Experimental report

03/02/2016

Proposal: **9-10-1414**

Council: 10/2014

Title: Pressure induced reverse micellization of PNIPAM based micelles

Research area: Soft condensed matter

This proposal is a new proposal

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Samples:
Poly(N-isopropyl acrylamide-co-N-tertbutyl acrylamide)-block-Poly(N,N-dimethyl acrylamide)
Deuteriumoxide

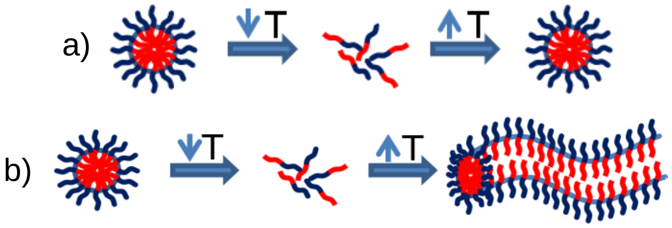
Instrument	Requested days	Allocated days	From	To
D11	3	2	21/07/2015	23/07/2015

Abstract:

We are interested in the pressure dependence of micelles in aqueous solution based on poly(N-isopropyl acrylamide). Linear precipitated PNIPAM-based chains showed a pressure-dependant solvation above its transition temperature. This should lead in case of micelles to a dissolution of the self-assemblies when using a PNIPAM-based core-forming block. Hence, pressure can then act as a stimulus to induce and reverse micellization. This would be to our best knowledge the first prove of an order-disorder transition of micelles upon induced pressure. A good method to detect the pressure-dependent changes of PNIPAM micelles in aqueous solution is SANS. The D11 instrument would provide a high contrast and the perfect q-value range to determine the pressure dependence of size and morphology of our micelles/dissolved diblock copolymers.

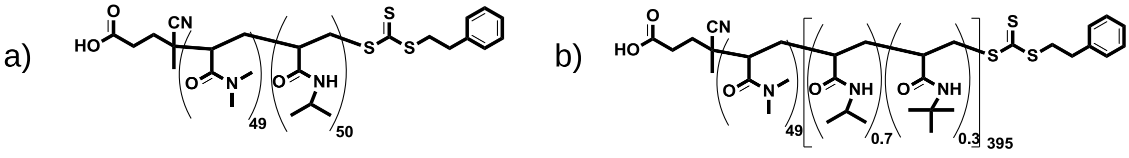
Pressure induced reverse micellization of PNIPAM based micelles

At ambient pressure, aqueous poly(*N*-isopropyl acrylamide) (PNIPAM) undergoes a phase transition at 32°C (its LCST). While below 32°C the polymer chains are hydrated, they tend to aggregate above 32°C. For diblock copolymers, this leads to micellar structures when stabilized by e.g. a soluble poly(*N*,*N*-dimethyl acrylamide) (PDMAM) block. Further, the PNIPAM LCST behaviour can be easily modified by copolymerizing with other acrylamides such as e.g. N,N-diethyl acrylamide (DEAM) or *N*-*tert*-butyl acrylamide (tBAM). The influence of pressure on the solvation of PNIPAM-based microgels at different temperatures was already studied with Fourier-transform infrared spectroscopy (FTIR) and SAXS in aqueous solution.[1] These measurements showed that raising pressure leads to rehydration at temperatures above 32°C.



Scheme 1 a) Reversible morphology change upon demicellization by temperature and b) irreversible morphology change upon demicellization by temperature and pressure

Here, we study PNIPAM-*b*-PDMAM based micelles and investigate whether the formed micelles dissolve upon an increase of pressure when chain rehydration should occur. With pressure-dependent SANS measurements, it is possible to determine changes of the form factor (which can be modelled with SasView) and the pressure dependence of the particle size and morphology. Pressure can then act as a stimulus to induce and reverse micellization. In contrast to classical amphiphiles, the hydrophobicity can be adjusted by temperature, anticipating the first observation of a pressure-induced demicellization. The project can be divided into a reversible morphology change upon demicellization and an irreversible morphology change upon demicellization (see Scheme 1). To achieve a reversible and an irreversible morphology change in the micelles, we use conventional star-shaped core-corona-type micelles and crew cut micelles (for polymer structure see scheme 2).



