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Polymers under Cylindrical Confinement

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Anodized alumina oxide (AAO) membranes offer a unique platform to investigate polymers under confinement. AAO membranes have been prepared where the diameters of the nanopores in the membrane have been varied from 8 to 50 nm by varying the anodization conditions. Capillary force is sufficiently large to draw high molecular weight polymers into the membrane, producing either nanotubes or nanorods. Polymer solutions can also be used to place a thin film on the walls of the nanopores, forming nanotubes. With pore diameters less than the radius of gyration, a quantitative understanding of perturbations to chain dynamics due to geometric constraints was examined. We found a weak molecular weight-dependent mobility of polymers confined within AAO nanopores having diameters smaller than the dimension of the chains in the bulk. The measured mobility of polymers in the confined geometry was much higher than the mobility of the unconfined chain. Rayleigh instabilities in thin polymer films confined within nanoporous alumina membranes were also found where periodic undulations on the film surface were found to increase with time, eventually bridging across the cylindrical nanopore, resulting in the formation of polymer nanorods with a periodic array of encapsulated holes. With microphase separated block copolymers, where the characteristic period of the BCP morphology is comparable to the pore diameter, significant deviations from the bulk morphology as revealed by electron tomography. Small angle neutron scattering was also used to investigate the influence of cylindrical confinement on the order-to-disordered transition. This work was done in collaboration with T. J. McCarthy (UMass), K. Shin (Seoul National University), H. Jinnai (Kyoto University), D. Chen, J. Chen, H. Xiang, T. Kim, and P. Dobriyal, and was supported by the DOE, NSF MRSEC, NSF CHM.