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| Experiment title: Pathways of micelle collapse and swelling of PMMA- <i>b</i> -PNIPAM diblock copolymers in aqueous solution triggered by a rapid change of pressure | Experiment number: SC-5318 | |
| Beamline: ID02 | Date of experiment: from: October 28, 2022 to: November 01, 2022 | Date of report: February 6, 2023 |
| Shifts: 9 | Local contact(s): William Chevremont | <i>Received at ESRF:</i> |
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Report:

In aqueous solution, diblock copolymers consisting of a permanently hydrophobic poly(methyl methacrylate) (PMMA) block and a thermo-responsive poly(*N*-isopropylacrylamide) (PNIPAM) block form spherical core-shell micelles. Our previous small-angle neutron scattering (SANS) experiments indicate that, at atmospheric pressure, the micellar shell of PMMA-*b*-PNIPAM strongly dehydrates and shrinks when heated above the cloud point of PNIPAM. In contrast, at higher pressures, e.g. at 75 MPa, the micellar shell remains hydrated and swollen. We previously characterized the collapse and swelling process by kinetics SANS measurements in combination with rapid changes of pressure (pressure jumps) and identified time scales in the range of 1s. Based on these results, the goals of the beamtime were (i) the determination of the temperature(s) at which the co-existence line of PMMA-*b*-PNIPAM in D₂O is crossed 2 times by changing the pressure by using static small-angle X-ray measurements, and (ii) the characterization of the collapse and swelling process by kinetic SAXS measurements in combination with pressure jumps of $\Delta p = 20, 40$ and 60 MPa, both at the left- and right-side of the maximum of the co-existence line and in both directions.

However, after the identification of suitable temperatures and pressures for these jumps, the piezo-electric actuator of the high-pressure cell broke down, preventing us from kinetic SAXS measurements. Thus, the time was used for a thorough characterization of the micellar structures of PMMA-*b*-PNIPAM in D₂O by pressure-resolved experiments in a large portion of the temperature-pressure frame.

Pressure-resolved SAXS experiments of a 3 wt% and 5 wt% solution of PMMA₂₁-*b*-PNIPAM₂₈₃ in D₂O were performed at 8 temperatures between 25 and 34 °C and at pressures increasing to 175 MPa in steps of 5 or 20 MPa and back (Fig. 1a). The same measurements were done on the solvent (D₂O) as a background. Samples were mounted in a polycarbonate capillary in the high-pressure cell. The detector was placed at a sample-

detector distance of 10 m, covering a q -range of 0.01-1 nm⁻¹. 10 frames with exposures times of 100 ms were measured at every point indicated in Fig. 1a.

