ESRF	**Experiment title:** **Studying conformational changes upon high-pressure induced hydration of thermoresponsive polymers under variation of solvent composition**	**Experiment number**: 3233
Beamline: ID02	**Date of experiment**: from: 28.09.2011 to: 01.10.2011	**Date of report**: 13.03.2011
Shifts: 9	**Local contact(s)**: Dr. Michael Sztucki	*Received at ESRF:*

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Report:

Polymers resulting from differently substituted acrylamides often undergo a phase separation with increasing temperature when dissolved in water. This phenomenon occurs at the so-called lower critical solution temperature (LCST). In case of poly(*N*-isopropylacrylamide) (PNiPAm) and poly(*N*,*N*-diethylacrylamide) (PDEAm), the LCST is located at about 32 °C. Studies were carried out on corresponding microgels, which are crosslinked hydrogels that have a radius in the swollen state of tens to few hundreds of nanometers. Instead of precipitation, they exhibit a strong decrease in size when the critical temperature is reached, which is coined volume phase transition temperature (VPTT). By applying pressure, the reverse behaviour is observable. PNiPAm and PDEAm are, for example, of particular interest as model systems for protein folding studies as well as temperature-sensitive compounds for the development of smart materials. The effects of pressure on the design of such materials is largely unknown. PNiPAm is also known to exhibit a cononsolvency effect. This effect leads to a decrease in the LCST when another solvent is added to the water, like e.g. methanol in which, if used as a pure solvent, the polymer is completely soluble without any LCST. [1]

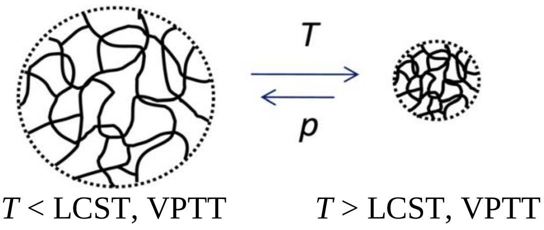

Fig. 1: Schematic drawing of the opposite effect of temperature and pressure on the swollen-to-collapsed-transition of the polymers.

In this study, we investigated the hydration and swelling properties as well as the phase behaviour of poly(*N*-isopropylacrylamide) (PNiPAm) and poly(*N*,*N*-diethylacrylamide) (PDEAm) derived microgels by small-angle X-ray scattering (SAXS). The polymers were measured using a home built high-pressure X-ray cell in a pressure range between 1 and 2500 bar at temperatures from 10 to 50 °C. [2] The high pressure SAXS measurements were performed at the ID02 beamline using a photon energy of 12.4 keV (wavelength $\lambda = 1$ Å).

The acrylamide polymers were treated as spherical particles. A first calculation of the particle size was carried out using the pressure dependent shift of the first minimum of the scattering curves. The scattering curves reveal that the polymer system gets more hydrated under high hydrostatic pressure conditions. The swelling is accompanied by a marked increase in particle size. All pressure-induced changes are fully reversible, which is an important property for putative technical applications, like stimulus-sensitive encapsulation of chemical compounds, enzymes or catalysts. A more detailed analysis of the temperature and pressure dependent strutural changes of the two polymer systems is underway.