Scheme 2 a) Polymer structure of reversible micelles (star-like micelles) b) polymer structure of irreversible micelles (of crew cut type)

The classical micelles and the crew cut micelles are synthesized by polymerization induced self-assembly in D_2O. Temperature dependent SANS measurements at ambient pressure (see Fig. 1) confirm the reversible morphology change. The structures dissolve upon the cooling to 25 °C and form again without any morphology change at 40 °C. The form factor is fitted with a hard sphere model with a repulsive square well structure factor.

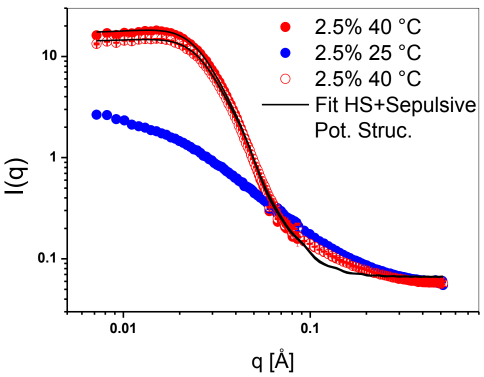


Fig. 1) SANS measurements at ambient pressure at 40 °C before cooling (filled red dot) at 5 °C (filled blue dot) and at 40 °C after cooling (open red dot)

The pressure dependant measurements of the reversible micelle morphology was conducted at 35 °C slightly above the LCST of PNIPAM, as previous measurements showed that the effect of the pressure is most pronounced near the LCST (see Fig 2a).[1]

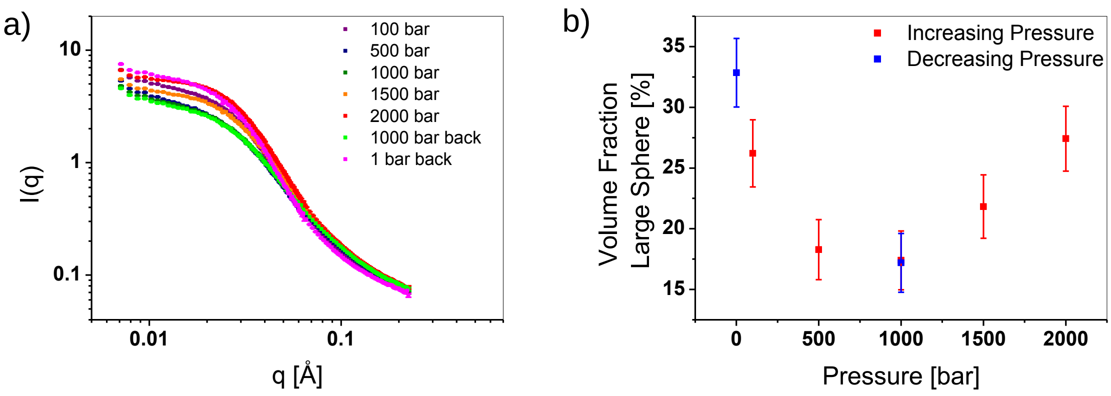


Fig. 2 a) SANS measurements at 35 °C at 100 bar (purple), 500 bar (blue), 1000 bar (dark green), 1500 bar (orange), 2000 bar (red), 1000 bar with decreasing pressure (light green) ambient pressure after decreasing pressure (magenta); b) Volume fraction of large spheres in binary hard sphere model for increasing pressure (red) and decreasing pressure (blue)

For the pressure dependent measurements, we do not observe a drastic change of the form factor as seen for the temperature trigger. Comparing the intensities, one can see that the intensity at low q drops slightly when the pressure is increased to 1000 bar. But when the pressure is increased to 2000 bar, the intensity increases again. This effect seems to be reversible. For a better understanding, the data is fitted with a binary hard sphere model, assuming that we have a two component system with micelles and dispersed random coils. Using this model, one can see that the volume fraction of the large spheres decreases when changing the pressure up to 1000 bar and increases when the pressure is further increased (see Fig. 2b). To verify that this is not an end group effect, we need now to apply pressure to reversible micelles with different block length.

