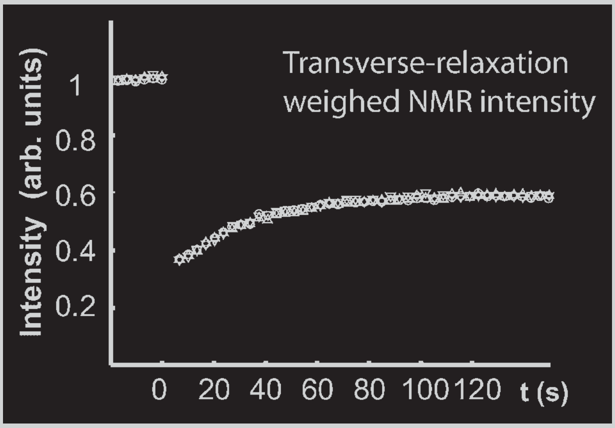
Summary: The time course of the coil-to-globule collapse and intermolecular aggregation of poly(*N*-isopropylacrylamide) in aqueous solution upon exceeding the lower critical solution temperature (LCST) are investigated by temperature-jump ^{1}H NMR spectroscopy. After the temperature jump, we record 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.



^{1}H NMR signal intensity of the methyl groups of 1 wt.-% PNIPAM dissolved in 0.1 M NaCl solution in D_2O in a temperature-jump experiment from 300 to 312 K. The data were recorded by the $90°-\tau-(180°-2\tau\text{-})_n$-detection of the CPMG pulse sequence.

Kinetics of Demixing and Remixing Transitions in Aqueous Solutions of Poly(*N*-isopropylacrylamide): A Temperature-Jump ^{1}H NMR Study

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Introduction

As is well established, poly(*N*-isopropylacrylamide) (PNIPAM) in aqueous solution[1] 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.[2,3]

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,[4,5] the PNIPAM chain in the collapsed state is composed of globular domains of a size in the order of $\bar{M}_w \approx 10^4$ with small extended portions of the chain in between them. This scenario is well supported by a wealth of experimental