

Interplay between Cubic and Hexagonal Phases in Block Copolymer Solutions

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The phase behavior of a styrene-isoprene diblock copolymer in a styrene-selective solvent was investigated by in-situ SAXS on isotropic and shear-oriented solutions, and by rheology and birefringence. A remarkable new feature in this phase diagram is the coexistence of both bcc and hcp sphere phases, in a region between close-packed spheres (cps) and hexagonally-packed cylinders (hex). By focusing on the transitions among these various ordered phases during heating and cooling cycles, we observed a strong hysteresis: supercooled cylinders persisted upon cooling. The stability of these supercooled cylinders is quite dependent on concentration and for high concentrations, the supercooled cylinders do not revert to spheres even after quiescent annealing for one month. The spontaneous formation of spheres due to the dissociation of cylinders is kinetically hindered in this case, and the system is apparently not amenable to any pre-transitional fluctuations of cylinders prior to the transition. This contrasts with the case of cylinders transforming to spheres on heating in the melt. Application of large amplitude shear to the supercooled cylinders is effective in restoring the equilibrium sphere phases.