Experimental Report

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Proposal: **9-11-1695** **Council:** 4/2014

Title: Kinetics of the pressure-induced coil-to-globule transition of PNIPAMmicrogels

This proposal is a new proposal

Research Area: Soft condensed matter

Main proposer: **PUETZ Yvonne**

Experimental Team:
LUELSDORF Stefan
GRASSBERGER Lena
ZAUSER DIANA
PUETZ Yvonne
SOTTMANN Thomas
HARBAUER Carola

Local Contact:
LINDNER Peter
SCHWEINS Ralf
PORCAR Lionel

Samples: Poly(N-isopropylacrylamid)

Instrument	Req. Days	All. Days	From	To
D11	2	2	09/10/2014	11/10/2014

Abstract:

PNIPAM is a thermoresponsive microgel which is interesting due to its lower critical solution temperature (LCST) which is located close to the temperature of the human body. There, PNIPAM undergoes a coil-to-globule transition which is connected to a dramatic change of volume. It is possible to deswell the particles applying pressure. However, the influence of pressure on the coil-to-globule transition and especially the kinetics of the pressure-induced structural changes have not been studied systematically so far. By performing DLS studies as a function of temperature and pressure we found that the LCST increases by approximately 2 K applying a pressure of 300 bar. In preliminary SANS measurements performed at the D22 we were able to confirm these findings. The next step would be the investigation of the kinetics of the swelling and deswelling behaviour upon a change of hydrostatic pressure. In order to conduct such kinetic studies we propose to perform time-resolved SANS measurements using our newly designed stroboscopic high pressure SANS-cell, which provides adjustable pressure cycles. Thereby the pressure can be varied between 1-300 bar with a maximum frequency of 10 Hz.

Kinetics of the pressure-induced coil-to-globule transition of PNIPAM microgels

Experimental Report No 9-11-1695

Abstract: Poly(*N*-isopropylacrylamid) (PNIPAM) is a thermoresponsive polymer which has attracted considerable interest in recent years due to its lower critical solution temperature (LCST) which is located around 32°C and therefore very close to the temperature of the human body[1]. Around this temperature, PNIPAM undergoes a coil-to-globule transition which is connected to a dramatic change of volume which is why this temperature is called volume phase transition temperature (VPTT) at concentrations which are not the critical concentration. It was already shown that it is possible to deswell the particles applying pressure at 298 K [2]. However, the influence of pressure on the coil-to-globule transition and especially the kinetics of the pressure-induced structural changes have not been studied systematically so far. By performing dynamic light scattering (DLS) studies as a function of temperature and pressure we found that the VPTT increases by approximately 2 K applying a pressure of 300 bar. This trend was validated by means of SANS experiments at atmospheric and elevated pressure and is contradictory to results by Lietor-Santos *et al.*[2] . By choosing an appropriate temperature, at which both the swollen and the dehydrated state are accessible at different pressures, it was possible to perform stroboscopic pressure jumps between the two states with small angle neutron scattering detection. Thus, we were able to follow both the hydration and the dehydration process of PNIPAM particles, finding that two processes occur. A fast one with $\tau_0 \approx 0.5$ s can be attributed to diffusion of water molecules, whereby $\tau_1 \approx 2.5$ s describes reordering of the polymer chains. All time constants seem to depend on the crosslinker content.

SANS measurements: In order to investigate the internal structure of the particles small angle neutron scattering (SANS) measurements at different temperatures and pressures were performed. Figure 1 shows the neutron scattering curves of PNIPAM particles with 5.6 wt% crosslinker (*N,N´*-methylenbisacrylamide) at atmospheric pressure (left) and at constant temperature and different pressures (right). The scattering curves were described by a combination of a polydisperse sphere form factor, a Lorentzian and a Gaussian scattering contribution whereby the Gaussian contribution was only used at temperatures at or below the VPTT.