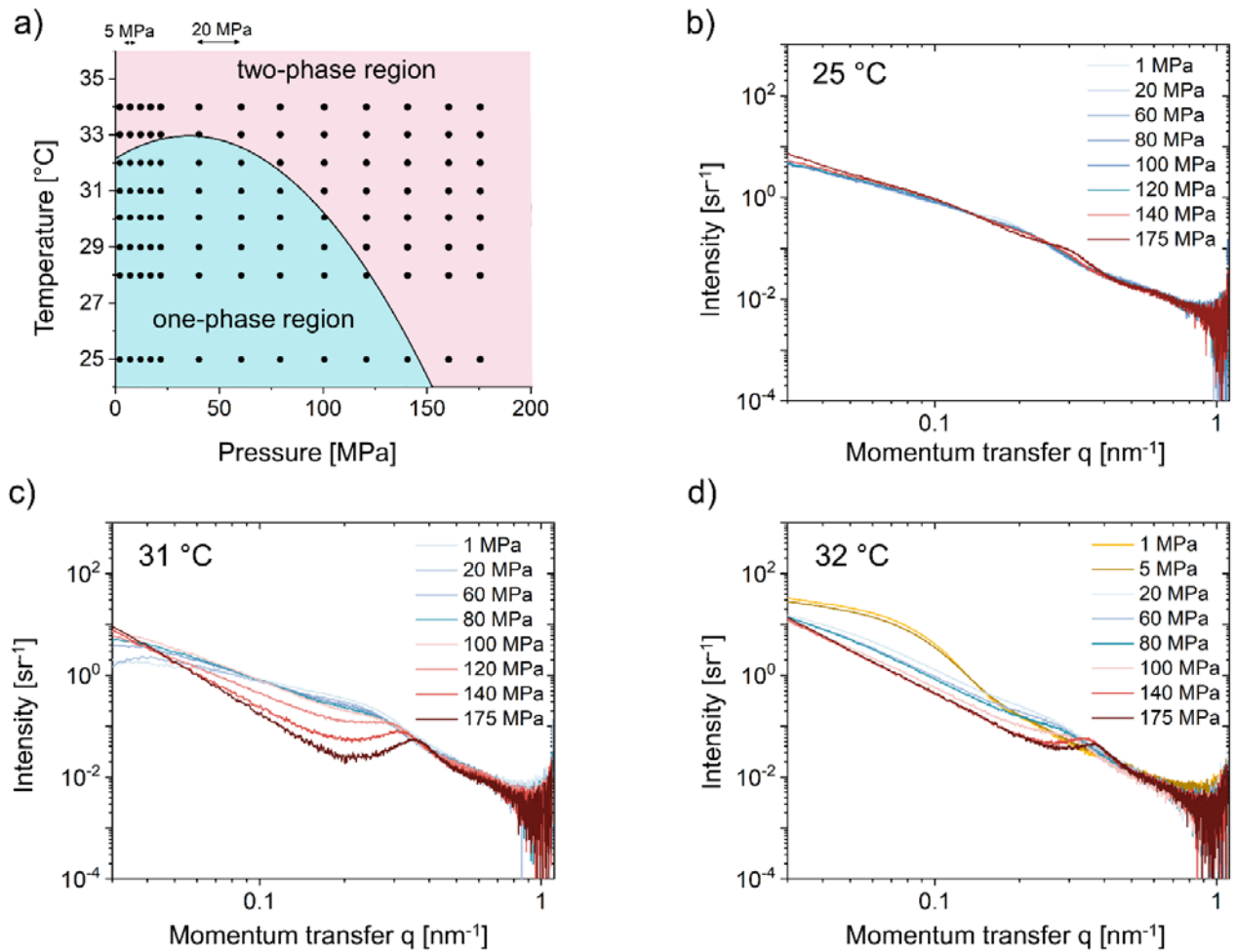


Figure 1: a) Phase diagram of 3 wt% PMMA₂₁-*b*-PNIPAM₂₈₃ determined beforehand by turbidimetry. The static SAXS measurements are marked with black circles. (b-d) SAXS profiles for the pressure-resolved experiments at b) 25 °C, c) 31 °C and d) 32 °C. Blue: curves from the one-phase region, yellow and red: from the two-phase region at the low- and high-pressure regime, respectively.

The SAXS profiles for the scans with increasing pressure at 25, 31 and 32 °C are shown in Fig. 1b-d. The SAXS profiles at 25 °C and 31 °C feature the transition from the one- to the two-phase region at 160 MPa and 100 MPa, respectively. The SAXS profiles in the one-phase region feature a weak shoulder at $q \cong 0.2$ nm⁻¹, which becomes weaker as the pressure is increased towards the co-existence line. The SAXS profiles in the two-phase region, on the other hand, feature a strong correlation peak at $q \cong 0.3$ nm⁻¹, which becomes sharper as pressure increases. At 32 °C, two transitions are observed, namely at 8 and 90 MPa, reflecting the re-entrant behaviour. The SAXS profiles at 1 and 5 MPa feature a strong shoulder at $q \cong 0.08$ nm⁻¹, that we assign to scattering from the relatively small aggregates formed in the low-pressure regime of the two-phase region. Moreover, the profiles in the high-pressure regime of the two-phase region, display correlation peaks. However, they are weaker than the correlation peaks observed at 31 °C, indicating a strong temperature-dependence of the micellar structures formed in the two-phase region. This temperature (32 °C) is thus ideally suited for kinetic SAXS measurements, since it is possible to cross the co-existence line both in the low- and the high-pressure regime. The SAXS profiles will be analysed by the following generic model:

$$I(q) = I_{\text{agg}}(q) + P(q)S(q) + I_{\text{int}}(q) + I_{\text{bkg}} \quad (1)$$

where $I_{\text{agg}}(q)$ describes the scattering of large aggregates, $P(q)$ and $S(q)$ are the form and structure factor of the individual micelles, $I_{\text{int}}(q)$ describes the scattering due to concentration fluctuations inside the micellar shell and I_{bkg} is a constant background. This way, we will characterize the micellar structure, the interactions between the micelles and the aggregation behaviour throughout the temperature-pressure frame. Also, this information provides an excellent basis for studying the kinetics and swelling of the micellar shell by time-resolved SAXS in combination with pressure jumps.

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