Experimental report

02/06/2016

Proposal: **9-11-1733** **Council:** 10/2014

Title: Orthogonally switchable block copolymers: effect of temperature and electrolyte on the self-assembled structures

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Christine PAPADAKIS**

Experimental team:
Bart-Jan NIEBUUR
Natalya VISHNEVETSKAYA
Margarita DYAKONOVA
Konstantinos RAFTOPOULOS

Local contacts: Isabelle GRILLO

Samples: poly(C12H24N2O4S-b-C7H12NO)

Instrument	Requested days	Allocated days	From	To
D11	2	2	25/06/2015	27/06/2015

Abstract:

Diblock copolymers consisting of a thermoresponsive and a zwitterionic blocks are switchable in water by changing temperature or electrolyte concentration. We propose to investigate the thermal behavior of poly(sulfobetaine-b-(Nisopropylacrylamide)), P(SB-b-NIPMAM), diblock copolymers in D2O using temperature-resolved small-angle neutron scattering (SANS). We expect to observe the cloud points due to the collapse of the PNIPMAM and the PSB blocks as well as possible changes due to the addition of electrolyte to the sample solution. We propose to carry out SANS experiments at D11 to study in particular the large-scale structures due to the formation of very large aggregates above and below the cloud points at low values of momentum transfer. We will compare and combine the results to the ones obtained by us previously at higher values of the momentum transfer.

We have investigated double thermo-responsive diblock copolymers consisting of a zwitterionic poly(sulfobetaine) (PSB) block [1] and a non-ionic block which had been synthesized by successive RAFT polymerizations. Two types of sulfobetaines (named here SPP and SBP), which differ in the length of the spacer between the two ionizable groups, were combined with poly(N-isopropylacrylamide) (PNIPAM) or with poly(N-isopropylmethacrylamide) (PNIPMAM).

In aqueous solution, the corresponding homopolymers feature upper and lower critical solution temperature (UCST and LCST) behavior, respectively. They are expected to feature three phases in dependence on temperature: micelles with a thermoresponsive shell and a PSB core and vice versa at low and at high temperatures and unimers at intermediate temperatures. The UCST of the zwitterionic homopolymers can be tuned by adding small amounts of electrolyte [2], which is expected to affect the phase transition temperatures of the diblock copolymers as well. In addition to the chemical nature of the blocks, we have varied the block lengths.

In this report, we show as an example the results from a 50 g L^{-1} solution of a $PSPP_{498}$-*b*-$PNIPMAM_{144}$ diblock copolymer (164,500 g/mol) in D_2O. Using turbidimetry, we have identified the cloud points at 29.5°C and 49.5°C, which are presumably due to the aggregation of the PSB (CP_{UCST}) and the PNIPMAM block (CP_{LCST}), respectively. Dynamic light scattering showed that the particle size changes accordingly. In the beamtime at D11, we investigated the large-scale structures due to the aggregation below CP_{UCST} (regime I), between CP_{UCST} and CP_{LCST} (regime II) and above CP_{LCST} (regime III) of the thermoresponsive $PSPP_{498}$-*b*-$PNIPMAM_{144}$ in D_2O as well as in 0.004 M NaBr solution in D_2O. Measurements were performed while heating from 15 °C to 59 °C. Sample-detector distances of 5.5, 8.0 and 34.0 m and a wavelength of 6.0 Å with a spread of 9 % were used, resulting in a q-range from 0.002 to 0.52 $Å^{-1}$. The scattered intensity maps were azimuthally averaged and corrected for background scattering from the solvent-filled cell and parasitic scattering. The data were reduced using the software LAMP [3].

