Experimental report

09/09/2015

Proposal: 9-11-1706 **Council:** 4/2014

Title: Structure determination of microcapsules with advanced temperature responsive behavior

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: silica-core/PNIPMAM-shell and corresonding hollow sphere
silica-core/PNIPMAM-PNIPAM- copolymer-shell and corresonding hollow sphere
silica-core/PNIPAM-shell and corresonding hollow sphere

Instrument	Requested days	Allocated days	From	To
D11	4	2	27/09/2014	29/09/2014

Abstract:

Nanocapsules are of special interest in the field of colloidal science. When synthesized from a thermoresponsive polymer like poly(N-isopropylacrylamide) (PNIPAM) a thermally induced uptake and release mechanism is imaginable. We performed the first small angle neutron scattering experiments including contrast variation measurements to investigate the structure of this unique species. Now we aim for advanced properties by introducing a second thermoresponsive polymer, namely poly(N-isopropylmethacrylamide) (PNIPMAM). Not only the different polymer type, but also the architecture in which both polymers are combined in the shell might have an influence on the capsule properties. Therefore we want to investigate capsules with a double-shell structure and a classical copolymer shell and compare these results with the homopolymer analogues.

During this beamtime at the D11 we studied the internal structure of microcapsules with advanced temperature responsive behavior.

These microcapsules are core-shell-shell (CSS) microgels with a silica core and two temperature-sensitive polymer shells with different volume phase transition temperatures (VPTTs) and the corresponding hollow double-shell (HSS) nanocontainers. They were prepared in a recent work in our group by Dubbert *et al*. [1] and analyzed by light scattering methods.

The inner polymer shell consists of poly(*N*-isopropylacrylamide) (PNIPAM) with a VPTT of 32 °C in H_2O [2] and the outer shell consists of poly(*N*-isopropylmethacrylamide) (PNIPMAM) which exhibits a VPTT of about 42 °C [3]. The hollow spheres were prepared by dissolution of the silica core.

The aim of this work was to compare scattering curves of the core-matched (62 wt% D_2O in D_2O/H_2O mixture) CSS particles with the scattering curves of the HSS particles. The measurements were performed at 52 °C, where both shells are collapsed, at 40 °C, where the outer PNIPMAM shell is swollen and the inner PNIPAM shell is still collapsed and at 20 °C where both shells are swollen.

To gain information about the swelling contribution of each individual shell, these measurements were also performed for the silica core – PNIPAM shell (CS) particles and the corresponding hollow PNIPAM spheres (HS) at 20 °C and 40 °C.

Additionally, the samples containing the silica core were also measured at full scattering contrast for comparison.

Samples were measured at three sample-detector distances of 1.2 m, 8 m and 39 m using wavelengths of λ = 6 Å and λ = 17 Å with a polydispersity of $\Delta\lambda/\lambda$ = 9% to cover the entire available *q*-range of the instrument. The scattering intensity was detected on a ^{3}He gas detector (CERCA) with a detection area of 96 x 96 cm^2 and a pixel size of 7.5 x 7.5 mm^2. Narrow Hellma quartz glass cells (type 110-QS) with 2 mm sample thickness were used. The incoherent scattering of water was measured as secondary calibration standard at 8 m sample-detector distance. All data were corrected for transmission, empty cell scattering and background scattering to receive absolute values for the differential cross section.

The samples were measured in a copper sample changer and the concentration was about 0.5 mg/mL. The sample temperature was measured inside a cell filled with water by an external thermometer and adjusted by an external thermostat.

All measurements where running fine and the data we received from these experiments are very good and are depicted in Figure 1.

The scattering curve of the silica core shows two local minima indicating very low polydispersity.

First, the particles with only one polymer shell will be compared. The scattering profiles of the HS and the core-matched CS particles at 40 °C look rather similar which indicates a similar structure. At 20 °C, however, the scattering curves of the HS and core matched CS particles clearly differ. Thus, removing the core influences the structure at temperatures below the VPTT of PNIPAM. This is in agreement with previous results from Dubbert *et al*. [4], who performed quantitative analysis of similar CS and HS systems. They could show, that below the VPTT of PNIPAM the shell swells into the void of the HS particles.

A similar behavior is observed for the system with two shells. At 52 °C, where both shells are collapsed, no clear difference between the scattering curves is observed. Lowering the temperature to 40 °C, which is below the VPTT of the outer PNIPMAM shell, leads to a swelling of the outer shell. The scattering curves of the HSS and core-matched CSS particles at 40 °C show a clear difference in the position of the second local minima. Thus, the swelling of the outer shell influences the void size in the HSS particles. At 20 °C, where also the inner PNIPAM shell is swollen, the scattering curve of the CSS particles at the matchpoint of silica look totally different as compared to the scattering curve of the HSS particles similar to the system with only one shell.

