Experimental report

14/03/2022

Proposal: **9-10-1646**

Council: 10/2019

Title: Pressure-induced phase transition of micelle-forming thermoresponsivePMMA-b-PNIPAM diblock copolymers in aqueous solution

Research area: Soft condensed matter

This proposal is a continuation of 9-10-1577

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Samples:
D2O
copolymer poly(methyl methacrylate)-b-poly(N-isopropyl¬acrylamide)

Instrument	Requested days	Allocated days	From	To
D11	3	3	02/09/2020 29/06/2021	04/09/2020 02/07/2021

Abstract:

Amphiphilic diblock copolymers from a hydrophobic block and a thermoresponsive block have a phase transition where the shell collapses and the collapsed micelles aggregate. The degree of dehydration of the shell can be tuned by applying pressure. We wish to continue our previous experiments by carrying out pressure jumps in the low-pressure and the high-pressure regime, i.e. under strong and weak dehydration conditions. Jumps will start at the same pressure in the one-phase region, just next to the coexistence line, and the target pressure will be varied in both cases. As a reference, a jump will be carried out in the one-phase regime as well. This time, the temperature shall be kept constant, so temperature as a parameter is ruled out.

Pathways of micelle collapse and swelling of PMMA-*b*-PNIPAM diblock copolymers in aqueous solution triggered by a rapid change of pressure

Diblock copolymers consisting of a short permanently hydrophobic and a long thermo-responsive block can self-assemble into core-shell micelles in aqueous solution, e.g. poly (methyl methacrylate)-*b*-poly(*N*-isopropylacrylamide) ($\mathrm{PMMA_{23}}$-*b*-$\mathrm{PNIPAM_{480}}$), consisting of the hydrophobic PMMA and the thermo-responsive PNIPAM. At atmospheric pressure, the micellar PNIPAM shell dehydrates, and the collapsed micelles form aggregates, when heating above the cloud point T_{cp} of PNIPAM [1]. The collapse and aggregation can also be caused by changing the pressure, because pressure alters the hydration state of PNIPAM: While the dehydration at the co-existence line is strong at atmospheric pressure, the chains remain partially hydrated at higher pressures [2].

In the present work, the micellar structure of a 1 wt.% solution of $\mathrm{PMMA_{23}}$-*b*-$\mathrm{PNIPAM_{480}}$ (Mn ≈ 57 $\mathrm{kg.mol^{-1}}$) in D_2O was characterized in the temperature-pressure frame by small-angle neutron scattering (SANS) measurements at D11. Moreover, the collapse and the swelling process of the micelles was studied by using rapid pressure jumps across the coexistence line in combination with kinetic SANS measurements with high time resolution. The pressure jumps were triggered by opening a pneumatic valve located between the sample holder and a pressure reservoir, which was pressurized to the target pressure. The opening of the valve activated automatically the acquisition of the data. In total, 85 measurements were taken after the opening of the valve. The duration of measurements was as low as 0.05 s, and the total duration was 1649 s. The neutron wavelength was 0.6 nm ($\Delta\lambda/\lambda \approx 0.1$), and sample-to-detector distances (SDD) of 3.0, 8.0 and 34 m were used. The measurements using a SDD of 34 m were repeated 3 times for better statistics.

The co-existence line of the 1 wt. % solution of $\mathrm{PMMA_{23}}$-*b*-$\mathrm{PNIPAM_{480}}$ was determined by turbidimetry (Fig. 1a). The location of the static SANS measurements carried out are indicated with red circles. At atmospheric pressure, SANS measurements ranged between 28.0 and 32.4 °C. At higher pressures (10, 20, 30 and 40 MPa), SANS measurements were done at 32.4, 32.6 and 32.8 °C. The SANS profiles at atmospheric pressure and 30 MPa are shown in Fig. 1b and c, respectively. At both pressures, a shoulder can be identified around 0.2 $\mathrm{nm^{-1}}$, which shifts to slightly lower q-values, as temperature increases. Also, forward scattering is observed in the whole temperature range, indicating the presence of aggregates, even in the one-phase region.

The SANS profiles were modeled by using the following equation:

$$I(q) = P_M(q)S_{SHS}(q) + I_P(q) + I_{OZ}(q) + I_{bkg} \quad (1)$$

where $P_M(q)$ is the form factor for spherical core-shell micelles with an exponentially decaying scattering length density (SLD) in the shell and $S_{SHS}(q)$ the sticky hard-sphere structure factor. The Porod term $I_P(q)$ was employed to describe the scattering of large aggregates of micelles in the low q region. The Ornstein-Zernike term $I_{OZ}(q)$ was utilized to describe the concentration fluctuations in the shell and a constant background I_{bkg} to describe the incoherent scattering.

