72g pH-Dependent Micellization of Peo-Containing Triblock Copolymers

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Novel PEO triblock copolymers consisting of poly(ethylene oxide) [PEO] end blocks and a center block consisting of urethane and carboxylic acid groups have been used to sterically stabilize colloidal dispersions of nanoparticles of magnetite. More recently, we have shown that these triblock copolymers form tunable micelles in aqueous solutions. As observed by dynamic light scattering, micellization is controllable by using pH and temperature, with ionic strength playing a lesser role. At pH 7 and 25 C, the copolymers are fully soluble unimers (hydrodynamic radius RH ~2 nm). At pH 2-3, protonation of the carboxylic acid groups in the core drives assembly of micelles with RH ~10 nm over a range of temperatures (5-40 C). At pH 7, micellization is induced upon decreasing the temperature to below 10 C, which is consistent with micellization driven by hydrogen bonding. Increasing ionic strength screens repulsion in the core and favors micellization. Static light scattering was used to measure the aggregation number and second virial of the micelles as well as the critical micelle concentration. We propose a simple model to describe micellization of these block copolymers as a balance between hydrogen bonding and electrostatic repulsion in the core and repulsion between PEO chains in the corona.