Experimental Report

28/01/2014

Proposal:	**9-11-1655**	**Council:**	10/2012
Title:	Contrast variation measurements ofcore-shell particles and hollow PNIPAM microgels		

This proposal is a new proposal

Research Area: Soft condensed matter

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Samples: poly-(N-isopropylacrylamide), polystyrene;

Instrument	Req. Days	All. Days	From	To
D11	3	2	08/03/2013	10/03/2013

Abstract:

Poly(N-isopropylacrylamide) microgels are stimuli-responsive polymer networks in the nanometer size range, swollen by a good solvent like water. At the volume phase transition temperature of 32°C in water, they change their size drastically. Different architectures of this polymer - like core-shell structures with different cores as well as hollow PNIPAM capsules have been synthesized.
However the structure of those hollow spheres has not been characterized by means of neutron scattering, yet. Our preliminary SANS measurements indicate a deformation of the hollow spheres. Therefore we want to investigate a system of Polystyrene (PS) core PNIPAM shell particles with deuterated cores. We want to compare the formfactor of the core shell particle in a D_2O/H_2O solvent mixture matching the core, with the scattering behaviour of the corresponding hollow capsules. To investigate the structure of the hollow particles in detail, temperature dependent SANS measurements in the q-range of 0.0015 1/Å to 0.15 1/Å are required. These conditions are provided at the ILL beamline D11.

Poly(N-isopropylacrylamide) (PNIPAM) microgels are cross-linked polymer networks in the nanometer to micrometer size range, which are swollen in a good solvent. They undergo a volume phase transition (VPT) in water at 32°C. The utilized amount of crosslinker in the precipitation polymerization process influences the softness and compressibility of the resulting particles and thus the swelling ratio.[1] Several core-shell architectures with both inorganic and organic cores have recently been synthesized and investigated. Ballauff et. al. for example studied the formation of core-shell structures of Polystyrene (PS) and PNIPAM in a photoemulsion polymerization process[2]. Using core-shell particles several approaches have been performed to establish hollow PNIPAM microspheres by dissolving the core in an appropriate solvent[3]. Hollow microgels have promising properties for the uptake and release of guest molecules. We employed the contrast variation technique to gain deep insight in the changes of the particle structure before and after the core dissolution. In Small Angle Neutron Scattering (SANS) the choice of an appropriate mixtures of D_2O and H_2O allows to highlight or hide parts of a particle consisting of different compounds with different scattering length densities (SLD). The employed particles were synthesized with a deuterated polystyrene core and a conventional protonated PNIPAM shell to have a pronounced difference of SLD in core and shell. The structure of the core-shell particles and the resulting hollow spheres both were investigated above and below the VPTT of PNIPAM in water. The calculated scattering length densities of the employed compounds are given in Table 1.

Table 1: Calculated scattering length densities for the employed polymers and solvents.

	CALCULATED SCATTERING LENGTH DENSITIES [1/Å²]
POLYSTYRENE-D8	$6.47 \cdot 10^{-6}$
POLY(N-ISOPROPYLACRYLAMIDE)	$8.69 \cdot 10^{-7}$
H_2O	$-5.6 \cdot 10^{-7}$
D_2O	$6.39 \cdot 10^{-6}$

The deuterated PS core should be best matched in pure D_2O according to the calculated values. This was confirmed during the measurements. The overall intensity which is mainly assigned to the scattering of the PS core is at a minimum in solvent composition of 100% D_2O as evaluated for three distinct q-values (Figure 1a).

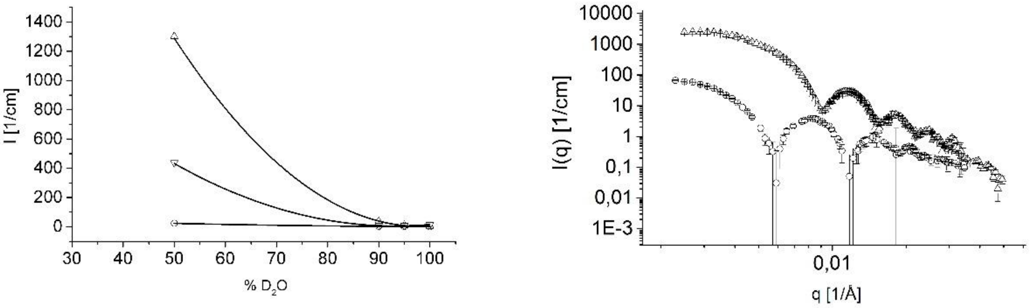

Figure 1a: Determination of the point of zero average contrast. The minimum of the parabola corresponds to a solvent composition of 100% D_2O for three different distinct q-values. Thus, in pure D_2O the PS-d8 core is matched. Figure 1b shows the core shell particle in full contrast (D_2O/H_2O =1, open triangles) and in D_2O where the core is matched (open circles).

Figure 1b shows the characteristic scattering curves of the core shell particles in two different solvent compositions. The open triangles correspond to the measurements in a mixture of D_2O/H_2O = 1. The open circles show the situation in pure D_2O where the core is matched. The distinct shift of minima to lower q-values indicate that the particles core is matched and the structure shows a hollow particle-like scattering behavior. Figure 2 shows the comparison of the core-shell particle in the core-matched state and the formfactor of the corresponding particles after the core was chemically dissolved. (Note that the intensity of the second curve is shifted for clarity reasons).

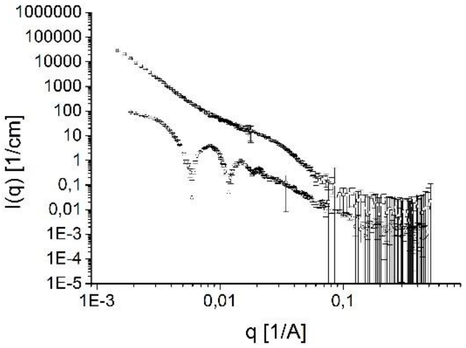

Figure 2: Comparison of formfactors of the core shell particles in the core-matched state (open circles) and the formfactor of the corresponding particles after core dissolution (open squares). The intensity of the upper curve is shifted by a factor of 25 for clarity reasons. The formfactors differ significantly, which is an indication that no simple hollow structure was formed after the core dissolution.

One can clearly see that the formfactors differ significantly and that dissolving the core does not yield in a simple hollow sphere that one could imagine after the dissolution of the core. However, it is not yet clear, whether the change of scattering behavior corresponds to a deformation of the particles or to a fracture of the PNIPAM shell during the core dissolution. A detailed quantitative analysis of the data is still under development at present.

[1] R. Pelton, *Advances in colloid and interface science* **2000**, *85*, 1-33.
[2] Y. Lu, A. Wittemann, M. Ballauff, M. Drechsler, *Macromolecular Rapid Communications* **2006**, *27*, 1137-1141.
[3] a) M. Peng, H. Wang, Y. Chen, *Materials Letters* **2008**, *62*, 1535-1538; b) S. Nayak, D. Gan, M. J. Serpe, L. A. Lyon, *Small* **2005**, *1*, 416-421.