POSS-Containing Block Copolymers With High Etch Contrast For Directed Self-Assembly

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We report the development of polyhedral oligomeric silsesquioxane (POSS) containing block copolymer (POSS-BCP) with high etch contrast and characterization of the self-assembled nanostructures on the topographically patterned substrates.

The POSS-BCP, polymethylmethacrylate-*b*-polymethacrylate POSS (PMMA-*b*-PMAPOSS), was synthesized by living anionic polymerization of methyl methacrylate and POSS methacrylate monomers. Excellent control of the molecular weights and polydispersity index of the resulting polymers in the range from 36,400 to 94,000 and less than 1.08, respectively (MALS) was achieved. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra showed the desired polymers were successfully obtained without any byproducts. The bulk morphology of the resulting PMMA-*b*-PMAPOSS was characterized, before examining the thin-film assembly. Well-ordered nanostructures such as lamellae and cylinders formed with long range ordering of the domains. The graphoepitaxial thin-film assembly of the PMMA-*b*-PMAPOSS BCP on topographically patterned substrate was examined. First, it was found that by appropriate choice of solvent, solvent annealing allowed control over both the vertical (annealed in CS_2) and parallel orientation (mixture of CS_2 and acetone) of domains. Second, for the lateral ordering of the nanostructures, the nature of the substrate makes a big difference. The patterned substrates composed of SiO_2 bottoms and Si_3N_4 sidewalls provided both laterally and vertically well-ordered cylinders, while the all SiO_2 substrate gave less ordered structures. The average *d*-spacings of was achieved 11.4 nm achieved on the SiO_2/Si_3N_4 substrate with 500 nm width. Furthermore, the nanostructures can be reversibly switched from the vertical to the parallel and vice versa by changing the annealing solvent.
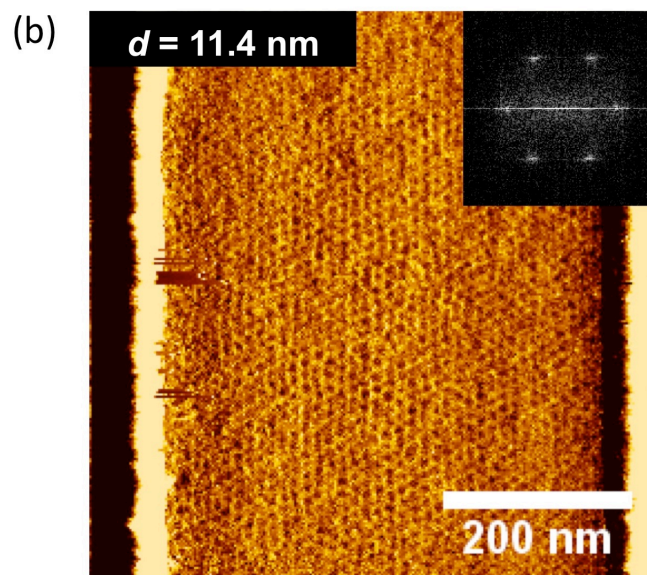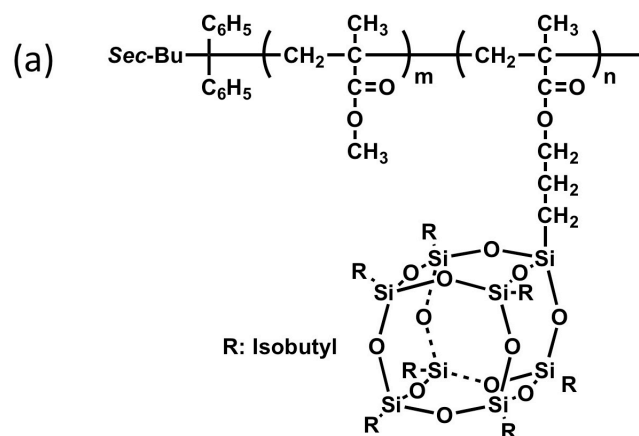
(a)

(b) *d* = 11.4 nm

200 nm

Fig.1: (a):Chmical structure of PMMA-*b*-PMAPOSS and (b) AFM Phase Images of PMMA$_{24}$-*b*-PMAPOSS$_{12}$ thin film after solvent annealing with CS$_2$ for 4 h. Polymer was spin-casted on Si(bottoms)-Si$_3$N$_4$(walls) topographic patterned substrate with 500 nm width.