Experimental report

09/02/2016

Proposal: **9-11-1754**

Council: 4/2015

Title: Kinetics of pressure-induced structural changes of thermoresponsive poly-N-n-propylacrylamide and related polymers

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Yvonne PUETZ**

Experimental team:
Thomas HELLWEG
Oliver WREDE
Thomas SOTTMANN
DIANA ZAUSER
Stefan LUELSDORF
Yvonne HERTLE

Local contacts: Ralf SCHWEINS

Samples:
poly-(N-n-proylacrylamide)
Poly-(N-isoproylacrylamide)

Instrument	Requested days	Allocated days	From	To
D33	0	0		
D22	0	0		
D11	4	3	30/10/2015	02/11/2015

Abstract:

Thermoresponsive polymers are interesting candidates for various applications including drug delivery, nanomembranes and temperature-controlled catalysis. Based on the volume phase transition temperature (VPTT), at which the particles undergo a dramatic decrease of volume, the properties of the material can be controlled by adjusting the temperature. However, examining the kinetics of such structural changes by fast temperature jumps is a challenge, especially to lower temperatures. Having shown that the VPTT of poly-(N-n-proplyacrylamid) (PNNPAM) can be shifted by 1.5 K to higher temperatures applying 300 bar, it is possible to access both the swollen and the dehydrated state at 300 and 1 bar, respectively, by choosing a temperature slightly above the VPTT at 1 bar. The narrow transition range of PNNPAM enables to clearly distinguish between both states. Performing pressure jumps between the two states should give detailed insights into the kinetics of structural changes. Thereby, the benefit of pressure is that it appears homogeneously and can be applied repeatedly in both directions. Thus, we propose to study swelling and deswelling kinetics of PNNPAM and related polymers.

Kinetics of pressure-induced structural changes of thermoresponsive poly-N-*n*-propylacrylamide and related polymers

Preliminary Experimental Report No 9-11-1754

Abstract

Thermoresponsive polymers have attracted considerable attention in recent years because they are promising materials for drug delivery systems, for temperature-controlled catalysis or as nanoactuators. Around a specific temperature, Poly-(N-*n*-propylacrylamide) (PNNPAM) microgel particles undergo microphase seperation which is connected to a dramatic decrease in volume. Only recently it was found that the volume phase transition temperature (VPTT) of thermoresponsive polymer brushes can be shifted to slightly higher temperatures upon applying a hydrostatic pressure.[1] We recently confirmed this trend for PNIPAM microgels (paper in preparation) and showed that the VPTT of PNIPAM can be shifted by about 1K per 100bar, depending on the cross linker content. In this study we performed similar experiments on Poly-(N-*n*-propylacrylamide) (PNNPAM) microgels. These systems are especially suited for pressure jump experiments, as it is possible to perform experiments which access both the fully swollen and the fully collapsed state at different pressures but at the same temperature due to their extremely sharp phase transition. With these experiments we obtained first promising results on the swelling/deswelling kinetics for PNNPAM microgels with different cross linker contents. For high cross linked particles we obtained two time scales for the swelling (τ = 3.7 ms) and deswelling (τ = 17.5 ms). For low cross linked particles both processes are much slower (τ = 208 ms).

Static SANS measurements

To investigate the internal structure of the microgel particles, small angle neutron scattering (SANS) experiments were performed at different temperatures around the VPTT and at different pressures at a temperature slightly above the VPTT. The obtained experimental data is shown in figure 1 for both measurement series.

