Mesoscopic Behavior of Polymer Chains in Mixed Solvents Away and Near the Critical Point

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We present results from an experimental dynamic light-scattering study of poly(ethylene oxide) (PEO), polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(butyl methacrylate) (PBMA) in mixed solvents away and near the critical point. When the temperature is far away from the critical point, polymer chains may show swelling-collapse-swelling transition at different solvent concentrations. The collapse of polymer chains is attributed to the preferential adsorption of hydrogen bonding. When the temperature is near the critical point, the critical fluctuations would play an important role in the conformation of polymer chains. This effect was predicted 35 years ago by de Gennes for a mixture of two good solvents and later confirmed experimentally. We released this limitation and studied the effect of solvent quality on the conformation of polymer chains near the liquid-liquid critical point of a nitroethane-isooctane solution. The components of the solution have very close refractive indices, which makes the critical opalescence relatively weak. Therefore, the weak scattering from critical fluctuations does not prevent the study of Brownian motion of polymer chains by dynamic light-scattering near the critical point.