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Routes to Frustrated Nanostructures with Block Copolymers

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Diblock copolymers of polystyrene and polybutadiene, PS-b-PBD were confined within nanoscopic cylindrical pores in alumina membranes. By capillary action, microphase separated symmetric and asymmetric PS-b-PBD were drawn into pores varying in diameter from 15 to several hundred nanometers. After thermal annealing, the alumina membrane was dissolved in a weak base, leaving nanorods of the PS-b-PBD that were then imbedded in epoxy, microtomed and stained with OsO_4. TEM on cross-sections taken parallel to and normal to the nanorod axis was used to investigate the morphology. For symmetric PS-b-PBD, when the pore diameter, d, was much larger than the copolymer repeat period, L_0, multiple concentric cylinders of PS and PBD oriented along the nanorod axis was obtained. When $d<2L_0$ and d/L_0 was non-integer, the morphology changed to a torroidal or stacked-disc type of morphology. For asymmetric PS-b-PBD (ϕ_{PBD} $\sim$0.3) when d/L_0 was large, cylinders of PBD in a PS matrix were found where the hexagonal packing was altered by the constraints of the walls. However, if $d<2L_0$, helices of PBD in PS running along the nanopore axis were found. Thus, using simple diblock copolymers, the frustration and curvature imposed on the copolymers forces new morphologies leading to novel templates and scaffolds for nanostructured materials. Supported by the NSF, MRSEC and NIRT at UMass, the Dept. of Energy, and the Hyperstructured Organic Materials Research Center in Seoul, Korea. *With K. Shin, H. Xiang, S. Moon, T. Kim and Thomas J. McCarthy*