film dewetting of both blend components from substrate can also occur,[17] resulting in complex patterns[18] that have a wide range of potential applications. Similar effects can be expected in
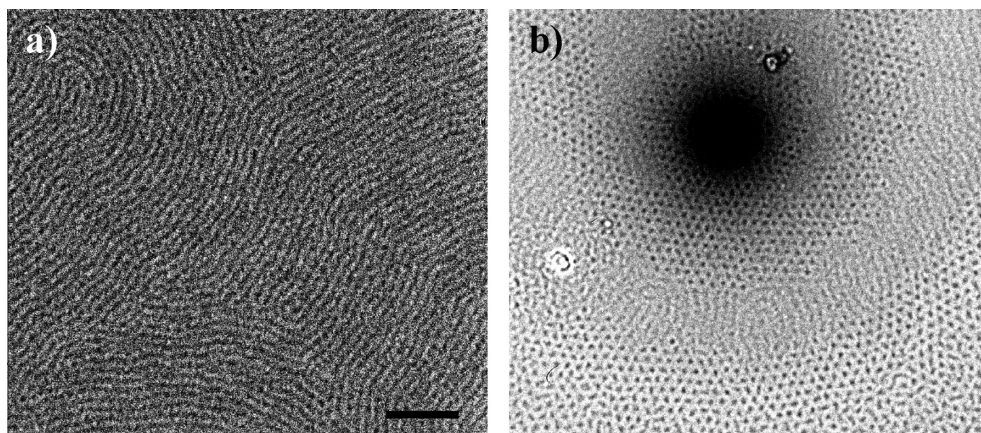
Figure 1. TEM images of PS-*b*-PMMA block copolymer films without particles (a) and with 150 nm silica particles (b) annealed at 164 °C for 22 h. Image shows local morphological orientations near an isolated particle. The scale bar in (a) corresponds to 200 nm and also applies to (b).

and annealing temperature. This is our "control" observation. The influence of the fixed particles on the self-assembled block copolymer morphology is illustrated in Figure 2. The film thickness, d_{film}, in this film is comparable to the particle radius, so the particle actually protrudes from the film (*i.e.*, $d_{film} \approx 0.4D_{particle}$). Annealing in a single step at $T = 164 \pm 0.9$ °C, as in the film without nanoparticles, yields a target-like pattern involving a periodic variation of the BCP cylinder morphology (cylinders standing up and laying down) centered about the isolated NP and the NP aggregates. An inspection of those images indicates that a close-packed morphology of cylinders (oriented perpendicular to the substrate) is nearly always observed near the nanoparticle/copolymer interface. Further, clusters of nanoparticles act as effectively large "particles"; that is, the pattern does not follow the local curvature of individual nanoparticles in the clusters. The distance of propagation of the close-packed vertical cylinders ranges from 2 to 14 times the BCP ordering repeat period of 25 nm, whereupon the BCP morphology "flips" to a morphology with the cylinders oriented parallel to the substrate (the morphology of the film in the absence of NP). This orientational transition repeated a minimum of two times (the typical value for isolated particles) and a maximum of five times (large particle aggregates). Evidently, the larger the core disturbance, the more rings that form. Our observation of a periodic morphology pattern of this kind in BCP film with fixed NPs is apparently unique, and the scale of the
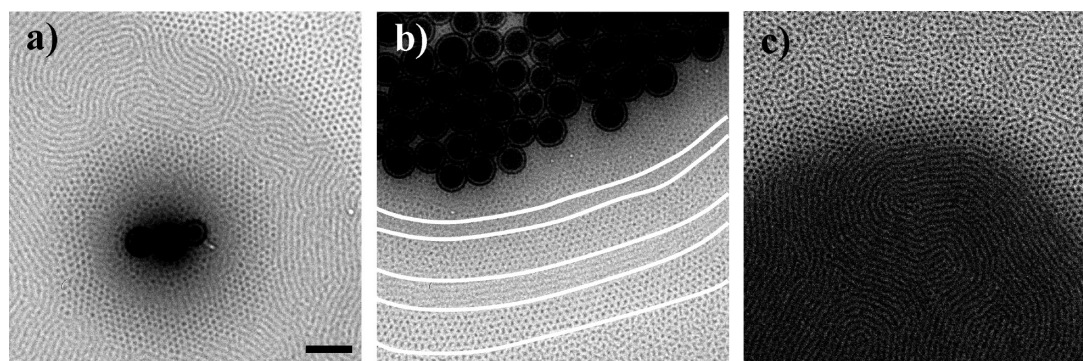
block copolymer films since the early stage pattern formation of polymer blends associated with phase separation can remarkably resemble block copolymer ordering.

