Solvent Vapor-Assisted Self-Assembly of Patternable Block Copolymers

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Proposal Title: Solvent Vapor Annealing of Block Copolymer Thin Films

Research Achievement

Block copolymer self-assembly presents a method for patterning and templating applications on the 10-50 nm length scale, smaller than is easily possible using photolithography. Here we investigate the use of polar-nonpolar block copolymers both as photopatternable self-assembling materials and also as vehicles for patterning by selective material infiltration into nanometer-scale polymer domains. Formation of block copolymer thin films with large areas of defect-free self-assembled morphologies, combined with careful control of the polymer domain orientation, are critical for patterning applications. The block copolymer self assembly process is facilitated by polymer chain mobility. The most common method for achieving this - thermal annealing - is a poor choice in our material systems due to thermal incompatibility of these polar-nonpolar block copolymers. Swelling the polymer in a solvent vapor (often termed solvent annealing) provides an alternate route to achieving sufficient chain mobility for self-assembly, and also has additional benefits not possible using a thermal annealing method.

We have used solvent annealing to promote self-assembly of a combined top-down/bottom-up block copolymer system comprised of poly(α-methylstyrene)-block-poly(4-hydroxystyrene), or PαMS-b-PHOST.[1] In this case, we designed photolithographic functionality into the block copolymers, allowing the majority component of the block copolymer to serve as a negative-tone photoresist. In this way we use lithography to control the precise location of the self-assembled block copolymer patterns. An added benefit of solvent vapor annealing is that we can reversibly change the self-assembled polymer film morphology by using the selectivity of different swelling solvents to the two blocks. The choice of solvent for annealing directs the formation of different morphologies in the dried film, demonstrated here to be either a spherical and cylindrical phase. This behavior is reversible and so therefore alternating annealing treatments results in repeatable pattern morphology changes within the film. Secondary ordering techniques applied in tandem with solvent vapor annealing can be used to

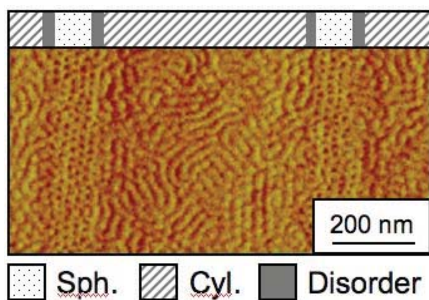
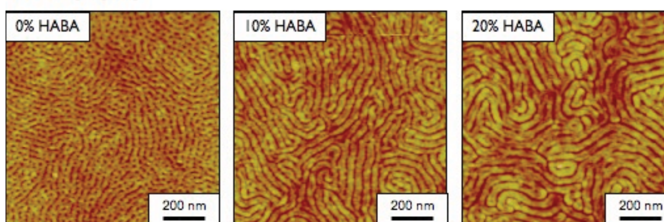


Figure 1. A single film of PαMS-b-PHOST displays two morphologies within high-resolution patterns in this atomic force microscopy height image. A spherical morphology is observed in 100 nm-wide stripes, surrounded by regions with parallel cylindrical morphology.

further control the self-assembly and give highly ordered block copolymer domains. For example, we have used surface topography (graphoepitaxy) to align these self-assembled block copolymer to patterns.

The combination of block copolymer self assembly with crosslinking by lithographic patterning was initially pursued to demonstrate an ability to control the precise location of the assembled patterns. We further combined solvent vapor annealing of PαMS-b-PHOST, used to reversibly tune the self-assembled morphology, with electron beam lithography, used to prevent switching in exposed regions.[2] This combined process has provided a method for selectively patterning 100 nm-wide domains of spherical morphology within regions of parallel-oriented cylindrical morphology, as seen in Figure 1. These results are achieved by first solvent vapor annealing in acetone to form a self-assembled spherical morphology in the entire film, and then patterning the film by expoure to an electron-beam. A second solvent anneal in tetrahydrofuran forms cylindrical morphology wherever the film had not been crosslinked by the electron beam.



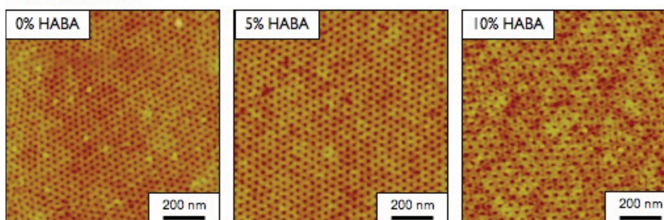


Figure 2. PS-b-P2VP solvent annealed in dioxane (A) display parallel cylinder morphology, while annealing in toluene (B) leads to spherical morphology. Varying the amount of 2-(4-hydroxyphenylazo)benzoic acid (HABA) blended with the PS-b-P2VP allows tuning of the morphology as well as formation of pores upon its extraction.

We have also investigated solvent vapor annealing of the block copolymer polystyrene-block-poly(2-vinylpyridine), PS-b-P2VP, blended with a hydrogen bonding material that selectively segregates into the polar block.[3] Blending the small molecule with the block copolymer provides a method of tuning the self-assembled domain periodicity upon solvent annealing, with morphology control again possible by choice of solvent and its associated block selectivity (Figure 2). Selective extraction of the blended material forms voids displaying the tunable periodicity, and such patterns can then be subsequently transferred by templating to inorganic materials.

Publications

1. Bosworth, J. K.; Paik, M. Y.; Ruiz, R.; Schwartz, E. L.; Huang, J. Q.; Ko, A. W.; Smilgies, D.-M.; Black, C. T.; Ober, C. K., Control of Self-Assembly of Lithographically Patternable Block Copolymer Films. *ACS Nano* **2008,** 2, 1396-1402.

2. Bosworth, J. K.; Black, C. T.; Ober, C. K., Selective Area Control of Self-Assembled Pattern Architecture Using a Lithographically Patternable Block Copolymer. *Submitted, ACS Nano*.

3. Bosworth, J. K.; Ober, C. K.; Black, C. T., Control of Self-Assembled Block Copolymer Film Morphology, Dimensions, and Packing Through Combined Selectve Molecule Blending and Solvent Vapor Annealing. *In preparation*.