Experimental report

21/09/2017

Proposal: **9-11-1827** **Council:** 10/2016

Title: Kinetics of aggregate formation insolutions of PNIPAM - pressure andtemperature jumps across the coexistence line

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: poly(N-isopropylacrylamide)

Instrument	Requested days	Allocated days	From	To
D11	0	3	27/02/2017	02/03/2017
D33	4	0		
D22	4	0		

Abstract:

Poly(N-isopropylacrylamide) (PNIPAM) is a thermoresponsive polymer which, in water, collapses at the cloud point with lower critical solution temperature behavior and subsequently forms large aggregates. In the temperature-pressure frame, the coexistence line follows an elliptical curve with a maximum at 60 MPa. At high pressure, the aggregation mechanism is fundamentally different from the one at atmospheric pressure, which we attribute to a difference in interactions. Pressure jumps at various pressures allow the investigation of early kinetics in the formation of aggregates, due to the fast response of the experimental set-up with respect to temperature jumps. We wish to study the aggregate formation using time-resolved SANS during pressure and temperature jumps at D22 or D33.

Poly(*N*-isopropylacrylamide) (PNIPAM) is a thermoresponsive polymer which, in aqueous solution, exhibits lower critical solution temperature (LCST) behaviour with an LCST 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 mesoglobules.[1] Their size and water content after crossing the LCST are strongly pressure-dependent: At elevated pressure (> 100 MPa), the mesoglobules are larger (~6 µm) and contain clearly more water than at atmospheric pressure (domain size ~1 µm).[2] Using time-resolved SANS, attempts were made to elucidate the growth process of the mesoglobules at atmospheric pressure during temperature-induced phase separation[1] and induced by the addition of a co-solvent.[3] The results in these cases may, however, be obscured by the slow heating and temperature gradients, and inhomogeneities in the system after mixing, respectively. In the present study, changes in pressure are used to induce phase-separation. Because pressure can be changed very rapidly (< 0.1 s), the early stages of the phase-separation process are accessible using this approach, and gradients are less severe, ensuring the reliability of the measurements. Moreover, the elliptical shape of the phase diagram of aqueous PNIPAM solutions in the temperature-pressure space[4] allows to cross the coexistence line at low pressure as well as at high pressure at constant temperature.

The pressure jumps were performed with a 3 wt% PNIPAM (36 kg mol^{-1}, dispersity index 1.26) solution in D_2O. Before each jump, the system was equilibrated close to the coexistence line in the one-phase region at 33.8 °C and 31.5 MPa, followed by jumps to lower pressures with pressure changes Δp = -15, -20 and -25 MPa into the two-phase region (low-pressure, LP, regime). In the high-pressure (HP) regime, the starting pressure for each jump was 87 MPa, and jumps to higher pressures into the two-phase region Δp = 15, 25 and 40 MPa were performed. The exposure time of the frames after each jump was increased logarithmically, starting at 0.05 s. The neutron wavelength was chosen at λ = 6.0 Å. A q range from 0.002-0.3 Å^{-1} was covered with sample-detector distances (SDDs) of 1.5 m, 8.0 m and 34 m. Measurements at SDD = 34 m were repeated at least 5 times to obtain sufficient statistics. The sample was mounted in a copper beryllium cell (21 PL 30 A 02) capable of withstanding pressures up to 350 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 and to bring the data to absolute scale. The dark current was measured using boron carbide. The software LAMP was used to perform the data reduction.

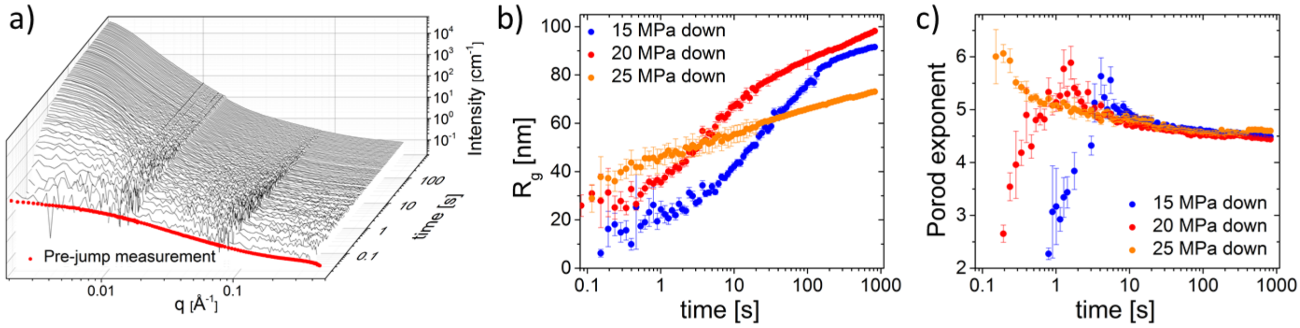

Figure 1. Results from pressure jumps in the LP regime: (a) Scattering curves after the jump with Δp = -20 MPa; (b) radius of gyration of the mesoglobules and (c) Porod exponent for jumps with the pressure changes indicated in the graphs.