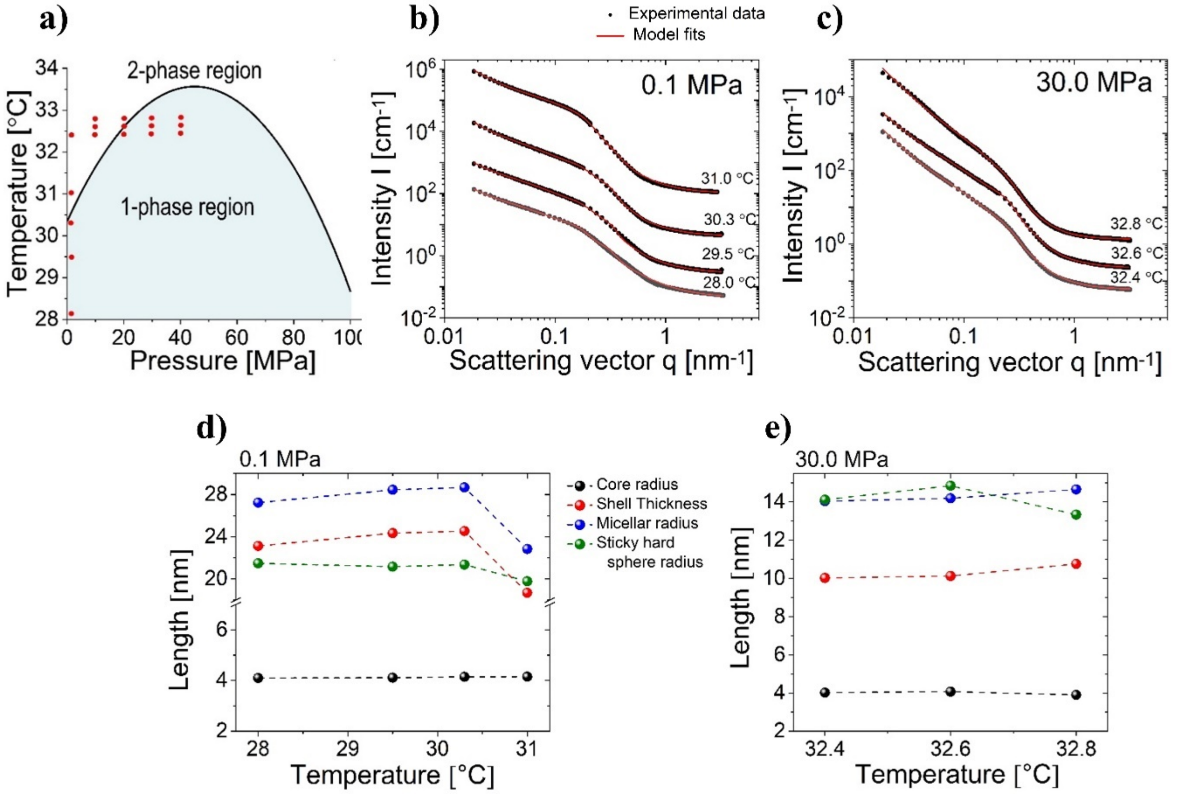

Figure 1: (a) Phase diagram of 1 PMMA_{23}-b-PNIPAM_{480} solution from turbidimetry. The static SANS measurements are marked with red circles. (b,c) SANS profiles with model fits at (b) 0.1 MPa and (c) 30 MPa. (d,e) Resulting parameters at (d) 0.1 MPa and (e) 30 MPa.

The resulting structural parameters are shown in Fig.1d and e. The core radius remains almost constant at ca. 4 nm. At 0.1 MPa, the micellar radius is ca. 28 nm and decreases at 31.0 °C, i.e. after crossing the co-existence line, indicating the micellar collapse. In contrast, at 30 MPa, the micellar radius remains constant at ca.14 nm in the entire temperature range. Moreover, at 0.1 MPa, the micelles inter-penetrate, since the sticky hard sphere radius is lower than the micellar radius. This is not observed at 30 MPa, indicating a repulsive interaction at higher pressures.

The pressure jumps are presented in Fig. 2a, all at 33 °C. For the jump from the two- to the one-phase region, the initial pressure was 16 MPa, while the target pressures were 28, 30 and 35 MPa. For the jump from the one- to the two-phase region, the initial pressure was 30 MPa, and the target pressures were 23, 15 and 10 MPa. Representative SANS profiles for the jump from 30 to 15 MPa are shown in Fig. 2b. The curve features a shoulder at $q \approx 0.3$ nm^{-1}, which shifts to lower q-values. The SANS profiles were modeled by Eq. 1; the collapsed micelles were modeled using the form factor of homogeneous spheres.

