Experimental report

29/08/2019

Proposal: **9-11-1849** **Council:** 4/2017

Title: Pressure as Stimulus for UCST-typePolymer Systems

Research area: Chemistry

This proposal is a new proposal

Main proposer: **Felix PLAMPER**

Experimental team:
Monia BRUGNONI
Felix PLAMPER
Steffen BOCHENEK
Maximilian Marcel SCHMIDT
Andrea MELLE
Marie Friederike SCHULTE
Andrea SCOTTI

Local contacts:
Ralf SCHWEINS
Leonardo CHIAPPISI

Samples: poly(ethyl acrylate) and poly(ethylene oxide) and poly(dimethylaminoethyl methacrylate)

Instrument	Requested days	Allocated days	From	To
D11	3	3	17/09/2018	20/09/2018

Abstract:

The pressure-sensitivity of microgels and block-copolymer micelles will be investigated, In all cases, polymers with an Upper Critical Solution Temperature (UCST) will be employed, meaning that the UCST-type polymers turn insoluble at low temperatures but are soluble at high temperatures. The UCST polymers comprise poly(ethyl acrylate) in (deuterated) isopropanol and aqueous poly(dimethylaminoethyl methacrylate) in presence of multivalent counterions (amino-containing block shows UCST-properties in presence of hexacyanoferrates). The former example will be achieved by help of poly(ethyl acrylate) microgels, while poly(dimethylaminoethyl methacrylate)-block-poly(ethylene oxide) is the polymer of choice in aqueous medium, which forms micelles at low temperatures. We expect a change of the UCST with pressure though the extent and direction of the phase separation temperature shift is unknown so far. Changes in swelling of the microgel and a pressure-invoked (de-)micellization will answer these open questions, giving a fundamental new insight into pressure-sensitive materials.

Pressure as Stimulus for UCST-type Polymer Systems

Experimental Report for Proposal 9-11-1849

Proposer: Prof. Felix Plamper (TU Bergakademie Freiberg, Leipziger Str. 29, 09599 Freiberg, Germany), Prof. Walter Richtering (RWTH Aachen University, Landoltweg 2, 52056 Aachen, Germany)

We were interested in the pressure-modulation of polymers, which exhibit an upper critical solution temperature (UCST). There have been some reports on the pressure-dependence of the solubility of polymers with a lower critical solution temperature (LCST), indicating in most cases an increase in the LCST and hence solubility upon application of hydrostatic pressure.[1,2] However, corresponding reports on the behavior of UCST-polymers are largely missing. Hence, we wanted to shed light on this issue by use of pressure SANS, following the structural changes by following changes in the form factor. We proposed several systems of interest and investigated the following: a) aqueous block copolymers based on poly(*N*,*N*-dimethylaminoethyl methacrylate) **PDMAEMA**, which act as representatives of charged UCST-type polymers in presence of multivalent salts[3] (hexacyanoferrates; poly(ethylene oxide) constitutes the solubilizing block of PEO_{110}-*b*-$PDMAEMA_{22}$, which was obtained by own procedure),[4] b) poly(*N*-acryloylglycinamide) **PNAGA** as a nonionic polymer in water (as microgels obtained from Sami Hietala, University of Helsinki)[5] and c) poly(ethyl acrylate) PEA in isopropanol as an example in organic solvents (linear **PEA** with M_w = 95000 g/mol; obtained from Sigma-Aldrich).

During the measurements, various difficulties arose, which led only to partially conclusive results. E.g. the sapphire window of the high-pressure cell broke once and needed repair, which took a considerable amount of our measurement time. In addition, we encountered unexpected sample damage during the high-pressure measurements, which would require fresh samples for each pressure and temperature (possible topic for a follow-up beam-time application), to obtain reliable data of the UCST system as such. Hence, most of the data is presented here as processed (absolute intensities), but without form factor fitting. In addition, full background control would be only possible when measuring the solvents at various temperatures and pressures (in some cases, the background would need correction, as only the background at certain temperature and pressure was measured and considered). Nevertheless, following preliminary observations can be drawn:

(i) Slightly charged PDMAEMA shows UCST-behavior in presence of hexacyanoferrate(III) due to ionic crosslinking between the polymer-bound ammonium groups and the negative charges located on the metallates.[3] This interaction weakens upon heating, as was seen for the micellization of PEO_{110}-*b*-$PDMAEMA_{22}$. It forms at low temperatures spherical micelles with an insoluble but still swollen PDMAEMA core and a PEO corona. Hence, the micellar form factor can be discerned in the scattering data at 20 °C and low pressure. We choose to apply a step-wise increasing pressure, but we realized that the scattering is reduced after the measurement series, even when going back to the initial conditions. In addition, the polymer solution transformed from yellowish to blueish, which might be caused by altered iron-complexes. Hence in the next series, we directly measured after ambient conditions the high-pressure condition (1750 bar), showing even an intensification of the scattering due to enhanced micellization. This suggests that pressure reduces the solubility of the PDMAEMA-UCST system. Again, the original scattering pattern could not be regained after several other measurements at elevated pressure, indicating sample damage. Hence, future experiments would require fresh samples for all high-pressure measurements assuring negligible degradation in the time scan of the data acquisition.

