Dynamics of Chain Exchange in Block Copolymer Micelles

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Block copolymer micelles are rarely at equilibrium. The primary reason is the large number of repeat units in the insoluble block, $N_{\text{core}}$, 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 have been using time-resolved small angle neutron scattering (TR-SANS) to obtain a detailed picture of the mechanisms and time scales for chain exchange, at or near equilibrium. Our model system is poly(styrene)-block-poly(ethylene-alt-propylene) (PS-PEP), in the PEP-selective solvent squalane (C$_{30}$H$_{62}$). Equivalent micelles with either normal (hPS) or perdeuterated (dPS) cores are initially mixed in a blend of isotopically substituted squalane, designed to contrast-match a 50:50 hPS:dPS core. Samples are then annealed at a target temperature, and chain exchange is revealed quantitatively by the temporal decay in scattered intensity. The rate of exchange as function of concentration, temperature, $N_{\text{core}}$, $N_{\text{corona}}$, and chain architecture (diblock versus triblock) will be discussed.