Hydration, Phase Separation and Nonlinear Rheology of Temperature-Sensitive Water-Soluble Polymers

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The molecular origin of temperature(heat)-sensitivity of poly(N-isopropylacrylamide) (PNIPAM) in water is theoretically studied on the basis of *cooperative (de)hydration*. The observed sharp collapse of a chain on heating above 32℃ and very flat LCST line (horizontal up to 20 wt%) are shown to be caused by the hydrogen bonds between water molecules and amide groups on the chain with cooperativity parameter smaller than $\sigma = 0.3$[1].

A PNIPAM chain exhibits peculiar conformational changes upon addition of a second water-miscible solvent such as methanol. Although the second solvent is a good solvent for the polymer, the chain collapses in the certain compositions of mixed solvent, followed by eventual reswelling under majority of the second solvent. The tendency for phase separation is strongly enhanced by the presence of the second solvent. The LCST drop is the largest, from 31.5 °C down to -7 °C, for the specific molar fraction $x_m = 0.35$ of methanol. This enhanced phase separation in mixed good solvents is known as *cononsolvency*. We propose a new mechanism of cononsolvency by introducing the concept of *competitive hydrogen bonds*: water and methanol strongly compete with each other to form hydrogen bonds with the polymer chain [2], and calculated the mean square end-to-end distance of a chain and the cloud point curves.

The solution properties drastically change when PNIPAM chains are hydrophobically modified. In particular, telechelic PNIPAMs exhibit a variety of associated structures, from flower micelles to gel networks. The LCST of these solutions is found to decrease along the sol-gel transition curve as a result of end-chain association (association-induced phase separation) . The LCST splits from the collapse transition line. We relate the magnitude of the LCST decrease to a hydration cooperativity parameter. The LCST decreases substantially (ca 100 K) in the case of random hydration (for PEO $\sigma = 1.0$), whereas only a small shift (ca 5 to 10 K) occurs in the case of cooperative hydration (for PNIPAM smaller than $\sigma = 0.3$)[3]. These results are compared with experimental observations of the cloud points of tel-PEO and tel-PNIPAM solutions.

Fig.1 Stress buildup in start-up shear flow: comparison of the theory with experimental data on telechelic PEO.

The nonaffine transient network theory is developed to study the time development of the shear and normal stresses under start-up shear flows in networks formed by self-assembled telechelic PEO and PNIPAM chains[4]. The initial slope, strain hardening, and overshoot of the shear stress are studied in detail in relation to the nonlinear tension-elongation curve of the elastically active chains in the network. The critical value of the shear rate for strain hardening (upward deviation of the stress from the reference curve defined by the linear moduli) is calculated as a function of the amplitude A of the nonlinear term in the tension of a chain. It is approximately 6.3 (in the time unit of the reciprocal thermal dissociation rate) for a nonlinear chain with $A = 10$. The overshoot time when the stress reaches a maximum, and the total deformation accumulated before the peak time are obtained in terms of the molecular parameters of the polymer chain. These theoretical results are compared with recent rheological experiments of the solutions of telechelic hydrophobically modified poly(ethylene oxide)s carrying short branched alkyl chains (2-decyl-tetradecyl) at both ends.
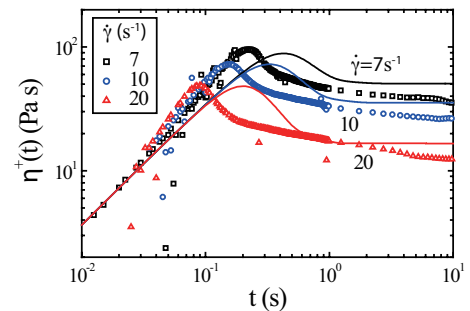
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