The temperature-dependent scattering curves show a clear trend to higher scattering intensities with increasing temperature. This is due to the increasing scattering contrast. The forward scattering intensity of the pressure-dependent scattering curves at $T = 36.5$°C decreases with increasing pressure which is expected since the particles become more hydrated with increasing pressure, thus loosing scattering contrast. This validates the previously mentioned DLS results and findings by Reinhardt *et al.* [3]. The fitting parameters are given in Table 1. The increasing contribution of $\Delta\rho$ with increasing T clearly points to an increase of scattering contribution of the sphere. The absolute value of $\Delta\rho$ is, however, rather low for all scattering curves. Hellweg *et al.* found that PNIPAM can be matched by a mixture of 10 % H_2O and 90 % D_2O, resulting in a SLD of about $0.13 \cdot 10^{-6}$ Å^{-2} [4]. The monomer has a scattering length density of $0.74 \cdot 10^{-6}$ Å^{-2}. Thus, if the particles were in pure D_2O the scattering contrast should be about $6 \cdot 10^{-6}$ Å^{-2} for completely dehydrated particles. Considering that water molecules inside the polymer decrease the scattering contrast this value is likely a bit lower. However, the results indicate that the substitution of 90 % of H_2O by D_2O is not sufficient for a good scattering contrast. Furthermore, the radius of the particles continuously decreases with increasing temperature. Comparing the values of R_0 and R_h (not shown) one finds a difference of almost 30 nm. This is reasonable since DLS measures the hydrodynamic radius whereas SANS tends to describe only the core of the scattering particle [5]. Analogous trends were found for particles with 1.9 wt% crosslinker.

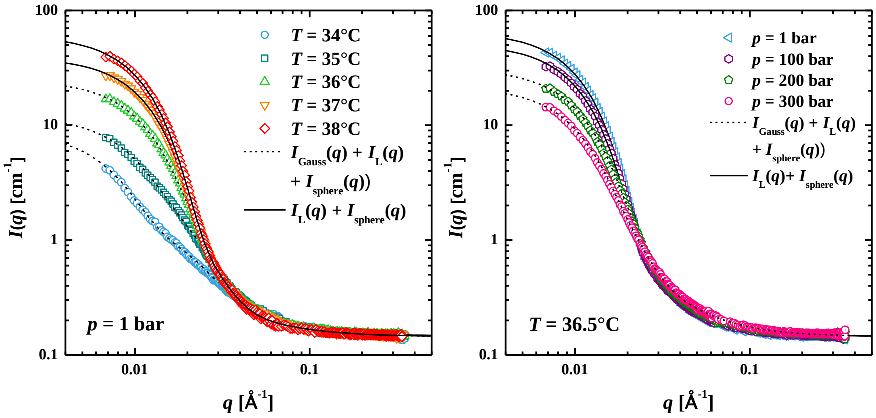

Figure 1: *Left:* Temperature-dependent scattering curves of PNIPAM particles with 5.6 wt% crosslinker (0.5 wt% in D_2O). While for the scattering curves at $T \geq 37$°C the spherical droplet form factor in combination with the Lorentzian was applied the scattering curves at lower temperature were described with an additional Gaussian contribution. *Right:* Scattering curves for the same PNIPAM particles at a constant temperature of 36.5°C and different pressures. With increasing scattering contribution of the gel network a Gaussian scattering contribution was taken into account for $p \leq 200$ bar to describe the scattering curves.

Table 1: Overview of fit parameters to describe the scattering curves shown in Figure 1 of PNIPAM particles with 5.6 wt% crosslinker. The scattering intensity $I_{sphere}(q)$ was used in combination with the Lorentzian shape $I_L(q)$ at temperatures above the VPTT. At temperatures at or below the VPTT the Gaussian contribution $I_{Gauss}(q)$ was also taken into account.

parameter		*sphere form factor*			*Lorentzian*		*Gaussian*	
T [°C]	p [bar]	R_0 [Å]	σ/R_0	$\Delta\rho$ [10^{-6} Å^{-2}]	$I_L(0)$ [cm^{-1}]	ξ_L [Å]	$I_{Gauss}(0)$ [cm^{-1}]	Λ [Å]
34.0	1	190	0.38	0.14	0.38	36.5	0.8	83
35.0	1	158	0.35	0.255	0.45	40	2.2	90
36.0	1	140	0.33	0.505	0.55	47	5.0	110
37.0	1	130	0.32	0.70	0.09	17	--	--
38.0	1	135	0.32	1.00	0.05	17	--	--
36.6	1	148	0.28	1.03	0.05	14	--	--
36.6	100	142	0.33	0.82	0.165	31	--	--
36.6	200	142	0.33	0.565	0.68	55	5.2	123
36.6	300	142	0.36	0.425	0.57	44	2.7	108

Kinetic SANS experiments: Pressure jump experiments using the stroboscopic high-pressure SANS cell were performed in order to obtain information on the kinetics of structural changes as a response to a sudden pressure jump. Pressure and temperature induce exactly the same structural changes but at different transition temperatures. Thus, these experiments can be compared to temperature jump experiments. Thereby, both structural changes, i.e. from gel to sphere and from sphere to gel, can be followed. Using temperature jump methods the application of fast cooling steps remains a challenge and has not yet been solved satisfactorily. Therefore, the measurements presented in the following contribute to the investigation of the kinetics of structural changes of PNIPAM microgel particles.