In the present work, we explore a superficially similar phenomenon in block copolymer (BCP) materials. Although we find a similar tendency toward the formation of wave-like compositional or "target" patterns as in the case of blends, these patterns are found to be strongly influenced by residual stress effects that arise during film processing, and correspondingly, the patterns occur at a scale significantly different than the characteristic scale of phase separation.

RESULTS AND DISCUSSION

Figure 1 shows that TEM images of particle-filled and unfilled PS-*b*-PMMA films after annealing for 22 h, following a single temperature step to $T = 164 \pm 0.9$ °C in a vacuum oven. For the BCP films without particles (Figure 1a), the cylinders are oriented parallel to the surface as found in previous studies for this film thickness

Figure 2. TEM images of PS-*b*-PMMA block copolymer films with 150 nm silica particles after annealing at 164 °C for 22 h. (a) Target morphology emanating from a small aggregate. (b) Target morphology induced by a large multiparticle aggregate. The boundaries between the regions having the different cylinder orientations have been marked by white lines for clarity. The cylinder "flips" on a scale on the order of a few nanometers. (c) Similar transition in morphological orientation is observed near the edge of an "island" found in a film having non-integral thickness. The island is the darker region. The reduced electron transmission is due to the increased thickness of the film. The scale bar in (a) corresponds to 200 nm and also applies to (b) and (c).

patterns suggests a relatively long-range interaction within the film in comparison to the repeat period of the block copolymer. Where do these mysterious patterns come from?

We then consider some of the basic phenomenological characteristics of these target patterns. First, we note that a significant factor controlling morphological orientation in thin films of cylindrical forming BCP is the packing of the cylinders within the film.[18] For films having a thickness that cannot accommodate an integral number of horizontally stacked cylinders, incomplete layers form at the polymer/air interface[19] that are commonly referred to as islands. A representative morphology at the edge of one of these islands is shown in Figure 2c for a BCP film without added NPs. The steep change in thickness at the island edge having an estimated gradient change in thickness of ≈13% (25 nm/200 nm) causes the close packing layers of cylinders to flip from the parallel to a perpendicular orientation within the island. As pointed out before by Fasolka et al.,[20] the packing frustration associated with a continuous change in the film thickness and the relatively small difference in surface energy between the two polymers (≈0.1 dyn/cm) leads to a "hybrid" morphological structure with a mixed "hybrid" orientation, that is, a coexistence of vertical and horizontal cylinder orientations. As a result, the preferred orientation within the islands (i.e., cylinders lying parallel to the substrate) transforms into close-packed vertical cylinders near the island edge. At large distances from the edge, the surface morphology adopts this hybrid structure. In contrast to this island-induced hybrid structure,[18] the cylinder orientation in our films oscillates in the form of concentric rings. The contour lines emphasized the rim boundaries in Figure 1. We observe wave-like interference pattern in these images, as in previous studies of composition waves in polymer blends containing NP spanning the film thickness.

