**Synthesis of High Etch Contrast Poly(3-hydroxystyrene)-based Triblock Copolymers for Sub-5 nm Features**

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Block copolymer (BCP) materials and their self-assembly has been widely studied in the last two decades. BCPs are advantageous in generating periodic patterns at nanoscale over large areas as well as providing access to a wide range of morphologies and size of features. Hence, BCPs are considered to be a promising candidate for microelectronics as sub-10 nm feature sizes over large areas can be achieved in a scalable and cost-effective manner. In this work, we demonstrate the synthesis and self-assembly of poly(3-hydroxystyrene)-*block*-poly-(dimethylsiloxane)-*block*-poly(3-hydroxystyrene) (P3HS-*b*-PDMS-*b*-P3HS) triblock copolymers. The incorporation of hydroxystyrene and PDMS not only dramatically increases the effective interaction parameter, but also offers inherent etch contrast between the blocks. The triblock architecture also has a higher tendency towards forming perpendicular nanostructures compared with the diblocks. Hydroxy-terminated PDMS polymers were functionalized to initiate the atom transfer radical polymerization of an acetal protected 3-hydroxystyrene monomer. The target triblocks were achieved after a subsequent deprotection of the acetal protecting group, under mild acidic conditions after polymerization. The resulting triblocks have dispersities ranging from 1.10 to 1.26 and the synthesis provides robust control over molecular weights and volume fractions. The large chemical incompatibility of the blocks enabled the formation of ordered structures at low molecular weights that yielded lamellar periodicities as small as 9.3 nm. Smaller dimensions were obtained by triblocks than that of the corresponding diblocks with similar molecular weights. The phase diagram of this triblock was mapped out based on the volume fractions and morphologies. The lamellar and cylinder morphology windows were observed at lower volume fractions of the P3HS block, relative to the diblocks. This phase diagram shift is ascribed to the dispersity of the middle block relative to the end blocks, which was confirmed by cleaving the end blocks for dispersity study. Thin-film study on diblock and triblock also confirmed the advantages of triblock architecture for thin-film assembly.