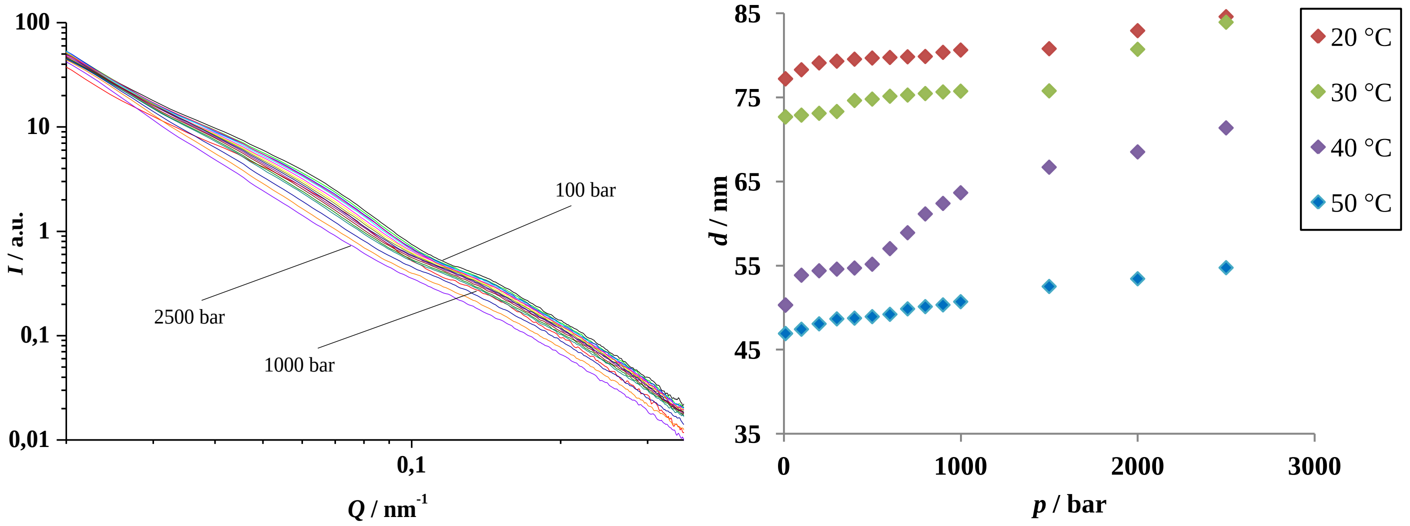

Fig. 2: Small-angle X-ray scattering curves of PNiPAm microgel in D_2O from 100 to 2500 bar at 40 °C (left). Corresponding pressure dependence of the size of PNiPAm microgel in D_2O at various temperatures (right).

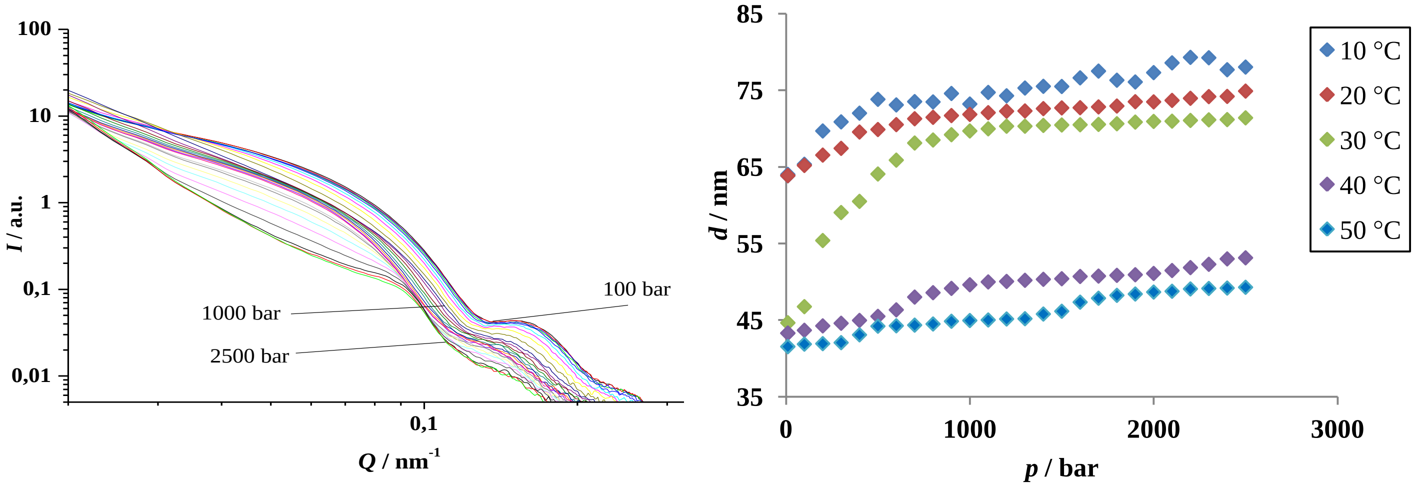

Fig. 3: Small-angle X-ray scattering curves of PNiPAm microgel in 10 mol % CD_3OD from 100 to 2500 bar at 40 °C (left). Corresponding pressure dependence of the size of PNiPAm microgel in 10 mol % CD_3OD at various temperatures (right).

References:

[1] Keerl, M.; Smirnovas V.; Winter, R.; Richtering, W. *Angew. Chem. Int. Ed. Engl.* 2008, *47*, 338 - 341.

[2] Kraineva, J.; Narayanan, R.; Kondrashkina, E.;Thiyagarajan, P.; Winter, R. *Langmuir* **2005**, *21*, 3559 - 3571.