The three regimes distinguished by turbidimetry are clearly discernible in the shapes of the SANS curves (Figure 1, left). In regime II, contrary to expectations, single chain scattering models are not applicable, but the SANS curves display a peak at a rather high q value, which is typical for polyelectrolytes in salt-free solution. The analysis of the SANS curves in regime II was carried out using a model containing (i) a solvation term, which was used to describe the scattering at high q values, and (ii) a Guinier term, describing the slight upturn at q values below 0.06 nm^{-1} at 49 ºC. The scattering level of the curves in regime I is higher than in regime II, which reveals aggregation in regime I. Moreover, the peak, which may be caused by electrostatic interactions in the PSPP block, is shifted to lower q values, compared to the one observed in regime II. At low q values, the scattering curves in regimes

I and II differ strongly, where large aggregates cause an increased forward scattering in regime I. The curves in regime I can be fitted using a similar model as in regime II, using the solvation term together with a Porod term, which describe the strong forward scattering at low *q* values due to very large aggregates. As an alternative, the curves were fitted using a model based on spheres correlated by a hard-sphere structure factor plus an Ornstein-Zernike term, describing the concentration fluctuations in the non-compact shell of the spheres, and the Porod term. The overall shape of the curve in regime III is significantly different, and the characteristic correlation peak of the polyelectrolyte systems is not evident any longer. The scattering observed at low *q* values (up to 0.1 nm^{-1}) points to self-assembly of the diblock copolymers on length scales not much higher than the mesh size of the polymer solution. The best model in regime III contains the form factor of core-shell spheres and the Ornstein-Zernike structure factor, whereas the hard-sphere structure factor and the Porod term were not needed.

