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Equilibration and metastability in block copolymer micelles

TIMOTHY LODGE, University of Minnesota

The strong incompatibility between a solvophobic block and the surrounding medium leads naturally to extremely slow chain exchange kinetics between micelles. The steric barrier between well-solvated coronas similarly inhibits micelle fusion/fission processes. Consequently, equilibration of block copolymer micelles is typically prohibitively slow. As a result, it is possible for one system to adopt quite different micellar shapes and sizes, depending on preparation method. However, by using low volatility solvents such as ionic liquids or paraffinic oils, combined with weakly solvophobic blocks, it is possible to design model systems with accessible critical micelle temperatures. This enables the study of both the mechanisms of chain exchange, by time-resolved small-angle neutron scattering, and the evolution of non-equilibrium structures, by dynamic light scattering. Examples of both approaches will be discussed.