Experimental report

12/01/2018

Proposal: 9-11-1770 **Council:** 4/2016

Title: Dynamics of PNIPAM microgels at high concentrations and low temperatures

Research area: Soft condensed matter

This proposal is a continuation of 9-11-1736

Main proposer: Emanuela ZACCARELLI

Experimental team: Paul MARCONNET
Hugues LASCOMBES DE LAROUSSILHE
Alice CHIODETTI
Robin PIONNIER
Maxime DEBERTOLIS
Joanna BERTEAUD
Antoine ROUX
ruben ROSSI-ZILOCCHI
Artashes ASOYAN
Marco ZANATTA
Monica BERTOLDO
Andrea ORECCHINI
Elena BURATTI

Local contacts: Jacques OLLIVIER

Samples: n-[C6H11NO + 0.051 C7H10N2O2] in D2O

Instrument	Requested days	Allocated days	From	To
IN13	11	0		
IN5	5	4	23/01/2017	27/01/2017

Abstract:

Microgels are colloidal-scale particles individually made by cross-linked polymer networks, which can swell and deswell in response to external stimuli. The widely studied PNIPAM microgels are nowadays used as model systems for the glass transition. Their dual colloid/polymer nature makes them very interesting because they should undergo two distinct glass transitions, at the level of colloids and of individual chains respectively. While the colloidal glass transition is extensively studied in the literature, the second one has been largely ignored. In a recent proposal, we have started such investigation finding promising results: not only we were able to clearly resolve the occurrence of the volume phase transition in all non-dry samples, but also we detected an interesting phenomenon at low temperatures. Namely, a sharp growth of the elastic incoherent scattering intensity was observed around 250K, suggesting the occurrence of a dynamic transition analogous to that observed for proteins. Here we propose to investigate further such transition at low temperatures and high concentrations and to compare the results with investigations with the chemically analogous macrogels.

We measured the temperature evolution of the $I(Q,\omega)$ on five PNIPAM microgels at increasing particle weight concentration. Microgels were prepared using hydrogenated PNIPAM particles and deuterated water, in order to highlight the dynamic contribution of the gelator network with respect to water. Measurements were performed around the volume phase transition (VPT) temperature T_{VPT} = 305 K. Samples and relative investigated temperature ranges are reported in Table 1. In addition, a pure D_2O was also measured.

	T range	*T* number
PNIPAM microgel 10%	280 K – 320 K	9
PNIPAM microgel 30%	280 K – 320 K	9
PNIPAM microgel 40%	280 K – 320 K	9
PNIPAM microgel 50%	280 K – 320 K	9
PNIPAM microgel 95% (dry)	280 K – 320 K	3
D_2O	280 K – 320 K	3

Table 1 – Samples measured during Exp. 09-11-1770.

The samples were loaded in Al slab cells as prepared and sealed with a In o-ring. The thickness of each cell was fixed to get a transmission of about 90%. Measurements were performed using the standard cryostat. The instrument was set to obtain an incident wavelength of 4.8 Å with a resolution of 96 μeV (FWHM, measured on a V sample).

Spectra were acquired after a thermalization of about 30' for each temperature. The integration time was between 1 hour to 1.5 hour, thus providing data with an excellent signal-to-noise ratio. A vanadium standard, the empty cell, and the signal from the empty cryostat were also measured. Fig. 1 and Fig. 2 show the experimental spectra measured on the PNIPAM 10% and 30% at Q = 1.0 A^{-1}. Increasing the temperature up to 304 K the quasi-elastic broaden and, above that T value, spectra become smaller. This is a signature of the occurrence of the VPT.

