Experimental report

12/01/2021

Proposal: 9-10-1580 **Council:** 10/2018

Title: Form factor of ultra-low crosslinked microgels in overcrowded environments

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Water suspensions of pNIPAM (C6H11NO)n/(C6D3H8NO)n

Instrument	Requested days	Allocated days	From	To
D11	3	1	07/02/2020	08/02/2020

Abstract:

We propose to use zero-average contrast and tracer-SANS to directly probe the form factors of ultra-low crosslinked (ULC) pNIPAM base microgels in overcrowded environments. For the first time we have been able to synthesize deuterated ULC microgels and we want to use them in ZAC and as matrix where embed few protonated ULC in the tracer experiments. The measurement will be performed at 20C, where the microgels are in the swollen, soft state. The data will. be fitted using the model for fuzzy spheres. This experiment will complete our understanding of the response of super-soft object in overcrowded environments and on the interplay between polymeric and colloidal nature of the ULC microgels.

Our goal was to use SANS with contrast variation to directly study the response of pNIPAM ultra-low crosslinked microgel to the increase of the particle concentration in a matrix of normal D3-pNIPAM-based microgels, $(C_6D_3H_8NO)_n$. The characteristic of these microgels is that they are synthesized without the addition of crosslinker and are, therefore, the softest that can be obtained by means of precipitation polymerization.

In contrast to other studies, here it was necessary to use a deuterated monomer with only 3 atoms of deuterium and not 7. The reason for this is that in the D7-pNIPAM the isopropyl group of NIPAM is deuterated and consequently the cross-linking is strongly restrained. As a consequence, the formation of microgels using D7-pNIPAM is precluded. Since we used a different monomer ($[C_6D_3H_8NO]_n$) with respect to the literature ($[C_6D7H_4NO]_n$), the match point of the deuterated ULC microgels has been determined experimentally. Figure 1(a) shows the scattered intensities of highly diluted solutions of D3-ULC microgels as a function of the scattering vector, q, suspended in various D_2O/H_2O mixtures, namely 0, 20, 50, 60, 80, and 100 wt% D_2O. For every selected q, the variation of the values of I(q) depends on the variation of $\Delta\rho$. For all the chosen q, a linear fit is performed. All the fits cross the zero-axes (dashed black line) in the very same point: 55.7±0.3 wt% D_2O that is the scattering length density of the deuterated ULC microgels. The samples for SANS with contrast variation have been then prepared in the D11 lab in this solvent and measured.

The volume fraction of the hydrogenated ULC microgels, ζ_H, is kept constant and equals 0.080 ± 0.003 in all the samples measured with SANS with contrast variation. The generalized volume fraction of the deuterated microgels composing the matrix where the hydrogenated ULC microgels are embedded, ζ_D, covers a range of concentrations between 0 and 2.14 ± 0.03. Consequently, the total generalized volume fraction, $\zeta = \zeta_H + \zeta_D$, covers a concentration range between 0.08 and 2.22 ± 0.03.

The data in Figure 1(c) are proportional to the form factors of the hydrogenated ULC microgels measured by SANS. The I(q)s in Figure 1 are shifted in the y-direction for clarity. The data are fitted using the model for a fuzzy-sphere (black solid lines), which has been shown to reproduce the form factors of ULC microgels. The characteristic lengths of the microgels (total radius, core radius, and length of the fuzzy shell) obtained from the fits of the data are used to plot the radial distribution of the relative polymer volume fraction within the microgel shown in Figure 1(d).

The results of this experiment, together with SAXS data collected at the instrument cSAXS at SLS, PSI, Villigen are the central body of the article " Phase behavior of ultrasoft spheres show stable bcc lattices" published on Physical Review E 102, 052602 (2020) DOI: 10.1103/PhysRevE.102.052602 by Scotti et al.

