



P.27 Computational studies on the effect of stereotacticity of poly(N-isopropylacrylamide) in aqueous solution

V Bojan and K Leonhard

Lehrstuhl für Technische Thermodynamik, RWTH University, Germany

In the present work the effect of polymer tacticity on the solubility and the lower critical solution temperature (LCST) of poly(N-isopropylacrylamide) (PNIPAM) chains in water is investigated by means of molecular dynamics simulations. The extent and type of stereoregularity of the polymer chains have a significant impact on the LCST of PNIPAM in aqueous solutions: the transition temperature, above which a polymer chain exhibits an abrupt and reversible coil-to-globule transition, is considerably reduced for the isotactic-rich polymers and scarcely increased for the syndiotactic-rich polymers compared to atactic polymers. Previous computational studies on the deswelling mechanism of stereoregular NIPAM-oligomers in water and water-alcohol mixtures, though indicating conformational entropy change associated with different stereoisomers, were all limited to dimers and trimers. It was shown, however, that in simulations a distinguishable coil-to-globule transition in a single polymer chain appears first with a chain length of at least 30 monomer units.

To investigate the effect of stereotacticity on the hydration of PNIPAM polymers atomistic molecular dynamics simulations of a single NIPAM-oligomer consisting of 30 monomer units solvated in water are used to model two limiting cases of iso- and syndiotactic isomers below and above LCST. The deswelling of PNIPAM chain is clearly observed at different temperatures for different stereoisomers. Conformational transitions in these two stereoisomers are evaluated using structural and dynamical correlation functions such as radius of gyration, pair correlation function, spatial distribution functions of water molecules and auto-correlation functions of intra- and intermolecular hydrogen bonds. Our results suggest that stereoisomers have different steric volume that greatly affects the conformational transition of chains and different LCST temperatures. The carbonyl oxygens located on the same side of the backbone of an isotactic PNIPAM chain hinders the formation of H-bonds between solvent and polymer to some extent and this effect should be also present in similar thermosensitive polymers, e.g. poly(N,N-diethylacrylamide). In addition, we calculate the radial and spatial distribution of water molecules around isotactic and syndiotactic solutes and indicate the difference in this distribution is mainly due to the steric effects. Thus, our study provides atomic-scale insights into the role of stereotacticity in deswelling transition of PNIPAM across LCST.