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Tuning the fast dynamics of PNIPAM-based systems with bio-cosolvents

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Responsive polymers as poly-N-isopropylacrylamide (PNIPAM) are known as "smart" materials due to their ability to respond to variations of parameters like temperature, pH, pressure, and many others. PNIPAM phase behaviour results from a highly temperaturesensitive competition between hydrophobicity of methyl and methylene groups and the ability of amide groups to make strong hydrogen bonds. When the temperature increases above a critical value (lower critical solution temperature, LCST), molecular agitation disrupts hydrogen bonds and leads to the breakdown of the local structure of water around PNIPAM chains. PNIPAM can be arranged in 3-D networks in order to form microgel particles which in correspondence of a critical temperature pass from a swollen, hydrated phase to a collapsed, dehydrated one, giving rise to the so-called Volume Phase Transition (VPT). Different environments can impact on this delicate balance between hydrophilic and hydrophobic interactions and strongly affect the LCST [1]. It is interesting to look at the transition of PNIPAM as an analogous to the cold denaturation of proteins: at high temperature PNIPAM is in a globular, folded state, but it unfolds to a coil as it is cooled below a critical temperature. It is known that changes of the environment by the addition of cosolvents has an impact on the protein behaviour, as they can act as cryopreservant (e.g., DMSO), denaturant (e.g., ethanol), stabilizer (e.g. glycerol) [2]. Despite the great interest in the understanding of the mechanisms underlying these effects, they are not yet completely understood. In this context, we use a multi-technichal approach to study how different solvent mixtures affect the PNIPAM hydration states and correlate with changes in the structure of PNIPAM-based microgel particles across the VPT. We use UV-Raman and neutron scattering measurements to get microscopic dynamical information to be correlated to macroscopic structural information obtained by PCS.

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Summary

Topic

1. Amorphous and soft matter

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