Experimental report

06/05/2017

Proposal: **9-11-1795**

Council: 4/2016

Title: Cononsolvency in PNIPAM - effect of pressure

Research area: Soft condensed matter

This proposal is a new proposal

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Samples:
poly(N-isopropylacrylamide)
fully deuterated methanol

Instrument	Requested days	Allocated days	From	To
D11	5	3	14/06/2016	17/06/2016

Abstract:

In aqueous solution, poly(N-isopropylacrylamide) (PNIPAM) is a responsive polymer which phase separates above a certain temperature, the cloud point. The cloud point increases with pressure up to 600 bar, then decreases. Addition of methanol alters the cloud point as well, and at high pressures, a coexistence region is encountered. We aim at investigating the chain conformation and domain structure in PNIPAM solutions, either in a mixture of water and methanol or in pure water. This will enable us to test theories about the change of chain conformation upon addition of methanol and will elucidate the effect of pressure on the hydrophobic effect and on the structure of water. SANS at D11 together with the use of deuterated solvents offers to cover a wide range of length scales, from the single chain to the domain scattering, which is of special interest in the coexistence region.

Poly(*N*-isopropylacrylamide) is a thermoresponsive polymer which, at atmospheric pressure, exhibits lower critical solution temperature (LCST) behavior in aqueous solutions at ca. 31°C.[1] At the LCST, the chain conformation sharply changes from a swollen coil to a collapsed globule, followed by the formation of aggregates.[1] The addition of an organic solvent decreases the cloud point of PNIPAM significantly. This effect, termed cononsolvency, was subject to numerous investigations during the past years. For example, it was shown that the presence of a co-solvent influences the aggregation behavior on mesoscopic length scales. After phase separation induced by the addition of methanol to aqueous PNIPAM solutions, the aggregates consist of a dense polymer shell surrounding a core which also contains a significant amount of solvent molecules.[2]

It has been shown that pressure destroys cononsolvency. Furthermore, the solubility of PNIPAM in mixtures of water and organic solvents is even enhanced at high pressures.[3] This effect is ascribed to the preferred binding of water to PNIPAM at high pressures because this leads to a decrease of the total volume of the system. Thus, the bulk solvent mixture contains more co-solvent, resulting in a higher amount of ordered water around the co-solvent molecules in the bulk solvent. Therefore, the hydrophobic interaction between hydrophobic side groups of PNIPAM and water, normally responsible for the phase separation, is reduced, leading to an enhanced solubility of PNIPAM at high pressure.[3]

The present study focuses on the influence of a co-solvent on the chain conformation and phase separation behavior in dependence on pressure. A 3 wt% PNIPAM solution in 74:6:20 v/v/v $D_2O/H_2O/CD_3OD$ (fully deuterated methanol) was measured in dependence on temperature at atmospheric pressure, 75 MPa, 150 MPa, 200 MPa and 265 MPa. A mixture of D_2O and H_2O was used to match the scattering length density of CD_3OD to avoid scattering originating from complexes formed by water and methanol. Experiments were performed in dependence on temperature around the respective cloud point (24.9 – 41.7 ˚C). The neutron wavelength was chosen at $\lambda = 6$ Å. A q range from 0.0015-0.2 Å^{-1} was covered with sample-detector distances (SDDs) of 3 m, 10 m and 39 m. The exposure times at these SDDs were 3 min, 12 min and 15 min, respectively. The sample was mounted in a copper beryllium cell capable of withstanding pressures up to 300 MPa. The sample thickness was 2 mm, independent of pressure. The signal of the empty pressure cell was subtracted from the data. H_2O was measured to determine the detector sensitivity. The dark current was measured using boron carbide. The software LAMP was used to perform the data reductions and to azimuthally average the data. Figure 1 shows the scattering curves at three selected pressures as a function of temperature.

