Experimental report

08/03/2019

Proposal:	**9-11-1848**	**Council:**	4/2017
Title:	Phase behavior and solution structure of new UCST- and LCST-type polymers		
Research area:	Soft condensed matter		

This proposal is a new proposal

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Samples:
(C4NOH7)n
(C7NOH13)m
(C9NOH15)m

Instrument	Requested days	Allocated days	From	To
D11	2	2	11/04/2018	13/04/2018

Abstract:

Copolymerization is a powerful strategy for the fabrication of new polymers with tailored functionality. For example, the copolymerization of acrylamide-based monomers with different substituents results in thermoresponsive polymers with either LCST- or UCST-type phase behavior. However not much is known about the solution structure of such polymers.

We used RAFT polymerization to synthesize a variety of different copolymers based on acrylamide. Depending on the polymer composition and degree of polymerization we find significant differences in the phase behavior. Here we would like to study the form factor, the dynamic correlation length and the aggregation number of different UCST- and LCST-type polymers in the dilute and semidilute regime. We want to perform measurements at different temperatures covering the phase transition to analyze the phase behavior.

The Small Angle Neutron Scattering (SANS) experiment performed at the D11 instrument at ILL aims at the investigation of structural changes during the phase transition (from soluble to insoluble or vice versa) of copolymers based on methacrylamide and differently substituted N-acrylamides. As known from previous publications the phase transition temperature can be tuned by means of variation of the side groups at the amide site. Additionally the molar ratio of the monomers does have an influence on the transition temperature and the transition type[1]. Still the phase transition process of thermoresponsive polymers is only partly understood and still updated, as seen for the well-known and intensely investigated thermoresponsive polymer poly(N-isopropylacrylamide) (PNIPAM)[2].

In general the phase transition for LCST-type polymers is expected to undergo from soluble to insoluble upon heating with the polymer coils becoming hydrophobic, releasing water and transforming into globules and aggregates, which can be observed visually via the formation of a turbid solution.

SANS is well suited to study the structural changes of thermoresponsive polymers during the phase transition because it delivers information from a wide q-range, i.e. on different length scales, and excellent contrast of hydrated polymers in deuterated environments also at very low concentrations.

In this experiment we studied LCST- and UCST-polymers of different molecular weight and monomer composition at temperatures below and above the phase transition temperature by SANS. Furthermore we systematically varied the concentration of the hydrated polymers in D_2O to study the phase transition behavior in the dilute and semidilute state.

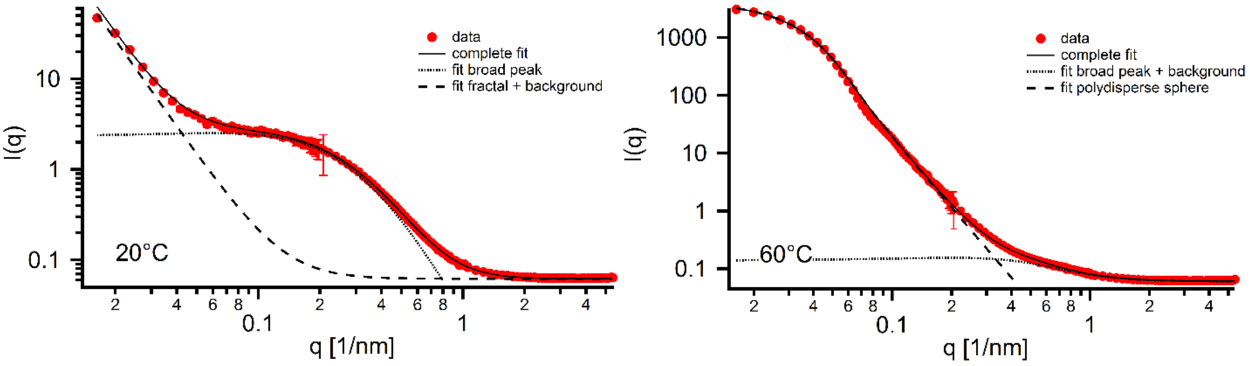

Fig.1: Scattering intensities obtained from SANS measurements from a LCST-polymer sample at 20°C and 60°C in red, additionally the contributions of the different fit models and the complete fit in black, concentration is 1%wt in D_2O

Figure 1 shows exemplary SANS profiles measured, for one of our LCST-type polymers at 20°C (left, below LCST) and 60°C (right, above LCST). A strong difference between the two scattering profiles can be depicted at first glance. At low *q* (0.01-0.03 nm^{-1}) a power law decay characteristic for fractal surfaces is obtained for the measurement at 20°C. This implies that the dispersion does not contain well-solvated isolated polymer coils, but rather large structures due to inter- and intrachain interactions are present already far below the LCST. The plateau in scattering intensity at approximately 0.2 nm^{-1} can be described by a broad peak contribution. From the fit we extract a correlation length of 3.2 nm and a scattering length density fluctuation on the lengthscale of 106 nm. The picture changes above the transition temperature. At 60°C a form factor for polydisperse spheres in combination with a broad peak model can be used to describe the scattering curves. The overall scattering profile is dominated by scattering from spherical aggregates, i.e. microphase separated collapsed globules, whereas the broad peak scattering contributes only a slight amount to the overall scattering. The polydisperse sphere contribution yields a size of 50 nm. From the broad peak contribution we derive a decrease of the correlation length from 3.2 nm at 20°C to 2 nm at 60°C. At the same time the lengthscale of the scattering length density fluctuation decreases to 25 nm. Currently we are analyzing all measured scattering profiles from the copolymers measured in dependence of temperature and concentration. As the examples in figure 1 have shown SANS and in particular the instrument D11 are ideally suited to study structural changes of thermoresponsive polymers in dependence of temperature. It also becomes obvious that the low q-range that the D11 instrument offers is required to cover all lengthscales appearing in our polymer dispersions. We would like to acknowledge the local contacts for the excellent support during beamtime and the ILL for allocation of beamtime.

Furthermore we would highly appreciate to use the D11 instrument at the ILL for our future SANS investigations.

[1]: F. Käfer, M. Pretscher, S. Agarwal, Macromol. Rapid. Commun. 2018, 39, 1800640
[2]: K. Yanase, R. Buchner, T. Sato, Phys. Rev. Mater. 2018, 2, 085601