We next take a closer look at the surface morphology with atomic force microscopy (AFM), a method that emphasizes the same phenomena at a large scale. The topographical scans in Figure 3 reveal a small, but measurable, variation in the local film height with a peak to valley distance of 3−4 nm after one step annealing in most cases. Near the particles, the thickness gradient (≈15%), which is comparable to the one at the edge of islands (≈13%), and the amplitude of the
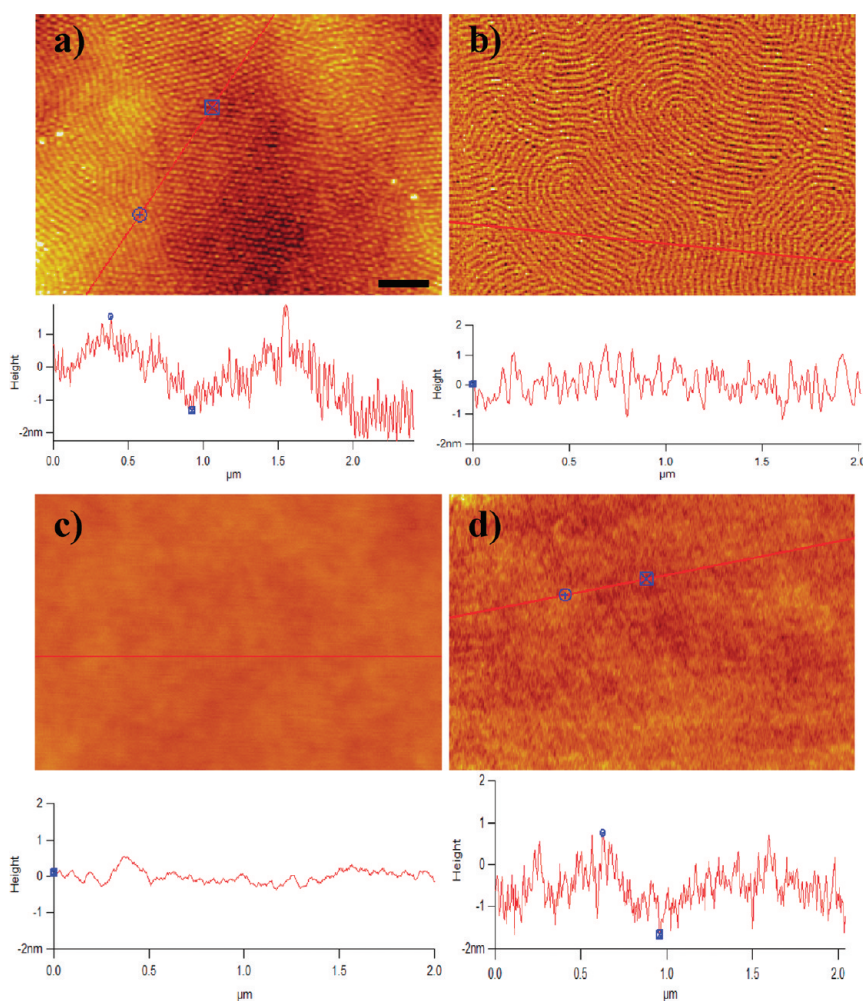

Figure 3. AFM height images of PS-*b*-PMMA block copolymers after annealing at 164 °C for 22 h. (a) Topography images of a BCP film with NPs. (b) Unfilled film with the thickness of 86 nm (b). AFM height images of pure homopolymer PS films cast on a silicon oxide surface with nanoparticles. Same film as-cast (c) and after annealing at 164 °C for 22 h (d). Lighter color regions indicate higher film regions, and one-dimensional height traces are provided below each image with the corresponding position on the image indicated by a red line. The scale bar in (a) corresponds to 200 nm and also applies to (b)−(d).

height undulations are larger, resulting in more ordered BCP regions and better defined surface patterns. At large distances from the NPs, the height gradients decay to a smaller value and the particle-induced pattern loses its coherence. In addition, the surface topography at large distance is complicated by complex interference between the waves originating from the separated particles. The formation of the periodic orientational change in PS-*b*-PMMA block copolymer films was found generally for films having a thickness range from 60 to 140 nm with large (150 nm) isolated nanoparticles, as well as nanoparticle aggregates. While the observed morphological oscillation is consistent with microphase separation in films having variable thickness, it is not clear whether the height undulations of these BCP patterns are a response to, or a driver of, the BCP ordering.

To gain insight into the relationship between topography and self-assembly in the BCP system, we cast a
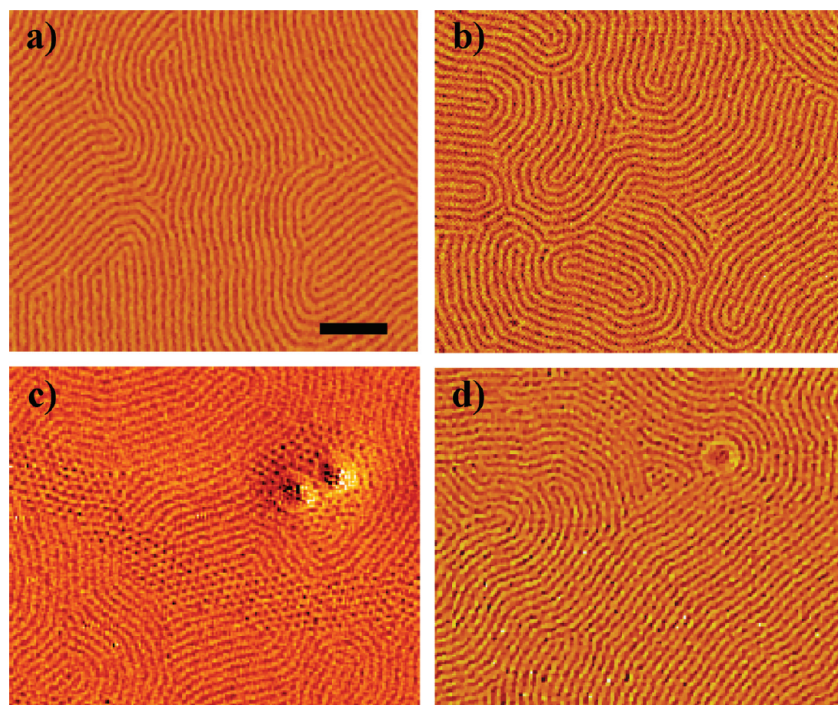
Figure 4. AFM phase images of PS-*b*-PMMA block copolymers cast on silicon oxide without NPs (a,b) and with 100 nm particles (c,d) after varying thermal history. Films annealed at 164 °C (a,c) are compared to those annealed at 129 °C for 22 h and then annealed at 164 °C for 14 h (b,d). The target patterns in the film annealed at one-step temperature (c) also dramatically reduced in the two-step thermal annealing history (d). The scale bar in (a) corresponds to 200 nm and also applies to (b)−(d).

