Experimental report

10/02/2017

Proposal: 9-10-1470 **Council:** 4/2016

Title: Pressure-induced demicellization of PNIPAM-based micelles

Research area: Soft condensed matter

This proposal is a continuation of 9-10-1414

Main proposer: Alexander STEINSCHULTE

Experimental team: Andrea SCOTTI
Steffen BOCHENEK
Sabine SCHNEIDER
Alexander STEINSCHULTE

Local contacts: Ralf SCHWEINS

Samples: D2O
Poly(N-isopropyl acrylamide)-block-Poly(N,N-dimethyl acrylamide)

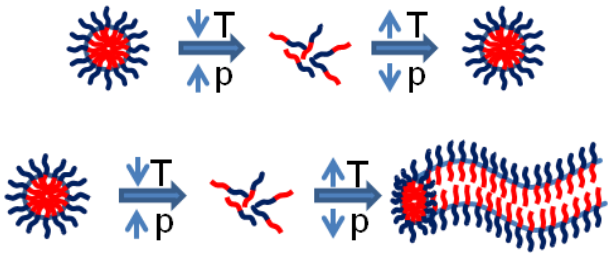
Instrument	Requested days	Allocated days	From	To
D11	4	3	27/06/2016	30/06/2016

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. We started to investigate this pressure influence in our last proposal 9-10-1414. Our obtained results showed that we can induce an irreversible morphology change by applying pressure. In this project, we would like to study reversible and irreversible morphology changes upon pressure application by help of PNIPAM-b-PDMAM-based micelles.
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.

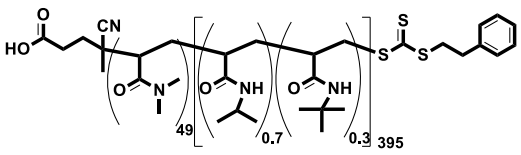
Pressure induced reverse micellization of PNIPAM based micelles

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 behavior can be easily modified by copolymerizing with other acrylamides such as e.g. *N*,*N*-diethyl acrylamide (DEAM) or *N*-tertbutyl 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. 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 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 classical micelles and crew cut micelles (for structure see scheme 2).



Scheme 2: Polymer structure

The classical micelles, crew cut micelles and vesicles are synthesized by polymerization induced self-assembly in D_2O. The demicellization is upon pressure and remicellization upon pressure release is followed by SANS for all three morphologies.

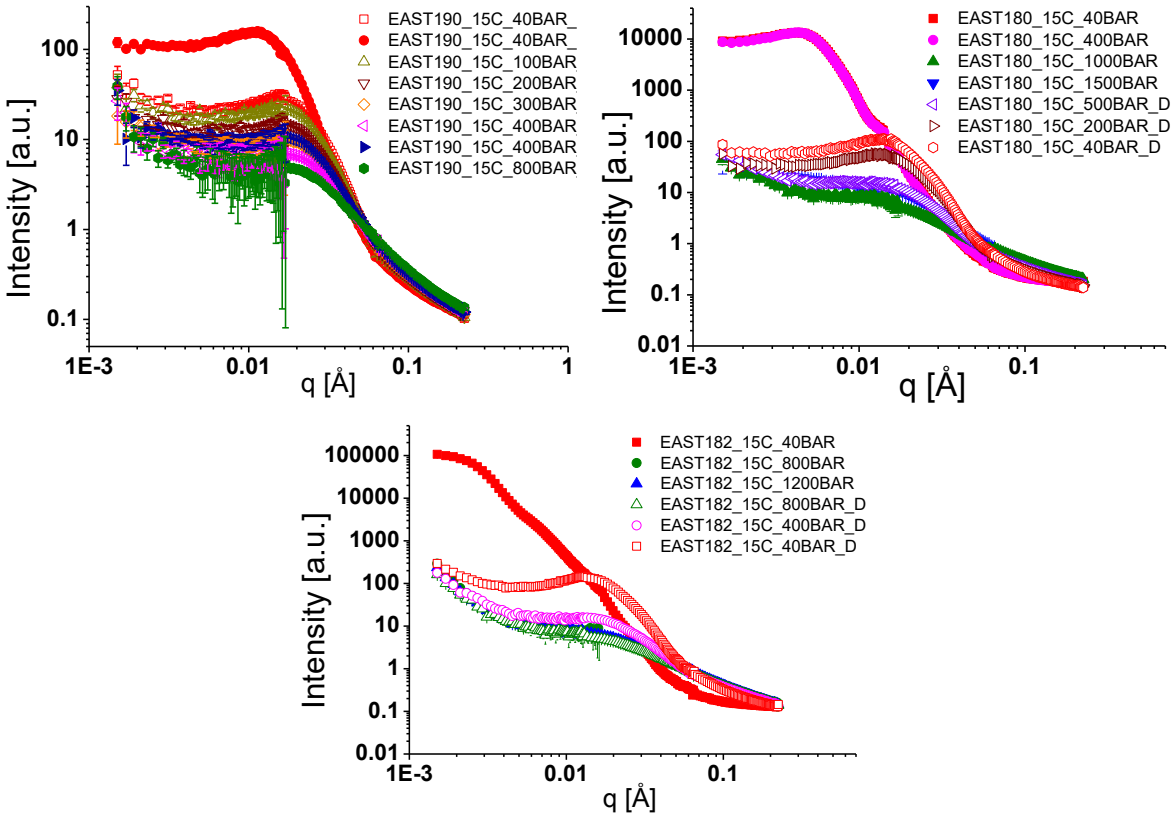


Fig. 1 SANS measurements at 15°C at different pressures of a) micelles b) crew cut micelles and c) vesicles.

The form factor of all three samples clearly changes upon pressure, indicating a structural change when applying pressure to the samples. A similar change was found when applying a temperature trigger to these stimuli responsive structures, indicating a dual stimuli response of the micelles.