Introduction

As is well established, poly(N-isopropylacrylamide) (PNIPAM) in aqueous solution exhibits a structural change upon increasing the temperature beyond a lower critical solution temperature (LCST) at approximately 305 K. As a consequence, PNIPAM solutions phase separate above the LCST while PNIPAM gels collapse (shrink). This fascinating thermo-responsive behavior stimulated extensive studies of PNIPAM solutions and gels for the preparation of stimuli-responsive devices and formulations with potential biomedical applications.

The molecular mechanism behind the PNIPAM transition, although still under intense investigation, seems to be dehydration and reduced hydrogen bonding of the amide moiety which renders water a poor solvent for the chain. Hence, the polymer, an extended coil below the LCST, collapses into a globular form above the LCST with a high degree of tight contact among the hydrophobic side chains. As established primarily by calorimetric studies, the PNIPAM chain in the collapsed state is composed of globular domains of a size in the order of $\mathcal{M}_w \approx 10^4$ with small extended portions of the chain in between them. This scenario is well supported by a wealth of experimental data.

Summary: The time course of the coil-to-globule collapse and intermolecular aggregation of poly(N-isopropylacrylamide) in aqueous solution upon exceeding the lower critical solution temperature (LCST) are investigated by temperature-jump $^1$H NMR spectroscopy. After the temperature jump, we record the time dependences of (i) the mobile fraction of the polymer chain as revealed by the intensity of the liquid-like NMR signal, (ii) the local mobility of those chains as revealed by the transverse relaxation time $T_2$, and (iii) their self-diffusion coefficient $D$. The same data are also reported at their temperature-dependent long-time limits. The results suggest a sudden, faster than one second, collapse and intermolecular aggregation into globules and a slower reorganization/redistribution of the individual chains among and within the globular and mobile states. We found that all molecular changes are reversible if the temperature remains less than ca. 6–8 K above the LCST for less than a few minutes; under those conditions, experiments upon sudden temperature quench below the LCST show that the aggregates disintegrate and swell into coils in less than a few seconds.