

Abstract Submitted
for the MAR06 Meeting of
The American Physical Society

Order-Disorder Transition and Critical Micelle Temperature in Concentrated Block Copolymer Solutions MOON JEONG PARK, KOOKHEON CHAR, Seoul National University, JIN KON KIM, Pohang University of Science and Technology, TIMOTHY P. LODGE, University of Minnesota — The phase behavior of symmetric styrene-isoprene diblock copolymers in selective solvents in the vicinity of the order- disorder transition (ODT) was investigated by SANS and rheology. To understand morphological changes in more detail, one of the blocks is deuterated and the scattering length density of the solvents used were identical to the corona chains. We examined two different ODTs: body-centered cubic/disorder and hexagonal cylinder/disorder, with similar SANS results in both cases. With increasing temperature, the micellar aggregation number decreases, and the core radius is roughly maintained by the increased solvent swelling of the core. The critical micelle temperature is experimentally described by an abrupt decrease in the size, aggregation number, and volume fraction of micelles, which is approximately 20-30 C higher than the TODT. Rheological measurements, however, revealed a distinct plateau in elastic modulus just above the temperature of cylinder/disorder. The structure is attributed to the micellar congestions due to the slow break-up of cylindrical domains into an equilibrium distribution of micelles. An isothermal frequency sweep in this regime indicated a very long relaxation time and the transient response significantly depends on solvent selectivity. Possible origins of the remarkable solvent selectivity dependence are also discussed.

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Date submitted: 29 Nov 2005

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