Kinetic experiments were performed at $T = 36.6$°C with the particles with 5.6 wt% crosslinker. The pressure cycle was adjusted to last for 10 s with 5 s at each pressure (300 and 5 bar) with a time resolution of 0.2 s. The pressure-dependent scattering curves in Figure 1 indicate that this pressure jump traverses the change from dehydrated to swollen sphere, as can be seen by the Gaussian contribution at high pressure. The scattering curves as a function of time and pressure for are shown in Figure 2 left.

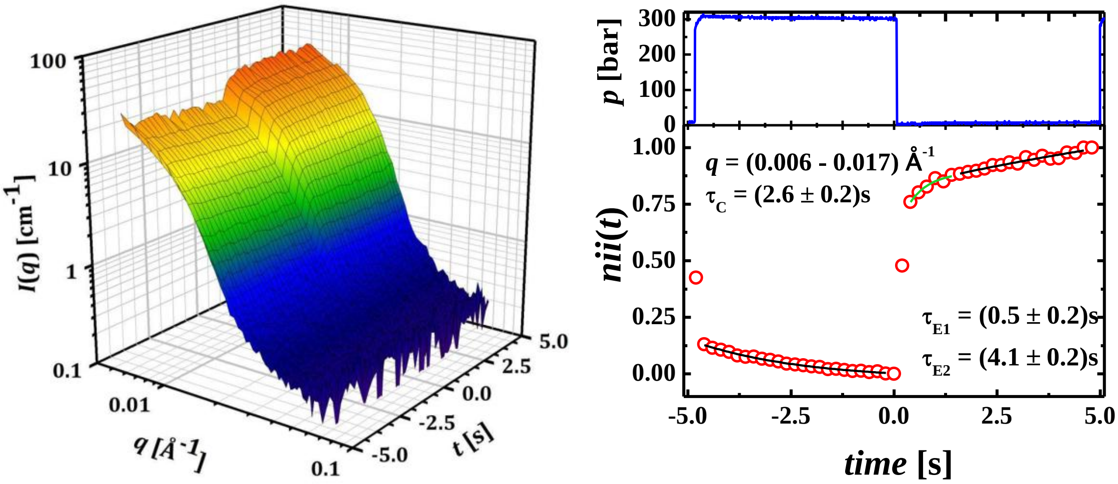

Figure 2: *Left:* Pressure-dependent scattering curves of PNIPAM particles with 5.6 wt% crosslinker as a function of time. A concentration of 0.5 wt% particles in D_2O was used. The scattering curves were recorded at $T = 36.6°C$. The pressure cycle starts at $p = 300$ bar which was held for 5 s, until at $t = 0.0$ s the pressure was changed to 5 bar for 5 s. A time resolution of 200 ms was applied. *Right:* Normalised integrated intensity (*nii*(*t*)) as a function of time for the scattering curves shown left in the *q*-range from 0.006 – 0.017 $Å^{-1}$. While the data points after compression were described by one exponential fit two functions were necessary to describe the data points after expansion. The solid lines represent these exponential fitting functions and are proportional to *exp*(-*t*/τ). The pressure profile shown at the top also applies to the plot shown left. Note that the error is within the size of the symbols.

Analysing the normalised integrated intensity *nii*(*t*) in Figure 2 right it was found that the process after compression can be described by means of one mono-exponential fitting function. The time constant found for this process is $\tau_C = (2.6 \pm 0.2)$ s. The data points obtained after expansion, however, were described by applying two fitting functions. Thus, a first and fast process occurs on a time scale of 0.5 s and is followed by a slower process ($\tau_{E2} = (4.1 \pm 0.2)$ s).

A similar experiment was performed with particles containing 1.9 wt% crosslinker. Here, only one time constant was found both after expansion and compression ($\tau_C = (2.3 \pm 0.3)$s, $\tau_E = (1.6 \pm 0.2)$s). Comparing these values it shows that the kinetics of structural changes are slower for particles with higher crosslinker content. Apparently, the processes after expansion occur with intermediate states. The process after compression, in contrast, only shows one process. Taking a more detailed look at the scattering curves it seems that the fast process after expansion represents diffusion of water molecules out of the polymer volume whereas the second, slower process describes reordering of the polymer chains. Regarding compression, one can assume that diffusion of water molecules into the polymer is faster than the applied time resolution and that the time constants describe the rebuilding of the gel state. This is in good agreement with results obtained by Sun *et al.* who performed correlation infrared spectroscopy and proposed a mechanism of the volume phase transition which can be supported by the new SANS results [6].

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