

## Smart, responsive materials: Co-nonsolvency

Responsive polymers exhibit abrupt property changes upon one or more external stimuli. A well-studied example is poly(*N*-isopropylacrylamide) (PNIPAM), a thermo-responsive polymer. In aqueous solution, linear PNIPAM shows a reversible coil-to-globule transition upon heating around a lower critical solution temperature (LCST) close to physiological conditions (ca. 32°C). Besides temperature, its chain conformation depends on external influences such as pH, salt concentration and cosolvents, as well as other factors, like the degree of polymerization, polymer concentration or crosslinker distribution. This combined tunability and multi-responsiveness has led to large interest across many disciplines of science, reflected in the manifold applications of responsive polymers. They are used as drug delivery systems, switchable cell substrates or matrices for optical arrays. Not least due to this versatility in macro- and nanoscale context, they are also called “smart materials”.

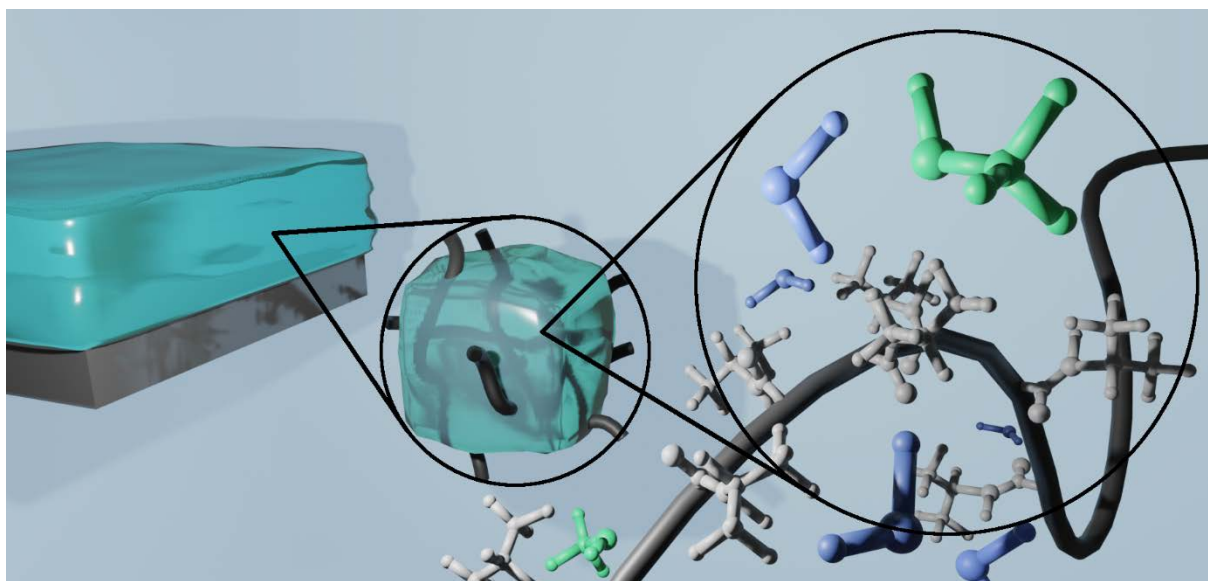


Figure 1: Sketch of a thin responsive polymer film exposed to cononsolvency conditions in mixed atmosphere.

When exposed to co-nonsolvency conditions, created by a mixture of water and organic cosolvent, thermo-responsive polymers in solution can undergo a coil-to-globule transition. For some poly(acrylamide)/water/alcohol systems, for example, this is accompanied by a shift of the critical temperature below room temperature. In this case, the phase transition can be observed by the naked eye: A clear solutions will become turbid as a result of polymer precipitation. At the molecular level, the cosolvent enters the hydration shell surrounding the polymer chain and disrupts intra and intermolecular forces. The coiled structure becomes unstable and ultimately the chain collapses. Similar to introducing salts, introducing cosolvents modifies the strength of hydrogen bonds within the hydration shell. In addition to this, as a unique aspect of the co-nonsolvency effect, the phase transition characteristics strongly depend on the local chemical structure of the responsive block, as hydrophobic moieties of organic cosolvents are able to directly bond to hydrophobic side groups and the backbone of polymers. The intricate mechanisms of the co-nonsolvency effect are not fully understood so far, and the research focus has been on solution systems. Thus, in an effort to explore the mechanisms and limitations of co-nonsolvency, our group is researching the influence of the co-nonsolvency effect on the behavior of responsive thin films in mixed vapor atmospheres.

We have particular interest in the sorption kinetics and self-assembly of responsive homopolymers, microgels and block copolymers with different architectures. To observe the diffusion of solvents and the aggregation of polymeric structures with high statistical significance we apply specialized neutron scattering methods. To learn how the co-

nonsolvency behavior is expressed in thin responsive films in contact with mixed vapor atmospheres, we have developed a vapor generation and mixing system and sample environment suitable for time-resolved time-of-flight neutron reflectometry (ToF-NR) and grazing-incidence small-angle neutron scattering (GISANS) measurements. Using time-of-flight neutron reflectometry (ToF-NR), for example, the stages of the solvation of a thin PNIPAM film can be resolved in detail. As a complementary method, Fourier-transform infrared spectroscopy (FT-IR) shows changing local polymer-solvent interactions. We found that the co-nonsolvency behavior of thin films in mixed vapors is a multi-stage swelling and contraction process, and greatly depends on the type of responsive polymer used and its uptake of water and cosolvent via the polymer-air interface [1-3]. Distinct states of the polymer films realized with a co-nonsolvency stimulus could be used in nanoswitches [4]. Using time-resolved small-angle neutron scattering (SANS) and quasi-elastic neutron scattering (QENS), the aggregation process as well as the solvent dynamics of the PNIPAM/water/methanol system under co-nonsolvency conditions were investigated [5,6].

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5. K.Kyriakos, M.Philipp, L.Silvi, W.Lohstroh, W.Petry, P.Müller-Buschbaum, C.M.Papadakis:  
*Solvent dynamics in solutions of PNIPAM in water/methanol mixtures – a quasi-elastic neutron scattering study*; J. Phys. Chem. B 120, 4679-4688 (2016)
6. K.Kyriakos, M.Philipp, C.-H.Lin, M.Dyakonova, N.Vishnevetskaya, I.Grillo, A.Zaccone, A.Miasnikova, A.Laschewsky, P.Müller-Buschbaum, C.M.Papadakis: *Quantifying the interactions in the aggregation of thermoresponsive polymers: The effect of cononsolvency*; Macromol. Rapid Commun. 37, 420-425 (2016)