Experimental report

04/08/2021

Proposal:	**EASY-632**	**Council:**	10/2019
Title:	Form factor analysis of thermorespsonsive core-shell microgels in the fully swollen and collapsed state		
Research area:	Soft condensed matter		

This proposal is a new proposal

Main proposer: **Matthias KARG**

Experimental team:

Local contacts: Sylvain PREVOST

Samples: Au, [C6H11NO]n, D2O

Instrument	Requested days	Allocated days	From	To
D11	12	12	15/08/2020	16/08/2020

Abstract:

PNIPAM microgels show a significant increase in light scattering when heated above the volume phase transition temperature. This behavior can be explained by the increasing polymer volume fraction - affecting the refractive index - dominating over the effect of significantly reduced particle size in the collapsed state. Although this observation is well-known, a quantitative description is still missing. Recently we were successful in theoretically describing the light scattering of core-shell microgels using finite difference time domain simulations. From these simulations we could extract the polymer volume fraction (shell) and the resulting refractive index for a broad range of swelling states covering the volume phase transition. With the proposed SANS experiment we want to study the form factor of different core-shell microgels in the fully swollen and collapsed state. This will allow us to get access to the polymer density profile of the shells experimentally. We want to study five core-shell systems (gold cores, PNIPAM shells with shell thicknesses in the range of 124 nm and 188 nm (hydrodynamic radius, swollen state) and cross-linker degrees of 5, 15 and 25%.

Experimental Report EASY-632

Title: Form factor analysis of thermoresponsive core-shell microgels in the fully swollen and collapsed state

Introduction:

We have measured core-shell (CS) microgels that feature a tiny gold core and a thermoresponsive, soft PNIPAM shell. The polymer shell varied in a size range between 111 and 190 nm in diameter and cross-linker densities of 5, 15 and 25 mol%. We labelled the particles as CS1-5 in our investigations. Samples CS1, CS2 and CS3 vary in shell thickness while possing the same crosslinking. However, sample CS4 has a lower and CS5 a higher crosslinking density compared to the other samples.

To study the form factor and, therefore, to get access to polymer density profiles of the microgels at their different states of swelling, we performed SANS measurements on the D11 instrument at the Institut Laue-Langevin (ILL, Grenoble, France) at four different temperatures of 25, 35, 37 and 50 °C. To cover a broad q range, the data for dilute CS samples in heavy water were collected at sample-to-detector distances of 1.4, 8 and 39 meters.

Results:

Figure 1 shows obtained scattering profiles of all CS microgels at four temperatures. The experimental data at different sample-to-detector distances were merged and analyzed by SASfit software by Kohlbrecher[1]. We used the fuzzy sphere model introduced by Stieger *et al*.[2] to fit our scattering curves. In this model, the microgel possesses an inner homogeneous crosslinked region with a radius R_{box}. The parameter σ defines the thickness of the fuzzy shell, and R_{SANS} gives the overall microgel radius by $R_{SANS} = R_{box} + 4\sigma$. The fits describe our scattering profiles very well. For temperatures below or close to volume phase transition temperature, σ values are greater than zero. However, at 50 °C, the microgels are in their fully collapsed state, resulting in $\sigma = 0$. At this state, the particles resemble the scattering of polydisperse homogeneous, hard spheres. A representative depiction of the core-shell particle morphology and its temperature-dependent evolution of the inner polymer region and shell thickness obtained by SANS data analyses is illustrated in figure 2. The fuzzy shell thickness shrinks with increasing temperature while the inner polymer core with R_{box} remains almost constant. Figure 2 (bottom) demonstrates calculated radial density profiles showing polymer volume fraction ϕ as a function of the radial distance from the microgel center. At the swollen state (25 °C), particles owning 15 mol% crosslinking possess approximately 80% of solvent. With increasing temperature, the particle undergoes a transition from an inhomogeneous fuzzy sphere to a homogeneous hard sphere with less than 60% solvent. However, the amount of solvent strongly depends on the crosslinking degree at lower temperatures. Sample CS4 (5mol%) possesses higher and CS5 (25mol%) lower amont of solvent than the other samples. Overall, all particle types show similar transitions from fuzzy sphere to a hard sphere-like scattering behaviour.

