Microrheological studies of solvent-response dynamics of polyelectrolytes

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We have developed a dialysis cell for microrheology, which provides unique capabilities for studying microstructural dynamics of macromolecular solutions due to sudden changes in solvent composition (e.g., ionic strength, pH, solvent/cosolvent ratio). The device was used to determine the response of sodium sulphonated polystyrene (NaPSS) solutions of different molecular weights to changes in counterion concentration. In general, polyelectrolyte chains collapse upon addition of counter-ions, but recent numerical simulations by Hsiao and Luijten (PRL 97, 2006) predicted reexpansion at high concentrations of multivalent counterions. We tested and confirmed these predictions for trivalent chloride salts (Al, In, Tl), although the effect is subtle and strongly varies between the cations investigated. Another study employed the dialysis cell to characterize pH-induced swelling and deswelling of colloidal microgel particles of a poly(N-isopropylacrylamide)-co-(acrylic acid) copolymer. The acid copolymer causes pH-responsiveness, swelling the particles at high pH due to deprotonation. In dilute suspensions of these particles, we studied the swelling response for different AAc fractions as a function of pH. In the concentrated suspensions, pH-induced particle expansion can cause transitions between fluid, glassy and crystalline phases. Data will be presented on the dynamics of the observed phase behavior.