Experimental report

16/05/2022

Proposal: 9-11-2007 **Council:** 4/2020

Title: Hollow microgel collapsed with hydrostatic pressure, a SANS study

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: C6H11NO

Instrument	Requested days	Allocated days	From	To
D11	3	2	15/06/2021	17/06/2021

Abstract:

Hydrostatic pressure can deswell regular microgels similarly to temperature. Here we propose to explore the effects of changes of hydrostatic pressure on the structure of hollow- and ultra-low crosslinked microgels. Hollow microgels possess a solvent filled cavity in their centre, which we can produce as both spherical or elliptical particles. Furthermore, we can implement a high number of charges in their polymeric networks. The ultra-low crosslinked microgels are microgels with the lowest number of crosslinks in their polymeric networks. To date, studies in the literature were limited to microgels with a more crosslinked core surrounded by a less dense polymeric shell. Here, we want to use D11 and the liquid pressure cell to investigate how changes in the hydrostatic pressure affect the structure of these hollow and ultra-low crosslinked microgels. In addition to static increase of the hydrostatic pressure we plan to apply pressure-jumps (0 to 300MPa) and probe the microgels architecture.

The goal of the experiment was to use the SANS to study the response of extremely soft poly(*N*-isopropyl acrylamide) (pNIPAM) microgels with different architectures to increase of hydrostatic pressure. To achieve it, a high-pressure SANS cell designed at ILL was used.

Two types of microgels were studied: ultralow-crosslinked (ULC) microgels, synthesized without the addition of crosslinker and therefore the softest possible using precipitation polymerization, and hollow microgels, which contain a solvent-filled cavity in the centre. The strong compressibility and deformability of such microgels makes them perfect systems to study the effect of hydrostatic pressure, because even small changes in solvent quality can result in significant changes of their form factor.

The volume fraction of the microgels suspended in D_2O was kept low at $\zeta = 0.08$, so that the scattering intensity $I(q)$ is directly proportional to the form factor of the microgels. The measurements were performed at three temperatures: 20, 30, and 35°C, corresponding to temperatures well below, close to, and above the volume phase transition temperature of the microgels in D_2O (VPTT=34°C, ambient pressure).

Figure 1 shows the $I(q)$ at T=20°C for the ULC (a) and hollow microgels (b) as a function of hydrostatic pressure. Black solid lines correspond to the fits using the polydisperse fuzzy sphere (a) or fuzzy core-shell model (b), which also provide the distributions of relative polymer density inside the microgels (insets). The data clearly indicate a gradual deswelling of both types of microgels with pressure.

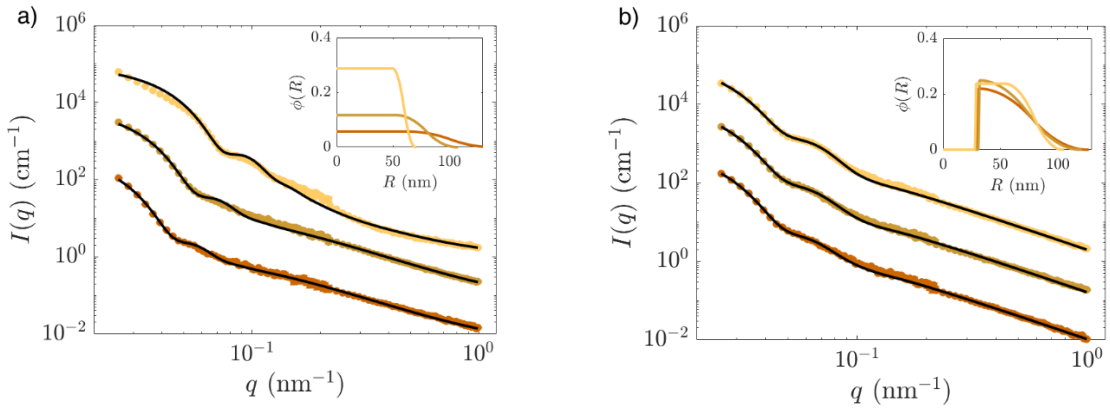

Figure 1. SANS intensities $I(q)$ at $T = 20$ °C versus scattering vector q of (a) ULC microgels at $P = 0.1$ MPa, 150 MPa, and 200 MPa (from bottom to top), and (b) hollow microgels at $P = 0.1$ MPa, 100 MPa, and 150 MPa (from bottom to top). Solid lines correspond to fits according to the fuzzy-sphere or fuzzy core-shell model. The insets show radial distributions of relative polymer volume fraction obtained by fitting of the corresponding SANS curves.

Figure 2 shows the $I(q)$ at T=35°C for the two types of microgels. The solid lines again correspond to the fits with the respective form factor models. At this temperature, a non-monotonic trend can be seen: the microgels that are collapsed at ambient pressure first reswell upon a mild increase in pressure, but then gradually deswell again. This results from an interplay between the decreasing solvent quality and a shift of the VPTT of microgels to higher temperatures.

Presently, a manuscript based on these data is under preparation. We plan to combine the scattering results with computer simulations of microgels to explain the change of the form factors of these extremely soft and responsive particles.

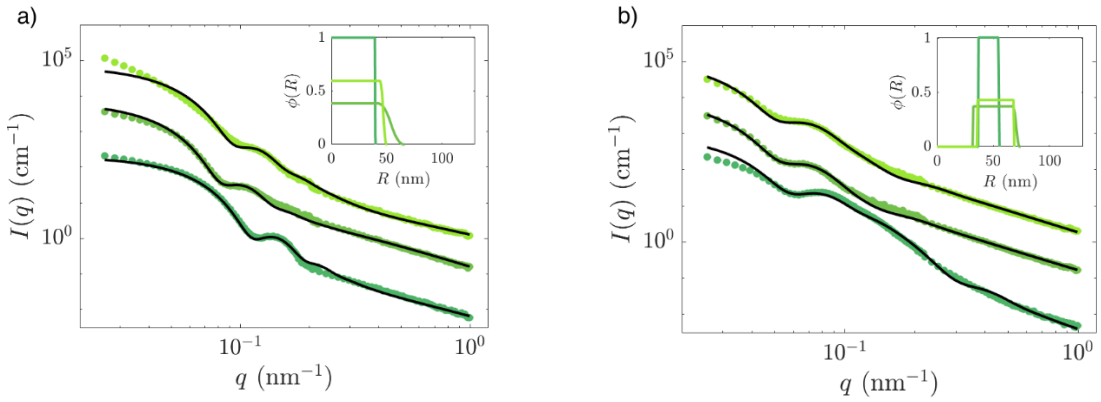

Figure 2. SANS intensities $I(q)$ at $T = 35$ °C versus scattering vector q of (a) ULC microgels at $P = 0.1$ MPa, 50 MPa, and 250 MPa (from bottom to top), and (b) hollow microgels at $P = 0.1$ MPa, 50 MPa, and 150 MPa (from bottom to top). Solid lines correspond to fits according to the fuzzy-sphere or fuzzy core-shell model. The insets show radial distributions of relative polymer volume fraction obtained by fitting of the corresponding SANS curves.