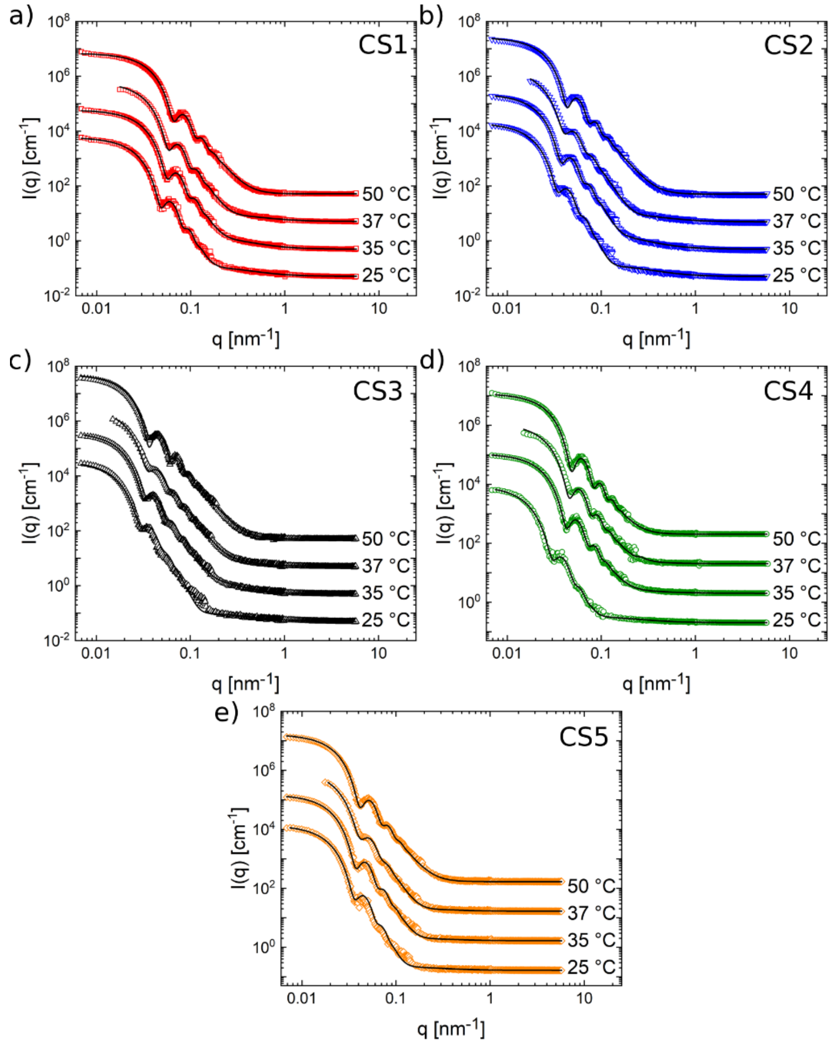

Figure 1: SANS results of all core-shell samples at the temperatures 25, 35, 37 and 50 °C. Symbols correspond to the experimental data, and solid black lines to the fuzzy sphere model fits from SASfit[1]. The spectra are shifted horizontally by multiplication by ×1, ×10, ×100 and ×1000, from bottom to top.

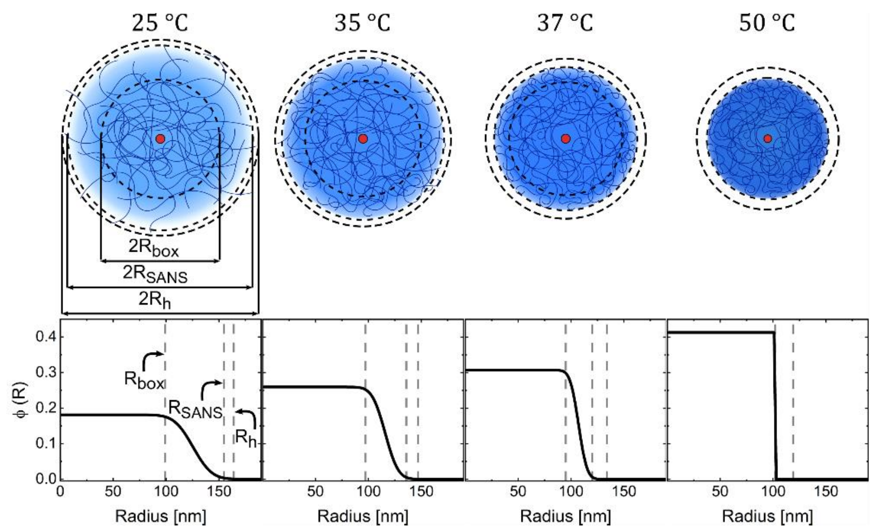

Figure 2: Top: schematic illustration of a core-shell particle at different temperatures. Black dashed lines highlight radii obtained by DLS and SANS. Bottom: corresponding radial density profiles.

Conclusion:

The performed measurements on D11 instrument at the Institut Laue-Langevin (ILL, Grenoble, France) gave us important insights into the morphology of the core-shell microgel. The obtained radii from SANS allowed us to obtain polymer volume fractions in dependence of the swelling state. For this we used data calibrated to absolute scale. Combined with our findings from temperature-dependent absorbance measurements, we are very confident to publish our results shown here very soon. The prepation of the manuscript is close to being finished.

We would like to thank the local contact for the great assistance with measurements, data reduction and normalization – in particular during the difficult times of the Corona pandemic where the experiment had to be performed without our presence at the ILL. We look very much forward to future measurements at ILL, in particular using the D11 instrument.

References:

[1] Kohlbrecher, J. *SASfit: A Program for Fitting Simple Structural Models to Small Angle Scattering Data*; Paul Scherrer Institut, Laboratory for Neutron Scattering, Villigen, Switzerland, 2008

[2] Stieger, M.; Richtering, W.; Pederson, J. S.; Lindner, P. Small-angle neutron scattering study of structural changes in temperature sensitive microgel colloids. *The Journal of Chemical Physics* **2004**, *120*, 6197-6206