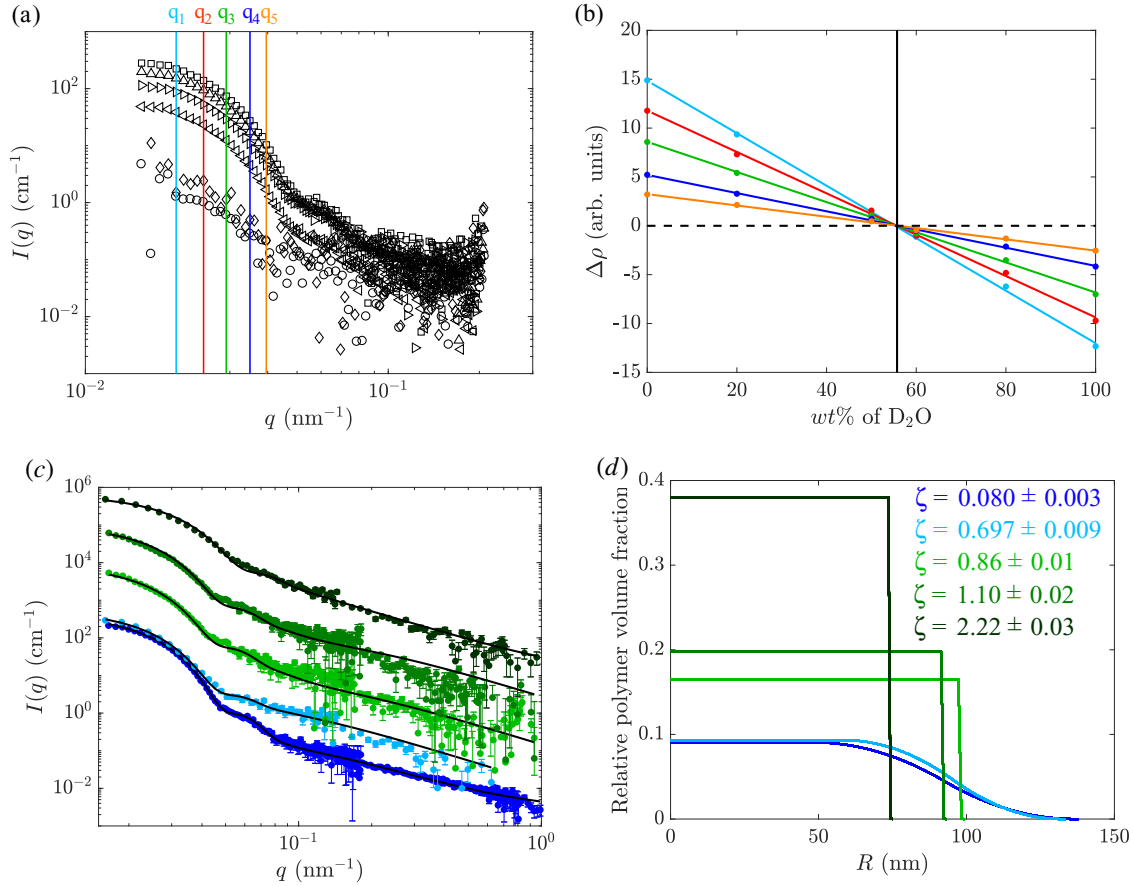

Figure 1 (a) SANS intensity, I(q), as a function of the scattering vector, q, of the deuterated-ULC microgels probed at 20.0±0.1 C suspended in D_2O/H_2O mixtures with: 100 wt% D_2O (upside triangles); 80 wt D_2O (left-side triangles); 60 wt% D_2O (circles); 50 wt% D_2O (diamonds); 20 wt% D_2O (right-side triangles); 0 wt% D_2O (squares). The colored vertical solid lines represent fixed qused to extract the contrast in panel (b). (b) Scattering length density contrast, $\Delta\rho$, as a function of the wt% of D_2O in the solvent. The different colors corresponds to the different qchosen in panel (a) to extract the contrast. The solid lines represent linear fits of the data. The dashed black horizontal line shows the zero contrast line. The black solid vertical line represents the match point of the deuterated ULC microgels: 55.7±0.3 wt% D_2O. (c) SANS intensity, I(q), versus scattering vector, q, of the ultra-low crosslinked hydrogenated microgels. Data are shifted in the y-direction for clarity. (d) Radial distribution of the relative polymer volume fraction as obtained by fits of the curves in (c) using the model for a fuzzy sphere. In panel (c), the concentrations from bottom to top are: ζ = 0.080 ± 0.003; 0.697±0.009; 0.86±0.01; 1.10±0.02; 2.22±0.03. All the measurements were performed at T = 20.0±0.01 C. The colors and concentrations in panel (b) correspond to those in panel (c).