similarly prepared film of pure homopolymer PS on a substrate with adsorbed NPs. Figure 3d shows the evolution of the film surface undulations after annealing a *pure* PS film with the same NP inclusions as in the BCP film study. While the undulations are somewhat less pronounced than in the BCP case (2−3 nm in amplitude, rather than the 3−4 nm value shown in the BCP films), the height fluctuations are significant in comparison to as-cast PS films and PS films annealed without NPs, where the root-mean-squared (rms) roughness is relatively small (<1 nm). Topographical scans of BCP films cast on the nanoparticles measured prior to annealing show a similar lack of periodic topology and rms roughness which was <1 nm. These observations indicate that the polymer film thickness undulations are essentially *independent* of the BCP microphase separation process.

We emphasize that, due to the extremely small amplitude of the surface undulations and the complex relation of the target wave interference patterns, it is challenging to follow the formation of these structures and their evolution in time. It is also not clear whether these patterns represent a thermodynamically stable, metastable, or transient state, although our annealing temperature and time are considered moderately high and long, respectively.

On the basis of these observations, we propose a working model to explain the NP-induced target patterns in our BCP films. In addition to being a

glassy material, the BCP film is thermodynamically in an ordering regime so that the BCP material is in a (weak) gel-like solid state even above the glass transition temperature. Subjecting the film to thermal annealing at an elevated temperature should cause the films to change from a glass to an elastic solid state, and appreciable film thermal expansion should accompany this process. This expansion naturally leads to stresses in the film, which can build up to such an extent as to cause film buckling if this stress is not released through chain diffusion and viscoelastic relaxation. The retention of residual solvent is another source of residual stress in cast polymer films, the amount of residual stress scaling in rough proportion to the amount of residual solvent trapped.[21] In a previous paper, we found evidence suggesting that a substantial amount of the casting solvent (toluene) is trapped in the as-cast film,[22] implying a potentially large amount of residual stress in these cast films. The impact of these residual stresses is apparently similar to observations on swelling-induced buckling patterns in gel films,[23] where swelling rather than thermal expansion is responsible for the induced stress within the plane of the gel layer. The buildup of elastic stresses in the plane of the block copolymer films is further enhanced by introducing fixed lateral constraints within the film (*i.e.*, the adsorbed NPs) that resist in-plane film swelling, a phenomenon with implications in nanofabrication, since inclusions or templates must play a similar role as the particles.

Due to adhesion to the bottom substrate, the thin polymer films expand primarily normal to the substrate, although the spatial placement of the particles is not expected to inhibit the lateral expansion of the film more than the underlying substrate. Expansion normal to the substrate should be locally limited by the particle curvature, a "wedge" effect. In response to this thermal expansion, regions near the edge of particles and particle aggregates will expand laterally, compressing the polymer locally around the particles. The surface compressive forces then induce an undulation in the film interface.

To further test our hypothesis that film surface undulations arise in heated films due to a combination of these thermally induced or residual solvent-induced stresses, we prepared BCP films by nominally the same procedures and varied the thermal history in such a way as to reduce these stresses. Specifically, by annealing the film at a temperature modestly above T_g, it should

be possible to greatly reduce both of these sources of stress within the film (residual stress is notoriously difficult to measure in ultrathin polymer films) *before* annealing the BCP film to induce its ordering. Our working model predicts a suppression of the film height variations in the nanocomposite film with this pre-annealing procedure.