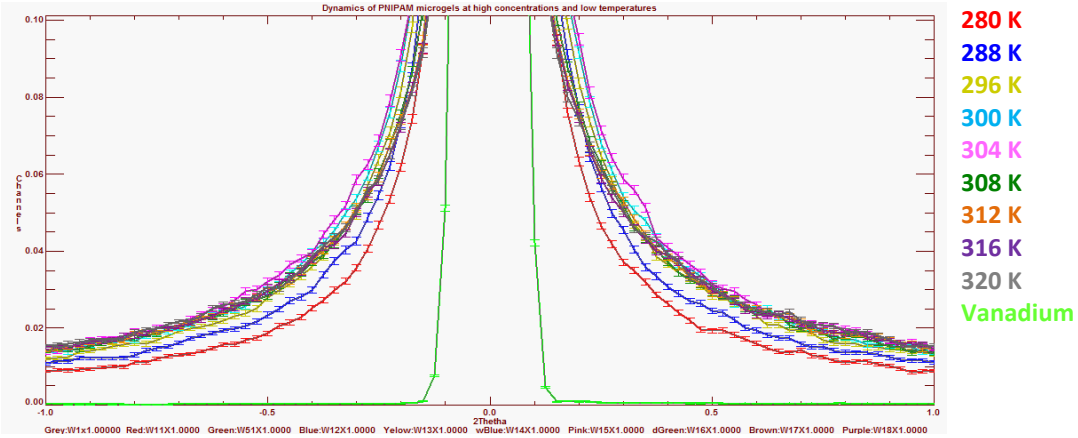

Figure 1. Temperature evolution of the experimental $I(Q,\omega)$ in a PNIPAM 10% microgel crossing the volume phase transition. Spectra are for Q = 1.0 A^{-1} and they are normalized to the elastic peak.

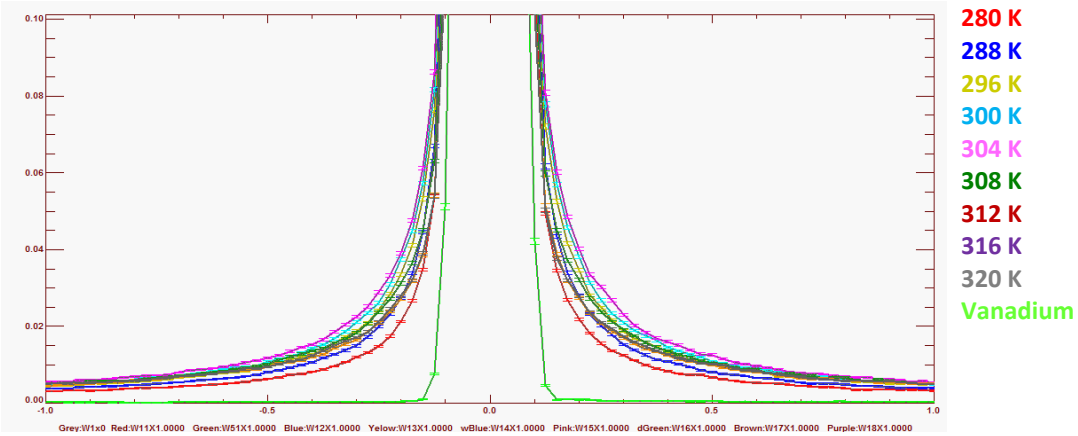

Figure 1. Temperature evolution of the experimental $I(Q,\omega)$ in a PNIPAM 30% microgel crossing the volume phase transition. Spectra are for Q = 1.0 A^{-1} and they are normalized to the elastic peak.

Previous experiment on the backscattering spectrometer IN13 (report 09-11-1736) shows that the high-Q region of the measured incoherent elastic intensities deviates from the Gaussian approximation. This might be due to the onset of anharmonic or relaxational motions. A careful analysis of results from present experiment can provide detailed insights on the specific nature of the microscopic motions involved in the dynamics of PNIPAM microgels.

The present experiment was focused on the VPT region. With respect to the submitted proposal, no low-temperature data were acquired due to time constraints. The investigation of PNIPAM microgels in this T-region may deserve a further experiment on IN5.