Polymers under Multiple Constraints

Kolloquium

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Kinetics of collapse and aggregation in thermoresponsive micellar block copolymer solutions

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Thermoresponsive, polymeric hydrogels respond in a controlled and reversible way with a volume change to a small change of temperature across the cloud point. These switchable and nanostructured materials are of great interest for controlled molecular ultrafiltration. A widely used thermoresponsive polymer is poly(N-isopropylacrylamide) (PNIPAM) which exhibits a cloud point at 32 °C. We investigate self-assembled, physically cross-linked thermoresponsive hydrogels formed by amphiphilic, symmetric triblock copolymers having short, fully deuterated polystyrene (P(S-d8)) end blocks and a large (PNIPAM) middle block. We focus on the structural properties as a function of temperature [1] as well as on the kinetics of the collapse of the micelles and their subsequent aggregation [2,3]. Small-angle neutron scattering (SANS) with contrast matching allowed us to reveal the core-shell structure of the micelles as well as the network structure. We found that, at the cloud point, the shell collapses and the distance between the P(S-d8) cores shrinks abruptly [1]. The changes are reversible upon cooling. Using in-situ, real-time SANS following a temperature jump across the cloud point, we characterized the collapse and the subsequent aggregation behavior in a micellar solution in D2O [2,3]. The collapse of the micellar shell is extremely fast (< 1 s). The aggregation process of the collapsed micelles is complex and involves several steps, such as the formation of small and loosely packed aggregates, their densification and eventually their coagulation. Thus, large aggregates are only formed after a certain time which may be at the origin of the slow reswelling behavior after prolonged heating of such solutions to high temperatures. Time-resolved SANS thus gives detailed information on the structure and dynamics as well as on the kinetics of switching.

Figure 1: Schematics of the setup for time-resolved small-angle neutron scattering measurements of the collapse and aggregation behavior of a thermoresponsive polymer during a temperature jump through the cloud point. The shell of the micelles formed by P(S-d8-NIPAM-d8-2-S) in aqueous solution collapses very rapidly. The aggregation of the collapsed micelles proceeds via a multi-step process [2].

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