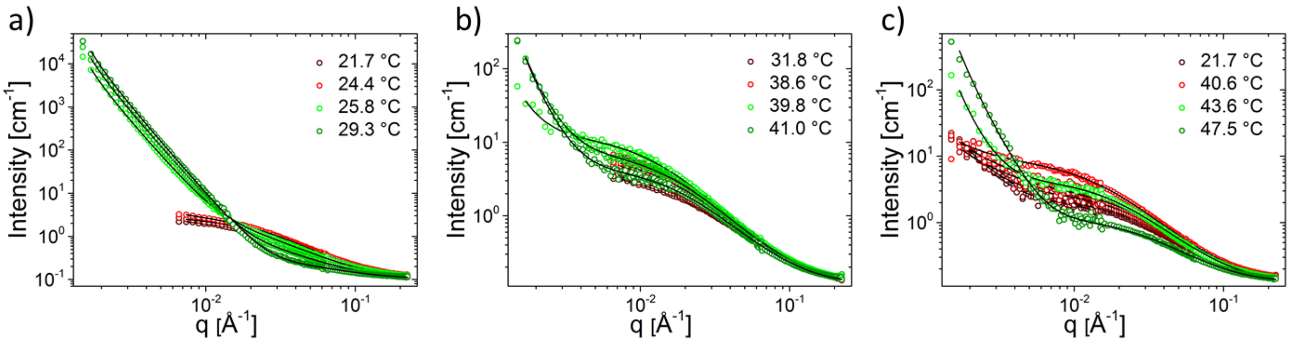

Figure 1. SANS curves of the 3 wt% PNIPAM solution in 74:6:20 v/v/v $D_2O/H_2O/CD_3OD$ at atmospheric pressure (a), 150 MPa (b) and 265 MPa (c). Symbols: experimental data (reddish: below T_c, greenish: above T_c), lines: model fits, see text.

At all pressures, the scattering at high *q* values increases, when the cloud point, T_c, is approached from below, and decreases above. Above the cloud point, a high scattering intensity at low *q* values (forward scattering) marks the presence of large aggregates. The main effect of pressure is, apart from the increased scattering at high *q* values, a shift of the forward scattering to lower *q* values. All scattering curves were successfully fitted with a combination of the Ornstein-Zernike structure factor, which describes concentration fluctuations at the nanometer length scale, and Porod's law, which accounts for large-scale concentration fluctuations below the cloud point and for aggregates above. Figure 2 shows selected fitting results. The correlation length, ξ, as well as the amplitude of the Ornstein-Zernike term, $I_{OZ}(q = 0)$, increase strongly when the cloud point is approached from below, an indication for the presence of critical behavior. This increase is the more pronounced the higher the pressure. Future work will address the determination of the critical exponents and their interpretation and may give insight into the influence of pressure on the hydrophobic interactions, reflected by the chain conformation.[1,4]

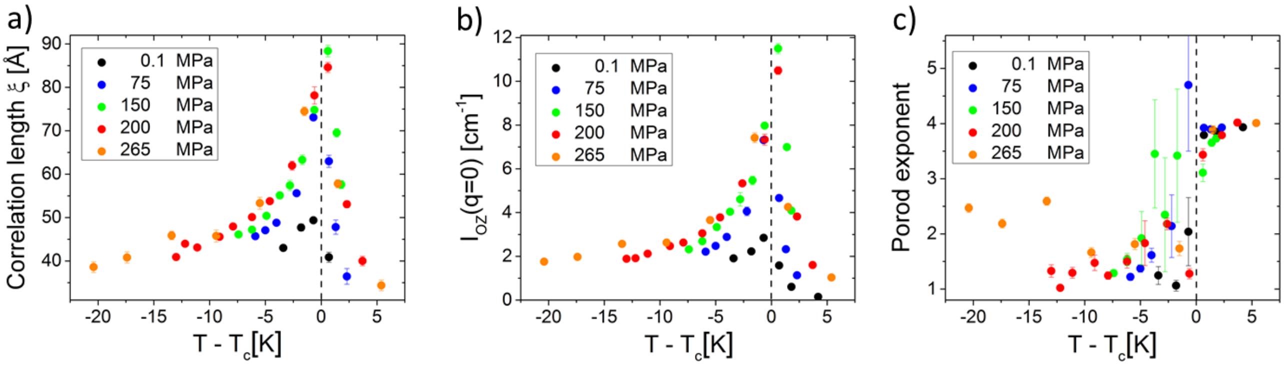

Figure 2. Results from fitting the scattering curves using a combination of the Ornstein-Zernike form factor and Porod's law. (a) Correlation length of concentration fluctuations, (b) amplitude of the Ornstein-Zernike term, and (c) Porod exponent of the forward scattering.

Above the cloud point, aggregates are formed. Fitting Porod's law gives the Porod exponent, characteristic for the inner structure and the surface of the aggregates. At all pressures, the Porod exponent is close to 4 above the cloud point; thus, the aggregates have smooth surfaces. Interestingly, also below the critical temperature, large structures are observed. The Porod exponent is between ~1 and 2.5, pointing to fractal (i.e. loosely connected) large-scale structures.

The SANS results will give further understanding of the influence of high pressure on the cononsolvency effect and thus on the packing of the solvent molecules along the chain.

Due to the excellent support of Dr. Ralf Schweins and Dr. Leonardo Chiappisi, the experiments were performed very efficiently.

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[2] Kyriakos, K.; Philipp, M.; Adelsberger, J.; Jaksch, S.; Berezkin, A.V.; Lugo, D.M.; Richtering, W.; Grillo, I.; Miasnikova, A.; Laschewsky, A.; Müller-Buschbaum, P.; Papadakis, C.M. *Macromolecules* **2014**, *47*, 6867-6879

[3] Osaka, N.; Shibayama, M. *Macromolecules* **2012**, *45*, 2171-2174

[4] Yuan, G.; Wang, X.; Han, C.C.; Wu, C. *Macromolecules* **2006**, *39*, 3642-2647