As an example, Figure 1a shows the scattering curves after the Δp = -20 MPa jump in the LP regime. At high q values, the decrease of the intensity of the chain scattering with time indicates the chain collapse, which goes along with a loss of contrast. At low q values, however, the intensity strongly increases almost directly after the jump, revealing the formation of mesoglobules. The curves are fitted with the Guinier-Porod model to describe large structures, and an Ornstein-Zernike structure factor to account for chain scattering. The radius of gyration R_g (Fig. 1b) clearly shows the presence of two growth processes. The initial fast growth is possible because the chains are hydrated and their mobility is high enough to form mesoglobules. The slow growth mode probably sets in when the chain hydration is significantly decreased, and coalescence is hindered by the low chain mobility. This scenario is supported by the observed differences between the different jumps. For jumps far into the two-phase region, the chains dehydrate rapidly, i.e. the slow growth mode sets in earlier. Directly after the jump, the Porod exponent (Fig. 1c) increases from ~3 to ~6, meaning that water molecules in the outer layer of the initially rough mesoglobules diffuse out, resulting in a strong SLD gradient at the surfaces. In the later stages, water is trapped inside the mesoglobules and can only diffuse slowly through the dense outer layer, marked by the gradual decrease of the Porod exponent.

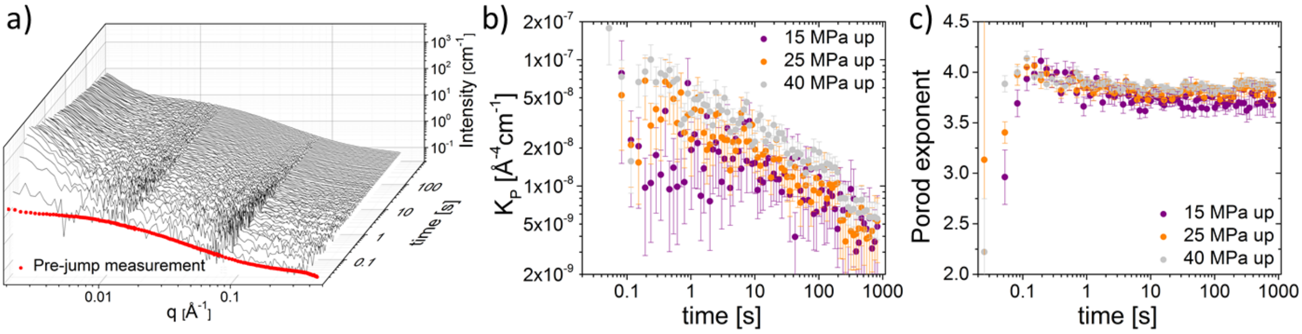

Figure 2. Results from the pressure jumps in the HP regime: (a) Scattering curves after the Δp = 15 MPa jump; (b) Porod amplitude and (c) Porod exponent for jumps with the pressure changes indicated in the graphs.

Figure 2a shows the scattering curves after the Δp = 15 MPa jump in the HP regime. In contrast to the jumps in the low-pressure regime, the intensity of the chain scattering at high q values does not drop after the jump, meaning that the chains stay hydrated when mesoglobules are formed. This is reflected by the weak intensity increase at low q values, caused by the low contrast between polymer-rich and solvent-rich phases. The mesoglobule size could not be resolved in the HP regime, therefore, the curves were modelled by a combination of the Porod approximation and the Ornstein-Zernike structure factor. The Porod amplitude K_p (Fig. 2b) decreases with time featuring only a weak dependency on Δp. Because K_p is proportional to $(\Delta\rho)^2 S/V$ with $\Delta\rho$ the SLD difference between polymer-rich and solvent-rich phases, and S/V the specific surface of the mesoglobules, this decrease can be assigned to their growth and/or the decrease of water content. As in the LP regime, the Porod exponent shows a maximum short time after the jump, the values of the Porod exponent are, however, smaller than at low pressure, i.e. the surfaces of the mesoglobules are rougher.

Further analysis and interpretation of the results will lead to an understanding of the influence of pressure on the growth behavior of mesoglobules formed by thermoresponsive polymers.

We thank Dr. Leonardo Chiappisi for excellent support during the measurements.

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