Thermo-Responsive Behavior of Poly(2-oxazolines)

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At their cloud point, thermo-responsive polymers react strongly on temperature stimuli, e.g. with a discontinuous change in volume and solubility. Poly(2-oxazolines) (POx) are very versatile and attractive polymers of this class, as their cloud point can be tuned. Along with their excellent biocompatibility this makes them attractive in medical applications, e.g. as a drug delivery agent.

We have investigated aqueous solutions (20 mg/ml) of poly(2-iso-propyl-2-oxazoline)50 (PiPrOx50), poly[(2-iso-propyl-2-oxazoline)48-(2-n-nonyl-2-oxazoline)2]gradient (P[iPrOx48NOx2]grad) and poly[(2-iso-propyl-2-oxazoline)46-(2-n-nonyl-2-oxazoline)4]gradient (P[iPrOx46NOx4]grad) by small angle neutron scattering (SANS), fluorescence correlation spectroscopy (FCS) and turbidimetry [1]. The results show that, below their respective cloud points, PiPrOx50 and P[iPrOx48NOx2]grad have Gaussian coil conformation. When approaching their cloud point, the polymers form small aggregates while Gaussian coil conformation is maintained. Directly above the cloud point, we encounter an intermediate regime, where these small aggregates remain stable. Only a few Kelvin above the cloud point, large aggregates become prevalent (Fig. 1). P[iPrOx46NOx4]grad, in contrast, forms compact spheres already below the cloud point, which we attribute to the two additional extremely hydrophobic NOx groups. They have to be shielded from hydrophobic interaction with the water. This polymer also exhibits the subsequent formation of small and large aggregates directly above the cloud point.

The solubility thus depends strongly on the NOx content. Moreover, we found an intermediate regime, thus aggregation is a two-step process.

Figure 1: Schematics of the phase transition of P[iPrOx46NOx4]grad. The chains aggregate below their cloud point. When crossing the cloud point, aggregates formed already below the cloud point, remain stable and only a few Kelvin above, large aggregates become prevalent.