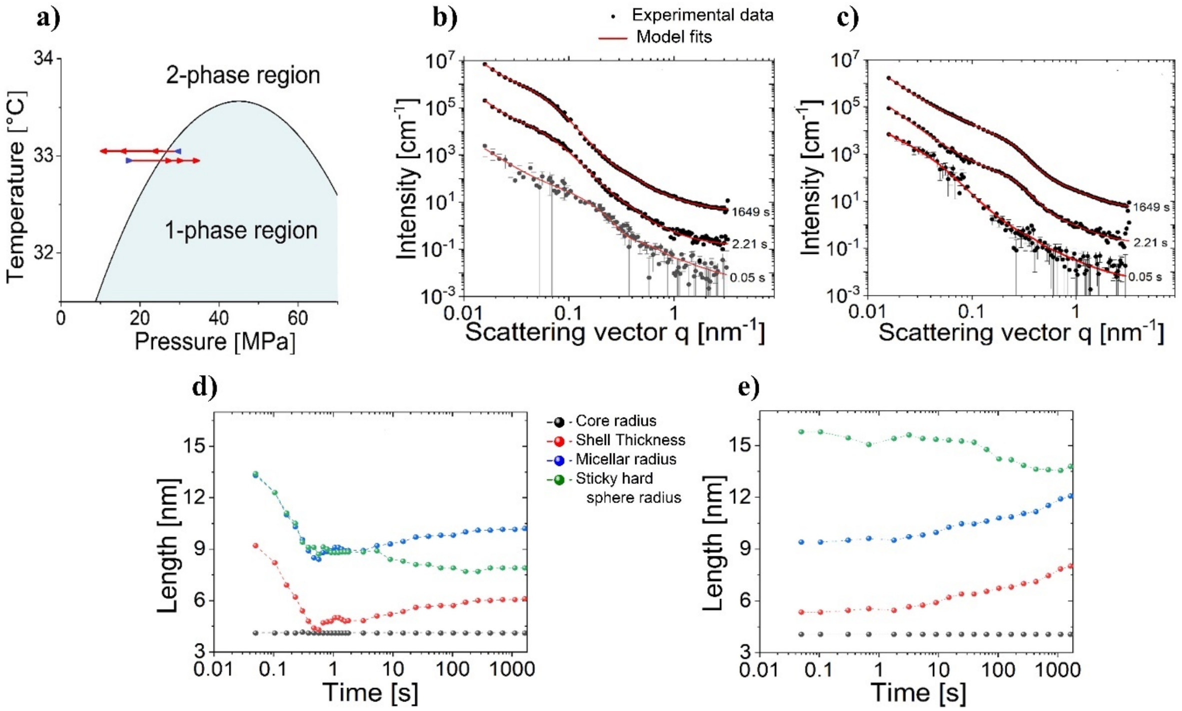

Figure 2: a) Pressure jumps experiments. The start and target pressures are indicated with blue and red arrows respectively. (b, c) Representative SANS profiles for pressure jumps b) from 30 to 15 MPa and c) from 16 to 35 MPa at the times given in the graphs. (d, e) Resulting parameters for jumps d) from 30 to 15 MPa and e) from 16 to 35 MPa.

Fig. 2d shows the micellar structural parameters after the jump from 30 to 15 MPa. Again, the core radius was kept constant at 4 nm. The shell thickness decreases strongly during the first 0.5 s due to partial dehydration of the PNIPAM shell. Afterwards, the micelles reswell slightly and interpenetrate. After the jump from 16 to 35 MPa (Figure 2e), an induction period of ca. 1 s is observed, after which, the micellar shell starts to grow.

In summary, static SANS measurements allowed us to characterize the micellar structures in the temperature-pressure frame. Moreover, we determined the pathways of the collapse and swelling of the micelles from PMMA-*b*-PNIPAM by rapid pressure jumps in combination with kinetic SANS measurements. Further analysis of the pressure jumps will reveal the effect of the pressure jump length on the rate and mechanism of the collapse and swelling of the micelles.

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References

[1] C-H. Ko, C. Henschel, G. P. Meledam, M. A Schroer, P. Müller-Buschbaum, A. Laschewsky, C. M Papadakis, Macromolecules **54**, 384-397 (2021).
[2] B.-J. Niebuur, K.-L. Claude, S. Pinzek, C. Cariker, K.N. Raftopoulos, V. Pipich, M.-S. Appavou, A. Schulte, C. M. Papadakis, ACS Macro Lett. **6**, 1180-1185 (2017).