## Understanding Critical Behaviour of pNIPAm: Hydration/dehydration, Solvent Deuterium Isotope Effects, and Cononsolvency

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As is well known, poly(N-isopropylacrylamide) (pNIPAm) has a lower critical solution temperature (LCST) in aqueous media [1]; when temperature (T) is raised, pNIPAm chains undergo a coil-to-globule transition at about 32-34 °C. In many small-angle neutron scattering (SANS) studies,  $D_2O$  is used as solvent [1][2]. However, solvent deuterium isotope effects are in a sense versatile depending on the system and sometimes cannot be neglected. First, we examined static structure of semi-dilute pNIPAm in H<sub>2</sub>O and D<sub>2</sub>O by means of simultaneous small- and wide-angle X-ray scattering (SWAXS) in the extended q-range of 0.072 - 20 nm<sup>-1</sup>. We show how solvent deuterium isotope effects affect  $T_c$  and the critical exponents of pNIPAm characterizing the divergence of the length-scale of density fluctuation and the osmotic compressibility. We also used dielectric relaxation spectroscopy (DRS) in the frequency range of  $0.2 \le \nu/GHz \le 89$  to monitor the kinetics of hydration and bulk water molecules in aqueous pNIPAm solution. SWAXS and DRS results demonstrate how dehydration of pNIPAm's sidechain groups at high T, mediated by hydrophobic interaction, is closely related to the formation of polymer-rich and water-rich domains and segregation of the polymer chains. Next, we investigated critical behaviour of pNIPAm in water/methanol mixed solvent by means of SWAXS at methanol molar fractions,  $X_m = 0.05$ , 0.10, 0.15, 0.20, 0.45, 0.80, and 1. As we mentioned, water can be either a good or poor solvent for pNIPAm depending on T. On the other hand, methanol is a good solvent independent of T below its boiling point. However, a mixed solvent comprising these two good solvents can be a poor solvent depending on solvent composition [3][4], which is called cononsolvency. Although the underlying mechanisms of cononsolvency of pNIPAm are still in debate, we found that the singular concentration for mixing schemes in methanol/water mixtures as revealed by previous DRS study seems to be linked with the phase boundary of pNIPAm in methanol/water mixtures. We observed critical behaviour depending on T as well as X, the correlation length  $\xi$  showing diverging behaviour when either a critical temperature or a critical composition is approached. Addition of methanol to water enhances hydrophobic interaction between the sidechain groups of pNIPAm. Finally, we move on the critical behaviour of pNIPAm-based microgels in dispersion. A series of microgel samples were prepared via aqueous free-radical precipitation polymerization using a water-soluble anionic initiator KPS, in which N,N'-methylenebis(acrylamide) (BIS) was used as a crosslinking agent. We observed simultaneous divergence of the correlation length, interpreted as the mesh-size of the transient polymer network, and the asymptotic Ornstein-Zernike forward intensity, being inversely proportional to the osmotic compressibility, when  $T_c$  is approached, whose features are, however, considerably different from those of the well-established pNIPAm-based bulk gels belonging to the Ising universality class. We try to explain why the microgels exhibit such unconventional behaviour.

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