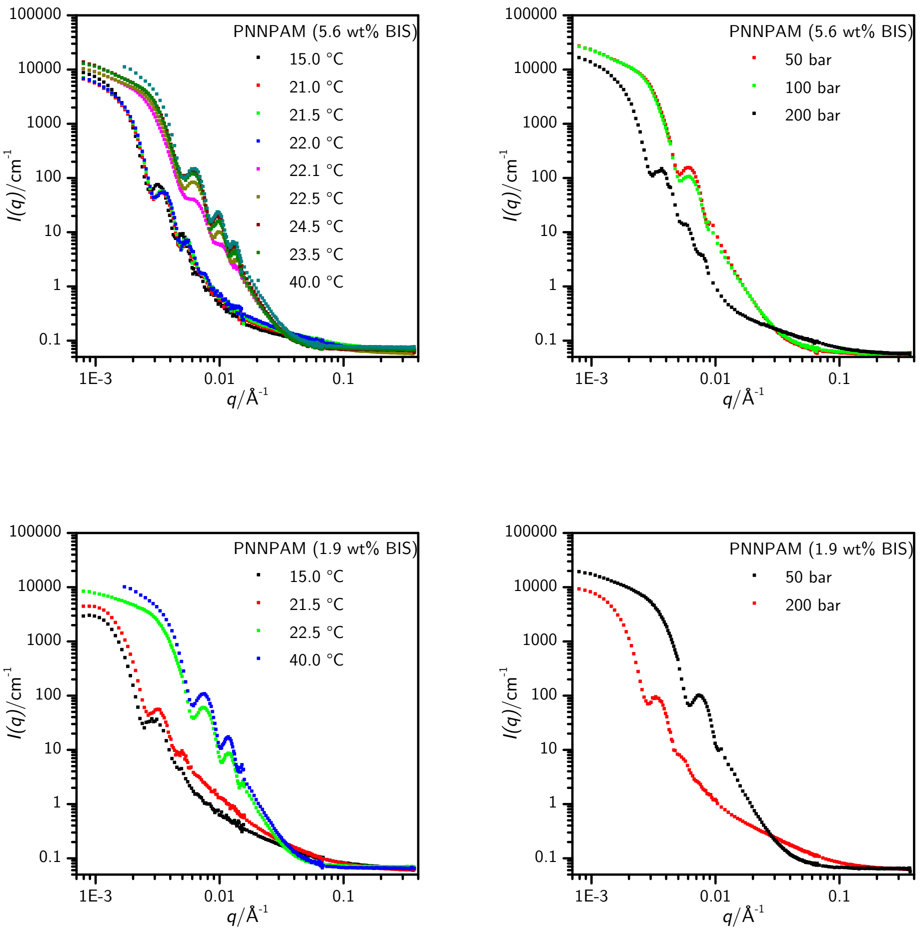

Figure 1: Small angle neutron scattering curves for PNNPAM microgels with 5.6 wt% (upper pictures) and 1.9 wt% cross linker content. On the left side the curves at p = 1 bar are displayed, on the right side the curves at p = 50 , 100 and 200 bar.

At hight temperatures the obtained scattering curves could be described by the hard sphere formfactor (eq. 1). At low temperatures an Ornstein-Zernike contribution for high q-values has to be added, to take into account the network composition fluctuations of the gel (eq. 2).

$$I(q) \propto \frac{1}{V} \cdot \left[\frac{3 \cdot V \cdot (\Delta\rho) \cdot (\sin(q \cdot R) - q \cdot R \cos(q \cdot R))}{(q \cdot R)^3} \right]^2 \tag{1}$$

$$I(q) \propto \frac{I_0}{1 + q^2 \xi^2} \tag{2}$$

On the left side of figure 1 the experimental results for the microgel with the highest (5.6 wt%) and the lowest (1.9 wt%, lower left side) cross linker content are shown at different temperatures. A comparison of the high pressure and low pressure curves show a similar overall size of the particles, but the apparent polydispersity seems to be higher in the high pressure experiments. This behavior might be worthwhile to investigate further. A second interesting point is, that for the low cross linked microgels changes in the internal structure seems to be present already before the main phase transition (comparison of the scattering curves for 15.0 °C and 21.5 °C).

Kinetic SANS measurements

To investigate the swelling and deswelling kinetics of NNPAM based microgels, periodic pressure jumps at a temperature slightly higher than the VPTT were performed. By this method it is possible to obtain scattering curves for the swollen microgel (at low pressures), the collapsed microgel (at high pressures) and the transition states with good statistics. The time resolution was selected according to the time scale of the swelling/deswelling kinetics.

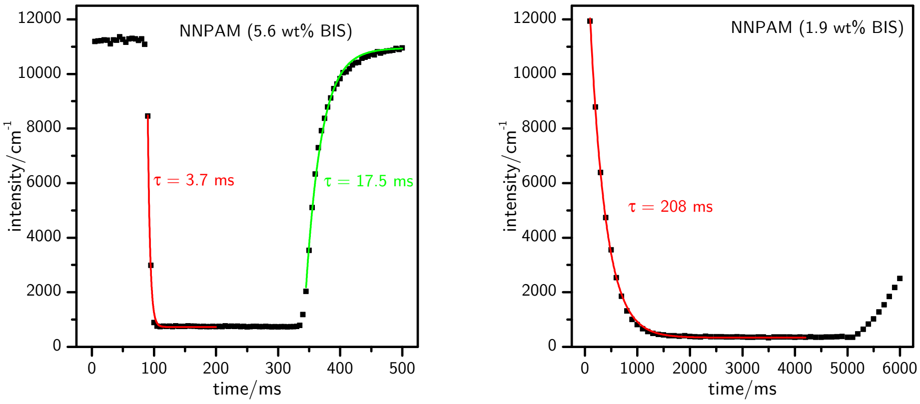

Figure 2: Integrated detector intensity as a function of time for high (left) and low cross linked microgels (right). The swelling kinetics (low measurements times) are faster than the deswelling kinetics (high measurement times). In both cases pressure jumps between 50 and 200 bar were performed (at at 22.5 Â°C for 1.9 wt%, at 22.9 Â°C for 5.6 wt% cross linker).

For high cross linked microgels fast kinetics in the low microsecond range (3.7 ms for the deswelling, 17.5 ms for the swelling process) were observed. Interestingly the swelling process is more than four times slower than the deswelling. For low cross linked microgels these processes exhibit even longer reaction times. For the deswelling of a microgel with 1.9 wt% cross linker, we observed a deswelling with a time constant of $\tau = 208$ms. A reason for this behavior might be the differences in the internal structure, which might be due a completely different density distribution inside the microgel (see static SANS results). In order to study this unexpected strong influence of the cross-linker concentration on the swelling/deswelling kinetics (which is in contrast to the theory of Tanaka and Fillmore) in more detail a follow-up experiment will be proposed.

References

[1] M. Reinhardt, J. Dzubiella, M. Trapp, P. Gutfreund, M. Kreuzer, A. H. Gröschel, A. H. E. Müller, M. Ballauff, R. Steitz, *Macromolecules* **2013**, *46*, 6541–6547.