

Directed Assembly of Symmetric ABA Triblock Copolymers on Chemically Nanopatterned Substrates

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Directed assembly of block copolymers on chemical pre-patterns has been demonstrated with high degrees of registration, increased feature density, and improved critical dimension control,¹ and listed as one of potential lithography solutions for sub-22 nm patterning in the 2007 International Technology Roadmap for Semiconductors.² However, the majority of past work on directed assembly of block copolymers on chemically nanopatterned surfaces (or chemical patterns) has focused on AB diblock copolymers. Here we report the first study on directed assembly of ABA triblock copolymers on chemical patterns. A distinct difference between triblock and diblock copolymers is that in triblock copolymers the central B blocks can form bridges between two different A domains.³ The bridging conformations in ABA triblock copolymers significantly improve their bulk mechanical properties,⁴ and, as shown in this work, also influence their assembly behavior in thin films. Directed assembly of thin films of symmetric poly(methyl methacrylate-*b*-styrene-*b*-methyl methacrylate) (PMMA-*b*-PS-*b*-PMMA) ($M_n=52-98-52$ kg/mol, MSM-198) triblock copolymers is shown to be capable of achieving a high degree of perfection, registration, and accuracy on striped patterns having periods, L_s , commensurate with the bulk period of the copolymer, L_o . When L_s is incommensurate with L_o , the triblock copolymer domains can equilibrate with dimensions up to ~55% larger or 13% smaller compared to L_o (Figure 1). This range over which triblock copolymers tolerate incommensurable L_s , is significantly larger than that (~10%) of the corresponding diblock copolymer material on analogous directed assembly systems. The assembly kinetics of the triblock copolymer was approximately 3 orders of magnitude slower than observed in the diblock system. Theoretically informed simulations are used to interpret our experimental observations; a thermodynamic analysis reveals that triblocks can form highly ordered, non-equilibrium metastable

¹ a) S. O. Kim *et al.*, *Nature* **424**, 411 (2003); b) M. P. Stoykovich *et al.*, *Science* **308**, 1442 (2005).; c) R. Ruiz *et al.*, *Science* **321**, 936 (2008).

² International Technology Roadmap for Semiconductors, www.itrs.net (2007)

³ a) M. W. Matsen, *J Chem Phys* **102**, 3884 (1995).; b) M. W. Matsen, M. Schick, *Macromolecules* **27**, 187 (1994).

⁴ a) M. W. Matsen, R. B. Thompson, *J. Chem. Phys.* **111**, 7139 (1999).; b) M. D. Gehlsen, K. Almdal, F. S. Bates, *Macromolecules* **25**, 939 (1992).

structures that do not arise in the diblock. Simulations also show that the fraction of the bridge/loop configuration varies with L_s on chemical patterns. The asymmetric expansion ($\sim 55\%$) and contraction ($<13\%$) of triblock copolymers in thin films when directed to assemble on chemical patterns is beneficial for the fabrication of complex structures with a mix of feature dimensions and provides a mean to fabricate integrated circuits and bit-patterned media using a single block copolymer.

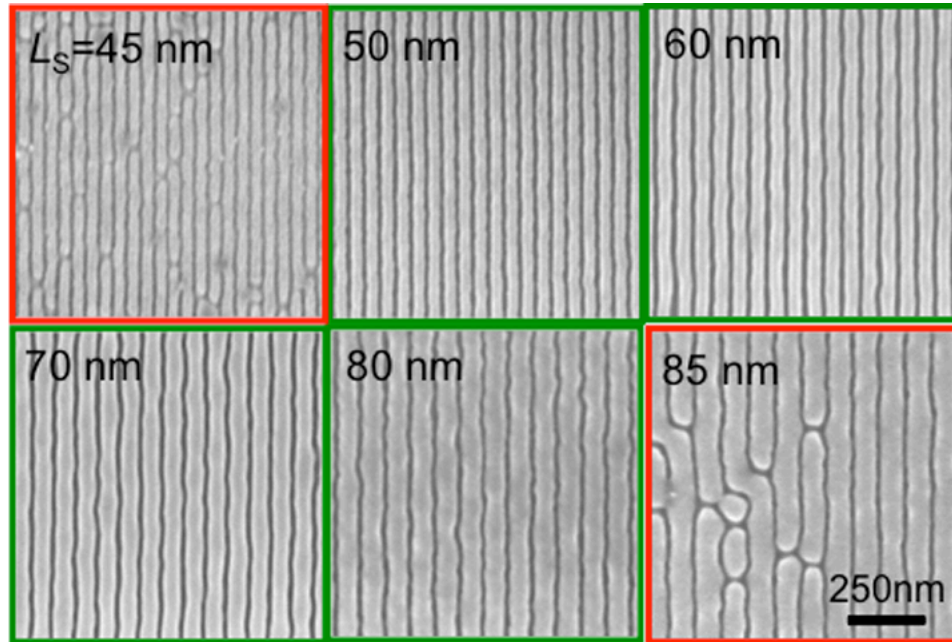


Figure 1. Top-down SEM images of MSM-198 films on chemical patterns with periods of 45-85 nm. Films were annealed at 230 °C for 36 hours. MSM-198 expanded up to 55% (80 nm) and contracted less than 13% (45 nm) on chemical patterns in thin films.