

MIT Chemical Engineering Department

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Equilibration and Dynamics in Block Copolymer Micelles



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66-110

Abstract: Block copolymers provide a remarkably versatile platform for achieving desired nanostructures by self-assembly, with lengthscales ranging from a few nanometers up to several hundred nanometers. In particular, block copolymer micelles in selective solvents are of great interest across a range of technologies, including drug delivery, imaging, catalysis, lubrication, and extraction. While block copolymers generally adopt the morphologies familiar in small molecule surfactants and lipids (*i.e.*, spherical micelles, worm-like micelles, and vesicles), one key difference is that polymeric micelles are typically not at equilibrium.

The primary reason is the large number of repeat units in the insoluble block, N_{core} , which makes the thermodynamic penalty for extracting a single chain (“unimer exchange”) substantial. Consequently, critical micelle concentration (CMC) is rarely accessed experimentally; however, in the proximity of a critical micelle temperature (CMT), equilibration is possible. We use time-resolved small angle neutron scattering (TR-SANS) to obtain a detailed picture of mechanisms and time scales for chain exchange, for systems at or near equilibrium. The dependence of the rate of exchange on key variables – concentration, temperature, N_{core} , N_{corona} , and chain architecture (diblock versus triblock) – will be discussed. Preliminary measurements of micelles prepared far from equilibrium, using dynamic light scattering, small-angle X-ray scattering, and TEM, will also be described.