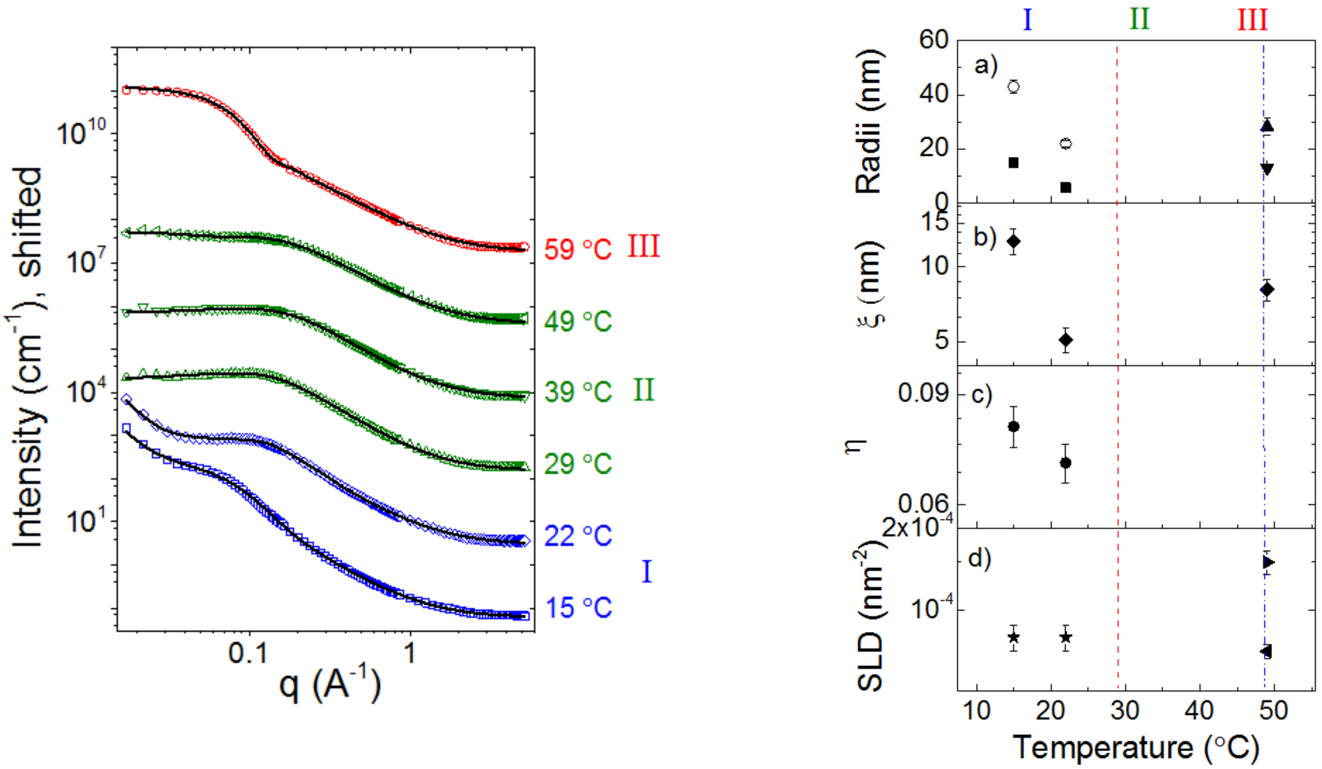

Figure 1. Left: SANS curves from a 50 g L^{-1} salt-free solution of PSPP$_{498}$-*b*-PNIPMAM$_{144}$ in D$_2$O (symbols), where only every third point is shown for clarity, together with the fitting curves (black lines). For better visibility, the curves are shifted vertically by factors of 50 with respect to each other. Regimes I, II and III are indicated by the blue, green and red color, respectively. Right: Temperature-dependent results from model fitting. (a) Micellar radius (squares), micellar radius (up triangles) and core radius (down triangles) of the core-shell spheres, and hard-sphere radius (open spheres); (b) correlation length, ξ (diamonds);

(c) volume fraction, η (closed spheres); and (d) SLD values of the spheres (stars) and the core (left triangles) and the shell (right triangles) of the core-shell spheres. Red dashed and blue dash-dotted lines represent the CP_{UCST} and CP_{LCST} values from turbidimetry. Regimes I, II and III are indicated on top of the graph.

The fitting results (Figure 1, right) reveal that, in regime II, both blocks are water-soluble with the solubility of the PSPP block being driven by the electrostatic interactions between water and the charged polymer chain. At the highest temperature in this regime (49 ºC), aggregates having a radius of gyration $R_G = 35 \pm 3$ nm are formed, which is due to the vicinity of CP_{LCST}. In regimes I and III, the diblock copolymer is amphiphilic, but with reversed hydrophilic and hydrophobic blocks, and forms micelles. In regime I, the PSPP coils overlap with each other, thus resulting in a molecularly crowded environment, and the solubility is driven by the PNIPMAM block. The spherical particles in regime I are comparably small with the radii increasing from ~6 to ~15 nm, as the temperature is decreased from 22 to 15 °C. Nevertheless, these spheres are correlated; moreover, they form large aggregates. The core-shell structure of the micelles expected in regime I could not be resolved. This may be due to the fact that the aggregation is governed by the electrostatic interactions in the PSPP block and that the PNIPMAM block being relatively short. Another reason might be that the PSPP and PNIPMAM blocks interact with each other, rather forming homogeneous micelle-like associates than distinct core-shell micelles. In contrast, in regime III, the micellar radius is very high (~28 nm), and a core-shell structure is evident. No aggregation is observed, which may be suppressed by the thick hydrophilic PSPP shell of the micelles, creating a steric hindrance for aggregation and keeping the system in the solvated state.

Overall, the experiment was very successful, the equipment was excellent, the measuring times were short, and the instrument responsibles were very helpful before, during and after the beamtime.

[1] M. Arotçaréna, B. Heise, S. Ishaya, A. Laschewsky, *J. Am. Chem. Soc.* **124**, 3787 (2002)
[2] M.B. Huglin, M.A. Radwan, *Polym. Int.* **26**, 97 (1991). P. Köberle, A. Laschewsky, T.D. Lomax, *Makromol. Chem., Rapid Commun.* **12**, 427 (1991)
[3] LAMP, the Large Array Manipulation Program, http://www.ill. eu/data_treat/lamp/the-lamp-book/.