Experimental report

27/12/2020

Proposal: **9-11-1939**

Council: 4/2019

Title: PNIPMAM - a thermoresponsive polymer under high pressure: Role of thehydrophobic effect for the phase separation

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: poly(N-isopropylmethacrylamide) in D2O

Instrument	Requested days	Allocated days	From	To
D11	3	2	05/02/2020	07/02/2020

Abstract:

We wish to investigate the thermoresponsive polymer poly(N-isopropylmethacrylamide) (PNIPMAM) in aqueous solution across the coexistence line in the pressure-temperature frame. In this polymer, the hydrophobic interaction between the alkyl groups is important. Pressure allows to vary the hydrophobic effect, and pressure scans at low and at high pressure will give information about the chain conformation and aggregation behavior. Rapid pressure jumps across the coexistence line along with kinetic SANS will give information about the collapse and aggregation behavior with ~100 ms time resolution.

PNIPMAM - a thermoresponsive polymer under high pressure: Role of the hydrophobic effect for the phase separation

Poly(acrylamide)-based thermoresponsive polymers have been widely investigated due to their importance in technological applications such as controlled drug release, in microfluidics, tissue engineering and sensorics [1]. Poly(*N*-isopropyl methacrylamide) (PNIPMAM) is a thermoresponsive polymer which exhibits a lower critical solution temperature (LCST) behavior and is chemically similar to the well-known thermoresponsive polymer poly(N-isopropylacrylamide) (PNIPAM) with an additional methyl group in its backbone. At the LCST transition, the chain conformation of PNIPMAM undergoes spontaneous and abrupt changes from an extended coil to a collapsed globule, which can be macroscopically observed as a cloud point. Contrary to the expectation that PNIPMAM would be more hydrophobic than PNIPAM, its cloud point T_{cp} is 42.5 °C, as determined using turbidimetry and differential scanning calorimetry (DSC), and is thus significantly higher than the one of PNIPAM, which is 32˚C. The solution structure is more complex than the one of PNIPAM, as evidenced using small-angle neutron scattering (SANS, [2]). Further, it has been reported that in addition to temperature, pressure also influences the phase behavior of PNIPAM as well as its collapse and aggregation behavior at T_{cp} [3,4]. The cloud point of a 3 wt% PNIPMAM solution in D_2O increases to 47.5 °C at 1200 MPa and to decrease again at higher pressures. In the present work, we investigate the role of the additional methyl group on the LCST transition of PNIPMAM as well as the effect of high pressure on its phase behavior.

SANS experiments were performed at D11 instrument on solutions of PNIPMAM (M_n = 6440 g mol^{-1}) in D_2O with two different concentrations, namely 1 and 3 wt%. The same pressure cell as in our previous experiments was used [4]. For the 3 wt% solution, temperature scans were performed from 38 to 51 °C at ambient pressure (0.1 MPa) in order to characterize the structural changes around the cloud point. A number of pressure scans were carried out, but did not reveal much change in the scattering curves. To understand the effect of concentration, temperature and pressure scans were carried out across the phase boundary on a 1 wt% solution of PNIPMAM in D_2O as well.

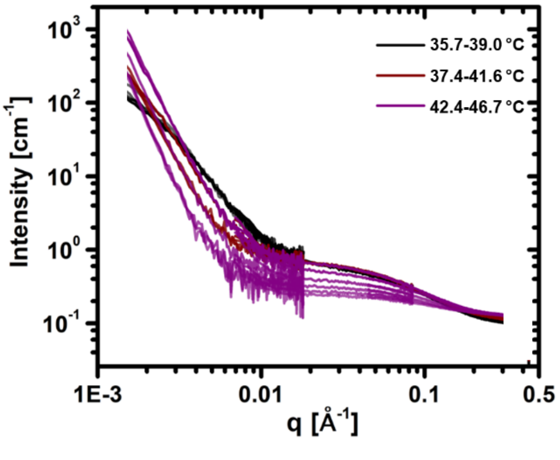

Figure 1. Representative small-angle neutron scattering profiles of a 3 wt% solution of PNIPMAM in D_2O at temperatures between 35.7 and 46.7 °C at a pressure of 0.1 MPa. The colors indicate the temperature range, as indicated in the legend.

