Title

Manipulating Block Copolymer Self-Assemblies in Bulk and Thin Films by Thermal and Solvent Annealing

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Abstract

The self-assembly of block copolymers (BCPs) into well-ordered nanoscopic arrays holds promise for new technological breakthroughs as templates and scaffolds for the fabrication of nanostructured materials. It is essential to establish convenient approaches to control the morphology of BCPs, since some applications require addressability, the BCP microdomains must be perfectly aligned and oriented. The theme of this thesis is the use of external forces, specifically thermal and solvent annealing, to guide the self-assembly of BCPs to obtain microphase separated morphologies for different applications. Three representative BCP systems, having lamellar, cylindrical and spherical microdomains are discussed. First, the self-assembly of lamella-forming brush block copolymers (BrBCPs) having polylactide (PLA) and polystyrene (PS) side chains were studied in the bulk and in thin films. The domain size increased approximately linearly with the molecular weight of the backbone, which indicated that the backbone was in an extended conformation that was confirmed theoretically. *In situ* small angle x-ray scattering (SAXS) measurements indicated that the self-assembly of the BrBCPs was quite rapid, due to the rigid nature of the backbone chain, Second, the directed self-assembly of cylinder-forming polystyrene-*block* -poly(ethylene oxide)s (PS-*b* -PEOs) in thin films were investigated. The polymer-surface interactions were tuned by hydroxyl end-functionalized polymers, so that the orientation of the PS-*b* -PEO microdomains was controlled during thermal annealing. Cylindrical PEO microdomains embedded in a PS matrix orientated normal to the silicon substrates were observed over a wide processing window when the substrates were modified by PS- *b* -PEO BCPs. PS-*b* -PEOs with an *o* -nitrobenzyl ester junction point (PS-*hv* -PEOs) were used to fabricate nanoscopic dot and line patterns having long-range lateral order. The cylindrical BCP microdomains were oriented perpendicular or parallel to the silicon substrates by varying the solvent annealing conditions. The third BCP system examined in this study was a sphere-forming polystyrene- *block* -polydimethylsiloxane (PS-*b* -PDMS). Solvent annealing in *N* -methyl-2-pyrrolidone was used to direct the self-assembly of the spherical microdomains into high areal density arrays on flat Si substrates, PS modified substrates and lithographically patterned substrates, respectively.

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