Dynamic Structure of Multiarm Star Polymers in the Ordering Region

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Star shaped macromolecules consisting of linear homopolymers covalently jointed to a common center represent model spherical polymer brushes with soft colloidal character. As a result of arm grafting, the monomer density distribution in multiarm stars is very inhomogeneous and liquid-like ordering can occur above the overlapping concentration c*. Three mechanisms are identified for the total concentration and order parameter (composition) fluctuations in multiarm stars vith high functionality in a good solvent with c ranging from below to well above c*. High quality intermediate scattering function data for model polybutadiene stars with f = 64 and 128 with different different degree of polymerization per arm (N = 120, 240, and 1340) were obtained over broad time range using photon correlation spectroscopy. Total concentration fluctuations relax, like in semidilute linear homopolymer solutions via fast cooperative diffusion exhibiting, however stronger c dependence due to the steeper increase of osmotic pressure near c*. The intermediate and slow processes relate to the dynamics of composition fluctuations decaying via structural relaxation and self diffusion probed due to the contrast between star cores and solution and functionality polydispersity.