The SANS profiles of the 3 wt% solution at temperatures ranging from 38 to 51 °C at ambient pressure are shown in Figure 1. At q-values above ~0.02 $Å^{-1}$, scattering due to concentration fluctuations is present at all temperatures, which becomes weaker, as temperature is increased. The forward scattering in the low q regime (up to ~0.01 $Å^{-1}$) indicates the scattering contribution from large-scale inhomogeneities. Unexpectedly, strong forward scattering is already observed far below T_{cp}, which had not been observed in our previous SANS investigations [2]. At T_{cp}, it changes shape from bent to straight in the double-logarithmic representation, i.e. the inhomogeneities grow beyond the resolution of the experiment.

Since the origin of the forward scattering below T_{cp} was unclear, a lower polymer concentration was chosen for subsequent experiments, namely 1 wt%. SANS profiles of the 1 wt% solution measured at two different pressures, namely 0.1 and 120 MPa at 25 °C, i.e. far below T_{cp}, are shown in Figure 2a. Forward scattering is still present, but compared to the data from the 3 wt% solution (Figure 1), the amplitude is reduced. For the 1 wt% solution, the intensity of the contribution in the high-q regime is increased at elevated pressure, which might be attributed to an enhanced hydration of PNIPMAM at high pressure, as observed for PNIPAM [3,4].

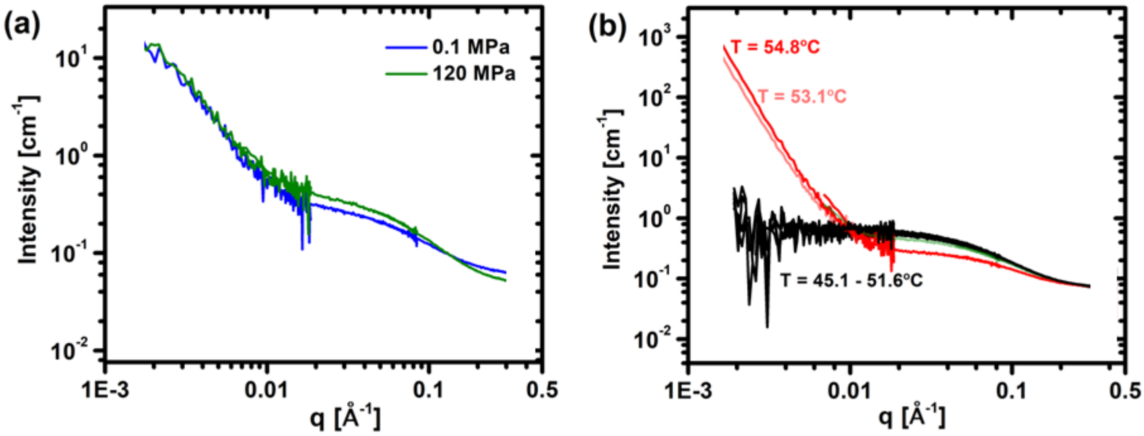

Figure 2. SANS profiles of a 1 wt% solution of PNIPMAM in D_2O at 25 °C and pressures of 0.1 MPa and 120 MPa (a) and at 120 MPa and at temperatures between 45.1 and 54.8 °C.

Scattering profiles measured at a pressure of 120 MPa at temperatures between 45.1 and 54.8 °C are shown in Figure 2b. At temperatures up to 51.6 °C, only chain scattering is observed, and forward scattering is absent. The amplitude of the forward scattering increases markedly above this temperature, which is attributed to the formation of large aggregates (named mesoglobules) at the cloud point. Thus, the appearance of forward scattering appears at significantly higher temperature than expected from turbidimetry and DSC. The data are currently being analyzed using the same models as in our previous work [2] and will give insights to the influence of pressure on the structural changes of PNIPMAM around the LCST transition.

The experiment was very successful. We thank Dr. Leonardo Chiappisi for the excellent support during the beam time.

[1] M. Islam, M. J. Serpe et al., *Anal. Chim. Acta* **2013**, *789*, 17.
[2] C.-H. Ko, C. M. Papadakis et al., *Macromolecules* **2020**, *53*, 6816.
[3] B.-J. Niebuur, C.M. Papadakis et al., *ACS MacroLett.* **2017**, *6*, 1180.
[4] B.-J. Niebuur, C.M. Papadakis, et al. *ACS Macro Lett.* **2018**, *7*, 1155.