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Molecular Exchange Dynamics in Block Copolymer Micelles¹ FRANK BATES, JIE LU, SOOHYUNG CHOI, TIMOTHY LODGE, University of Minnesota — Poly(styrene-b-ethylene propylene) (PS-PEP) diblock copolymers were mixed with squalane $(C_{30}H_{62})$ at 1% by weight resulting in the formation of spherical micelles. The structure and dynamics of molecular exchange were characterized by synchrotron small-angle x-ray scattering (SAXS) and time resolved small-angle neutron scattering (TR-SANS), respectively, between 100 °C and 160°C. TR-SANS measurements were performed with solutions initially containing deuterium labeled micelle cores and normal cores dispersed in a contrast matched squalane. Monitoring the reduction in scattering intensity as a function of time at various temperatures revealed molecular exchange dynamics highly sensitive to the core molecular weight and molecular weight distribution. Time-temperature superposition of data acquired at different temperatures produced a single master curve for all the mixtures. Experiments conducted with isotopically labeled micelle cores, each formed from two different but relatively mondisperse PS blocks, confirmed a simple dynamical model based on first order kinetics and core Rouse single chain relaxation. These findings demonstrate a dramatic transition to nonergodicity with increasing micelle core molecular weight and confirm the origins of the logarithmic exchange kinetics in such systems.

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