We then prepared two as-cast films according to thermal histories: the method used before and a two-step annealing procedure to remove residual stresses. In particular, both films were first annealed at 164 ± 0.9 °C under vacuum, but the temperature of one of the samples was ramped up quickly as in Figure 2, while the other was first annealed at a lower temperature (129 °C) for a day, prior to heating to 164 °C (a two-step annealing procedure). The second sample should have a greatly reduced residual stress within the film, and no or limited pattern formation is then expected. Figure 4 compares films with and without NPs. The orientation of morphology of the unfilled samples is independent of thermal path, where both samples exhibit cylinders lying parallel to the substrate, the expected morphology under these conditions.[24] In the case of the NP-filled samples, the two-step temperature annealing, which essentially eliminates the height variations, indeed results in almost a *complete suppression* of the target patterns and supports our proposed residual stress model of the BCP pattern formation.

CONCLUSION

We have observed the formation of surface patterns composed of oscillating BCP cylinder orientation in the presence of immobile particles that span the film thickness. These target patterns are radially concentric and emanate from the center of isolated particles or particle aggregates. The oscillations in BCP morphology appear to follow oscillations in film thickness, creating a large-scale wave-like interaction between the particles. The height oscillations in the films after annealing are proposed to arise from residual stresses, which in turn arise both from the trapping of solvent within the film (and its evaporation during annealing) and from thermal expansion of the film upon heating. Our working model of this phenomenon gives insight into the complex interaction of polymer film expansion, residual stresses arising in the course of film casting, and the effect of fixed constraints (adsorbed particles) on BCP ordering. Height variations in the film are directly responsible for the target pattern formation.

We have further found that we can control this type of surface pattern formation by altering the thermal annealing history to allow for a relaxation of residual stresses in the particle-filled films. Specifically, if we first anneal the films at 129 °C for 22 h, cool for overnight, and then reheat the film to 164 °C for 14 h, the target patterns are no longer apparent. This is consistent with residual stresses having been dissipated after thermally annealing the film at a temperature near T_g.

The particles in the present measurements play the role of fixed constraints within the film since the Si particles are strongly bound to the substrate through physical adsorption, and their presence evidently enhances the buildup of residual stresses within the films during film formation and processing (heating the films). Post-like structures, channels, or other fixed structures within heated and cast polymer films are also fixed constraints within the film and should have a similar effect of inducing stresses within heated cast polymer films, an effect of significant interest in manufacturing applications where this effect might give rise to defect formation in the block copolymer material or device failure because of the breaking of vital structural elements within the film associated with these stresses. On the other hand, the formation of these patterns might have some practical benefit to the nanofabrication process in some cases. It is also possible that these target patterns might be useful as a *diagnostic* for the buildup of residual stresses in block copolymer films during thermal and solvent processing, perhaps even providing a new method for detecting large residual stresses in thin polymer films.

EXPERIMENTAL DETAILS

Preparation of Nanoparticles Fixed in Random Positions on a Silicon Wafer. The particle-filled films were prepared *via* spin coating from a 0.05% by mass particle solution in water onto substrates. By simple adhesion to the underlying substrate, the particles are rendered immobile and are only removed by extended sonication. The silica nanoparticles (NP) with diameters of 100 and 150 nm were obtained from Polysciences Inc.[25]

Preparation of BCP Thin Films. Poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) with a total relative molecular mass of 47.7 kg/mol and a mass fraction of PS of 0.74 was purchased from Polymer Source, Inc. Polystyrene having a total relative molecular mass of 50 kg/mol was purchased from Pressure Chemical Company. The relative molecular mass and relative block lengths are chosen to create a cylinder forming morphology, where the minority PMMA block forms the cylinders in a matrix of PS.[24] The block copolymer (BCP) film was flow coated[26] onto the NP-coated substrate from a 4% by mass BCP solution, and the samples were placed in an oven for one-step (164 °C for 22 h) or two-step (129 °C for 22 h followed by 164 °C for 22 h) annealing.

Atomic Force Microscopy (AFM). AFM images were obtained in both height and phase contrast modes with an Asylum MFP-3D scanning force microscope in the tapping mode. The tapping mode cantilevers with spring constant ≈50 N/m and resonance frequency ranging from 100 to 200 kHz were used.

TEM. The samples were prepared for TEM by floating the films from the carbon-layer-coated mica on a pool of deionized water, then transferring onto the copper TEM grid. The plan-view image was obtained without RuO₄ staining because electron irradiation induced thinning of the PMMA block produced sufficient contrast.[27]

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