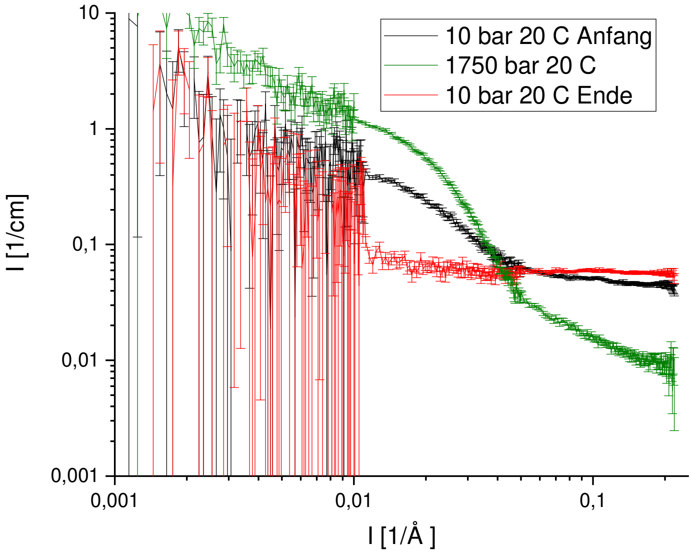

Figure 1: Pressure-induced changes of PEO_{110}-*b*-$PDMAEMA_{22}$ scattering (1.2 g/L polymer in 0.1 M NaCl at pH 7 in presence of $[Fe(CN)_6]^{3-}$, which equals four times the amount of DMAEMA units); initially, a micellar form factor is visible, which even intensifies upon pressure application; however, after several measurements the micellar form factor vanishes even under pressure (and when going back to ambient conditions); this indicates damage to the sample by pressure and/or neutron irradiation

(ii) As a next step, we used non-ionic PNAGA microgels in water.[5] We can see clearly the size increase of the microgels with increasing temperatures (20 °C and 70 °C) due to a leftward shift of the major scattering decay toward smaller q values, though a pronounced polydispersity blurs the microgel form factor (probably even some aggregation is present). The pressure response is however much less pronounced. At low temperature, one might discern a minor compaction upon pressurizing up to 2500 bar (again, the major scattering decay is shifted to the right).

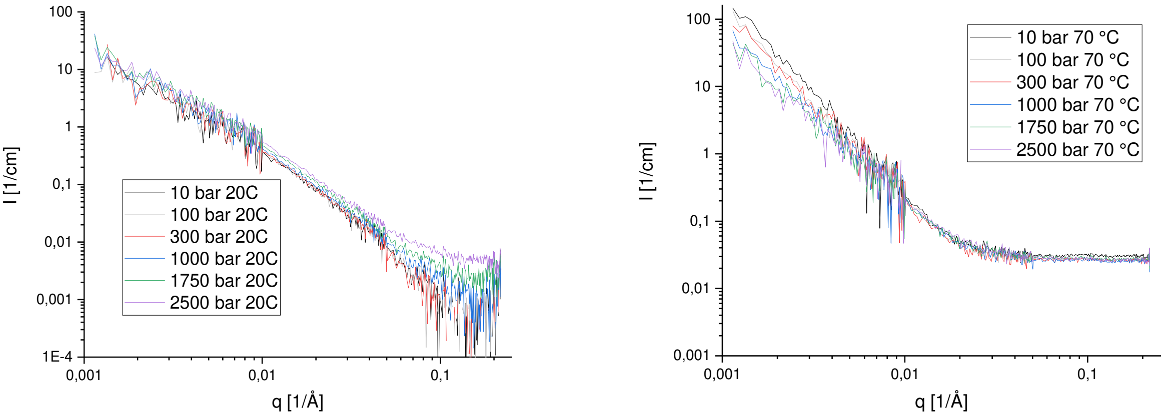

Figure 2: Pressure dependence of the scattering of PNAGA microgels (with 3 mol% crosslinker; 1g/L in deuterated water) at low and high temperature (the change in size with temperature is more gradual and not stepwise as for most LCST polymers);[5] the temperature effect is visible, but any pronounced pressure effect cannot be discerned.