It is important to decrease the transition temperature to values below room temperature for the irreversible morphology change. This allows easy handling of the (non-equilibrium) samples without inducing the irreversible morphology change. To decrease the LCST to a value below room temperature, we copolymerized

NIPAM with tBAM (resulting LCST ~7 °C). The irreversible morphology change upon the temperature trigger is observed by SANS at ambient pressure (Fig. 3a)

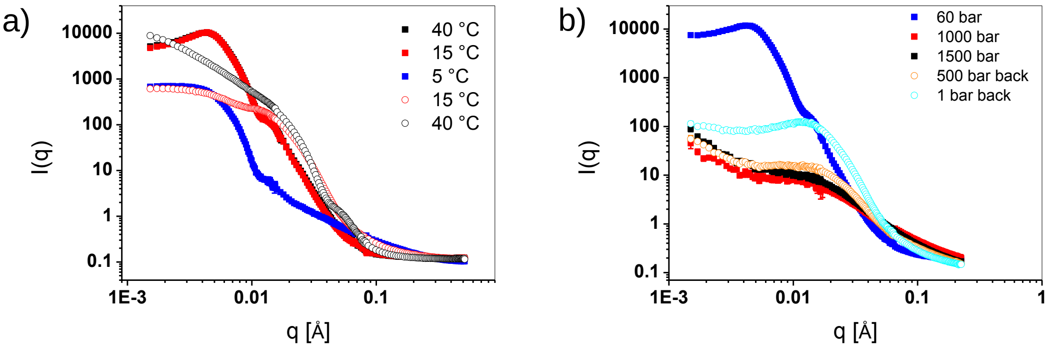
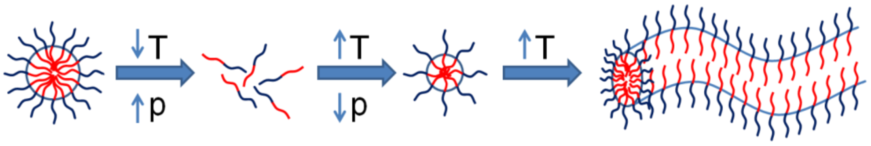


Fig. 3a) SANS measurements at ambient pressure at 40 °C cooling (filled black square) 15 °C cooling (filled red square) at 5 °C (filled blue square) at 15 °C heating (open red dot) and at 40 °C after cooling (open black dot); b) SANS measurements at 15 °C at 60 bar (blue), 1000 bar (red), 1500 bar (black), 500 bar with decreasing pressure (orange) ambient pressure after decreasing pressure (turquoise)

The form factor at 40 °C and 15 °C can be fitted with a hard sphere model with a repulsive square well structure factor. At 5 °C, a high amount of the spherical structures is dissolved. But a certain amount is still observable. Therefore the equilibration time at 5 °C was probably not long enough. When the temperature is then increased to 15 °C the form factor changes compared to the form factor at 15 °C before cooling. One can fit this with a combination of the form factor of the non dissolved spheres and smaller spheres. The measurement at 40 °C after cooling is fitting to the flexible cylinder model. This behavior is sketched at scheme 2.



Scheme 2) Sketch of irreversible morphology change upon demicellization by temperature and pressure

The pressure-dependent measurement is recorded at 15 °C and shows already a complete dissolution of the micelles at 1000 bar. The fact that these micelles completely disperse under pressure while the reversible ones do not disperse is not yet understood. As the core-forming block is 8 times longer for the irreversible micelles, we expected the opposite effect. Moreover, it seems that the pressure is the faster trigger for these micelles as the complete dispersion of the micelles was reached without any equilibration time while the temperature trigger does not lead to a complete dispersion after equilibrating for 30 min. When reducing the pressure to ambient pressure, the morphology changed to a spherical morphology, which can by compared with the small spheres detected at 15 °C after the temperature trigger. This behavior is summarized in scheme 2. For further verification of this scheme, the measurement of the temperature behavior needs to be repeated in a way that the micelles have enough time to dissolve at low temperatures. A further important measurement would be a pressure switch at 25 °C to show that it is possible to obtain worm like structures after the pressure switch. As the demicellation of the irreversible micelles is that successful, we need to investigate whether this is due to the fact that we used P(NIPAM-*st*-tBAM) as core forming block. Therefore it is important to investigate either reversible micelles containing P(NIPAM-*st*-tBAM) or irreversible micelles containing only NIPAM as core forming block.

[1] S. Grobelny, C. H. Hofmann, M. Erlkamp, F. A. Plamper, W. Richtering and R. Winter, Soft Matter, 2013, 9, 5862-5866.