References:

1. Dubbert J, Nothdurft K, Karg M, Richtering W (2015) Core-shell-shell and hollow double-shell microgels with advanced temperature responsiveness. Macromol Rapid Commun 36:159–164. doi: 10.1002/marc.201400495

2. Pelton RH, Chibante P (1986) Preparation of aqueous latices with N-isopropylacrylamide. Colloids and Surfaces 20:247–256. doi: 10.1016/0166-6622(86)80274-8

3. Pelton R (2000) Temperature-sensitive aqueous microgels. Advances in Colloid and Interface Science 85:1–33.

4. Dubbert J, Honold T, Pedersen JS, et al. (2014) How Hollow Are Thermoresponsive Hollow Nanogels? Macromolecules 47:8700–8708. doi: 10.1021/ma502056y

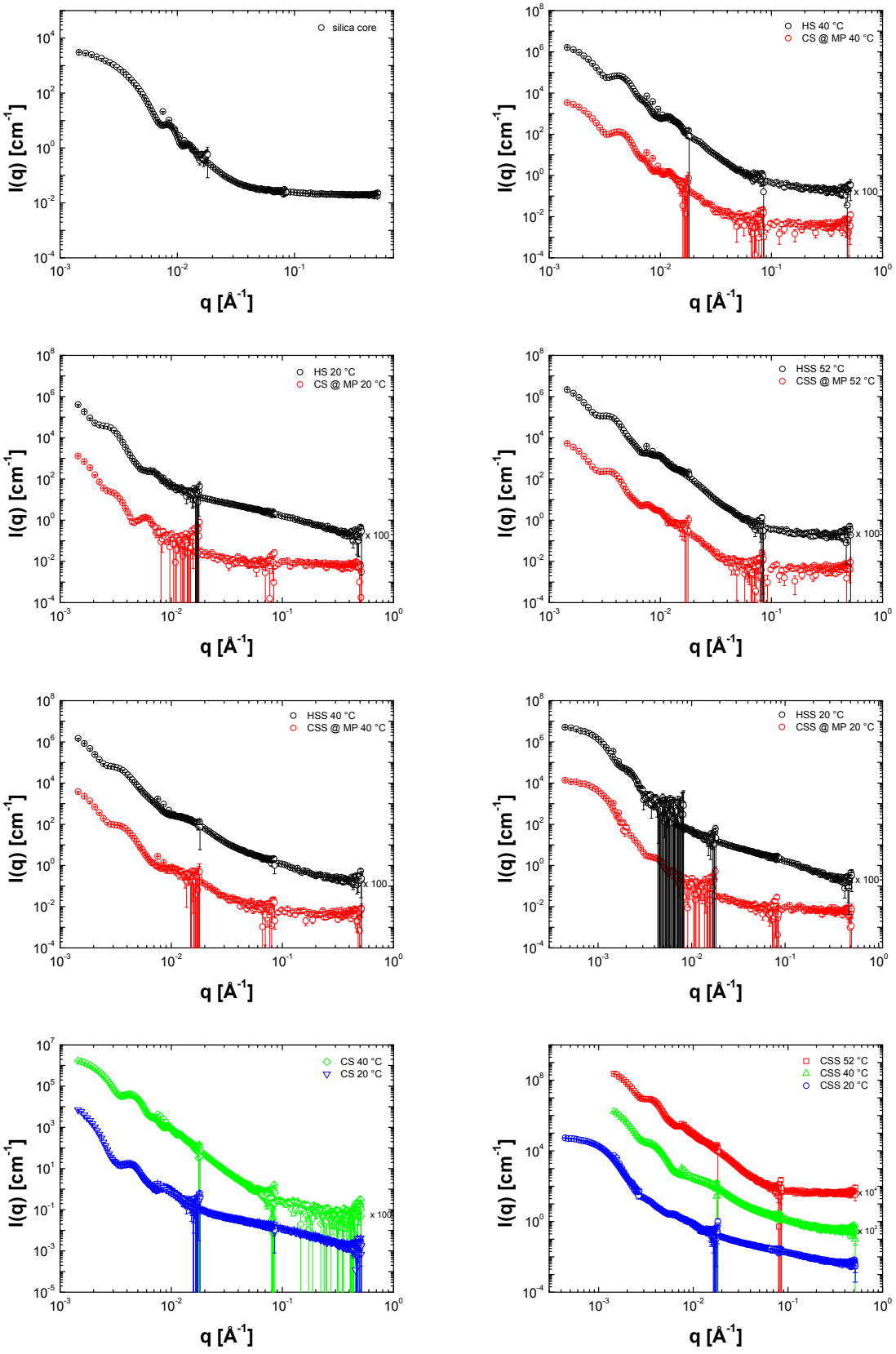

Figure 1 Experimental scattering curves of the silica core, the core-shell (CS), the core-shell-shell and the corresponding hollow spheres (HS) and hollow double-shell particles at different temperatures and at full scattering contrast (in D2O) and at the matchpoint (MP) of the silica core