Self-assembled nanostructures with ring arrays and square pattern from organometallic-containing triblock terpolymers

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Microphase-separation of block copolymers into periodic nanoscale structures has drawn considerable attention as a method for pattern generation in nanolithography. The use of triblock terpolymers allows the formation of more complex pattern geometries compared to their diblock counterparts, which are typically restricted to forming arrays of parallel lines, or closepacked dots or holes with hexagonal symmetry. In this study, we demonstrate the generation of two morphologies: closepacked rings, and square arrays of dots. Moreover, since the features are made from an organometallic block, they have a high etch contrast and etch resistance compared to the organic blocks of the triblock terpolymer, making them useful for pattern transfer. Arrays of hollow rings with a period of 54 nm were obtained from a core-shell cylindrical-morphology poly(styrene-*b*-ferrocenylsilane-*b*-2-vinyl pyridine) (PS-*b*-PFS-*b*-P2VP) triblock terpolymer. Using oxygen plasma, the PS core and P2VP matrix blocks were partly removed simultaneously, as shown in figure 1, leaving ring patterns made from oxidized PFS. Subsequently, the remaining PFS ring pattern was successfully replicated in a PS layer by imprinting. Results will be compared with those obtained from triblock terpolymers in which all three blocks contains organic segments[1]. A second organometallic polymer, poly(isoprene-*b*-styrene-*b*-ferrocenylsilane) (PI-*b*-PS-*b*-PFS), was also investigated. In bulk, this forms a square packed arrangement of PI and PFS cylinders in a PS matrix. By controlling the film thickness and annealing conditions, thin films were prepared consisting of short cylinders perpendicular to the substrate. Areas of both close-packed and square symmetry PFS cylinders were produced, as shown in Figure 2. The center-to-center distance for hexagonal and square packing is 57 nm and 41 nm, respectively. The square symmetry array, which is not found in diblock copolymers, has applications in via formation, magnetic patterned media, and other applications.

[1] Chuang et al., *ACS Nano*, **2008**, *2*, 2007.

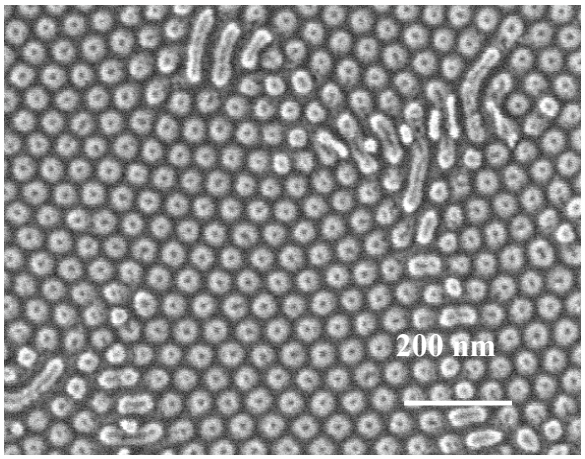

Fig 1: SEM image of a thin film of PS-b-PFS-b-P2VP on Si after annealing in a mixture of chloroform and acetone vapor at room temperature, followed by etching with oxygen RIE to remove the PS and P2VP. This reveals a pattern of robust ring-shaped structures made from oxidized PFS.

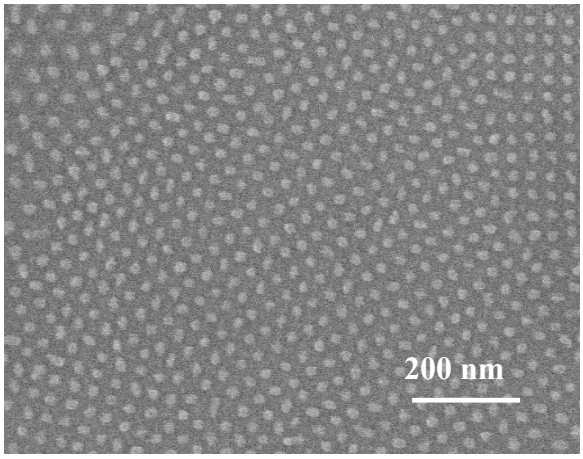

Fig 2: SEM image of a thin film of PI-*b*-PS-*b*-PFS on Si after annealing in chloroform vapor at room temperature, followed by etching with oxygen RIE to remove the PI and PS. The PFS forms a square array of cylinders perpendicular to the substrate.