At high temperature, the size of single microgel is unaffected by rising pressure, but some aggregation is reversed by pressure application. We can state that PNAGA does not exhibit a strong pressure dependence on its thermoresponsive properties. This might be caused by the gradual temperature-induced changes in size,[5] which leaves only a small handle for any pressure effects.

(iii) Finally, we investigated linear PEA in deuterated isopropanol. We choose two temperatures, one slightly above the cloud point (34 °C) and one slightly below the cloud point of PEA (31 °C). Above the cloud point, pressure does not significantly affect the scattering pattern. Below the cloud point, we see that aggregation is reversed upon pressure application. This could be in line with an increased solubility at high pressure.

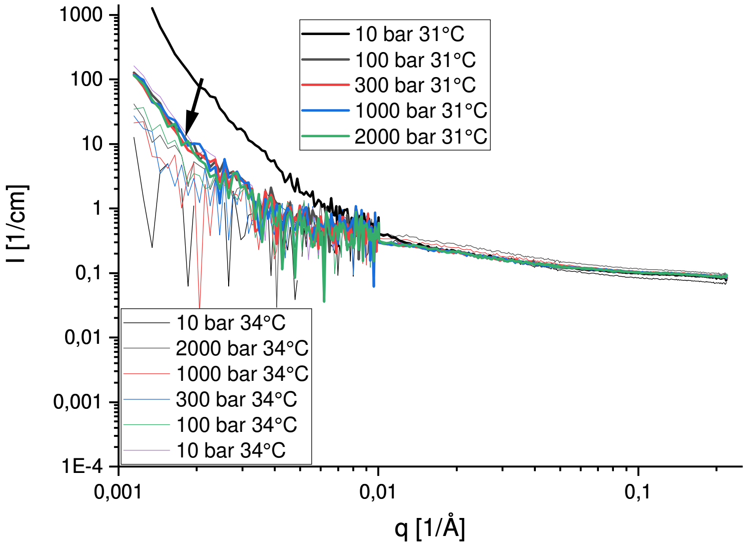

Figure 3: SANS patterns of PEA (1 g/L in deuterated isopropanol) at two different temperatures (thick lines at 31 °C, thin lines at 34 °C) and various hydrostatic pressures. Above the UCST, the scattering changes are minor, while an increase in pressure clearly leads to less aggregates below the UCST (31°C).

Concluding, we cannot draw a uniform picture with this set of experiments but surely they represent an interesting starting point for further experiments we are planning. For PEA, it seems that pressure enhances the solubility, while in aqueous solutions the opposite is true (PNAGA compacts under certain conditions, while the number of micelles increases with pressure for the PDMAEMA-based system).

References

(1) Grobelny, S.; Hofmann, C. H.; Erlkamp, M.; Plamper, F. A.; Richtering, W.; Winter, R. Conformational changes upon high pressure induced hydration of poly(N-isopropylacrylamide) microgels. *Soft Matter* **2013**, *9*, 5862–5866.
(2) Reinhardt, M.; Dzubiella, J.; Trapp, M.; Gutfreund, P.; Kreuzer, M.; Groeschel, A. H.; Mueller, A. H. E.; Ballauff, M.; Steitz, R. Fine-Tuning the Structure of Stimuli-Responsive Polymer Films by Hydrostatic Pressure and Temperature. *Macromolecules (Washington, DC, U. S.) FIELD Full Journal Title:Macromolecules (Washington, DC, United States)* **2013**, *46*, 6541–6547.
(3) Plamper, F. A.; McKee, J. R.; Laukkanen, A.; Nykänen, A.; Walther, A.; Ruokolainen, J.; Aseyev, V.; Tenhu, H. Miktoarm stars of poly(ethylene oxide) and poly(dimethylaminoethyl methacrylate). *Soft Matter* **2009**, *5*, 1812–1821.
(4) Steinschulte, A.; Xu, W.; Draber, F.; Hebbeker, P.; Jung, A.; Bogdanovski, D.; Schneider, S.; Tsukruk, V. V.; Plamper, F. A. Interface-Enforced Complexation between Copolymer Blocks. *Soft Matter* **2015**, *11*, 3559–3565.
(5) Yang, D.; Viitasuo, M.; Pooch, F.; Tenhu, H.; Hietala, S. Poly(N-acryloylglycinamide) microgels as nanocatalyst platform. *Polymer Chemistry* **2018**, *9*, 517–524.