Equilibration of Block Copolymer Micelles: How Difficult Can It Be?

Block copolymers provide a remarkably versatile platform for achieving desired nanostructures by self-assembly, with lengthscales ranging from a few nanometers up to microns. 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, Ncore, which makes the thermodynamic penalty for extracting a single chain (“unimer exchange”) substantial. As a consequence, the 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 the mechanisms and time scales for chain exchange, for systems at or near equilibrium. The dependence of the rate of exchange on the key variables — concentration, temperature, Ncore, Ncorona, and chain architecture (diblock versus triblock) — will be discussed. Interestingly, almost none of the observed features are captured by available theory. Dissipative particle dynamics simulations provide a hint of the underlying physics. Then, when micelles are significantly larger or smaller than the equilibrium size, fragmentation and fusion mechanisms, respectively, can become operative. We will describe measurements using dynamic light scattering, small-angle X-ray scattering, and liquid-phase TEM to follow the fragmentation process in detail.

Bio

Tim Lodge graduated from Harvard in 1975 with a B.A. cum laude in Applied Mathematics. He completed his PhD in Chemistry at the University of Wisconsin in 1980, and then spent 20 months as a National Research Council Postdoctoral Fellow at NIST. Since 1982 he has been on the Chemistry faculty at Minnesota, and in 1995 he also became a Professor of Chemical Engineering & Materials Science. In 2013 he was named a Regents Professor, the University’s highest academic rank, and he was named the inaugural Prager Chair in Macromolecular Science in 2021.

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