Experimental report

01/04/2016

Proposal: **9-11-1736** **Council:** 4/2015

Title: Fast and slow dynamics in PNIPAM microgels.

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: n-[$C_6H_{11}NO$ + 0.051 $C_7H_{10}N_2O_2$] in D_2O

Instrument	Requested days	Allocated days	From	To
IN13	6	7	09/11/2015	16/11/2015
IN5	4	0		

Abstract:

Microgels are colloidal-scale particles individually made by cross-linked polymer networks, which can swell and deswell on short time-scales as compared to "macrogels".

The widely studied PNIPAM microgels are nowadays used as a model system for the glass transition. Their dual colloid/polymer nature makes PNIPAM microgels very interesting because one can actually think of two well-separated glass transitions: one at the level of the colloidal particles and one at the level of the individual polymer chains.

A recent study has put forward the hypothesis that in glass-formers a clear correlation exists between the fast atomic mean-squared displacements within the cage of close neighbors and the slow structural relaxation. However an experimental confirmation of this correlation in a colloidal system is still missing.

Here we propose to investigate PNIPAM microgels across both the colloidal and the polymeric glass transition. Such an investigation will provide a test of the hypothesized dynamical correlation between fast and slow dynamics. In addition, it will pioneer the new concept of a double-glass-transition system.

We measured the temperature evolution of $I(Q,\omega = 0)$, the elastic incoherent neutron scattering (EINS), on four PNIPAM microgels at increasing particle weight concentration. All the 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. The explored temperature ranges are reported in Table 1. An additional sample of dry macrogel was not measured due to lack of time.

	T range
PNIPAM microgel 10%	283 K – 320 K
PNIPAM microgel 30%	283 K – 318 K
PNIPAM microgel 50%	153 K – 400 K
PNIPAM microgel 95% (dry)	153 K – 430 K

Table 1 – Samples measured during Exp. 09-11-1736.

The samples were loaded in Al slab cells as prepared and sealed with a Pb o-ring. The thickness of each sample was fixed to get a transmission of about 90%.

Fig. 1 shows the EINS intensity as a function of temperature for the different measured samples. In order to get a good signal to noise ratio, **an integration time of about 3 hours for each temperature** was needed. The elastic intensity of 50% and 95% were normalized by linearly extrapolating their low-*T* behaviour and imposing that $I(Q,\omega = 0) = 1$ for $T = 0$ K. This is not applicable for PNIPAM 10% and 30%, which were thus normalized to the elastic intensity of the 50%, using the common *T*-interval between 285 K and 300 K.

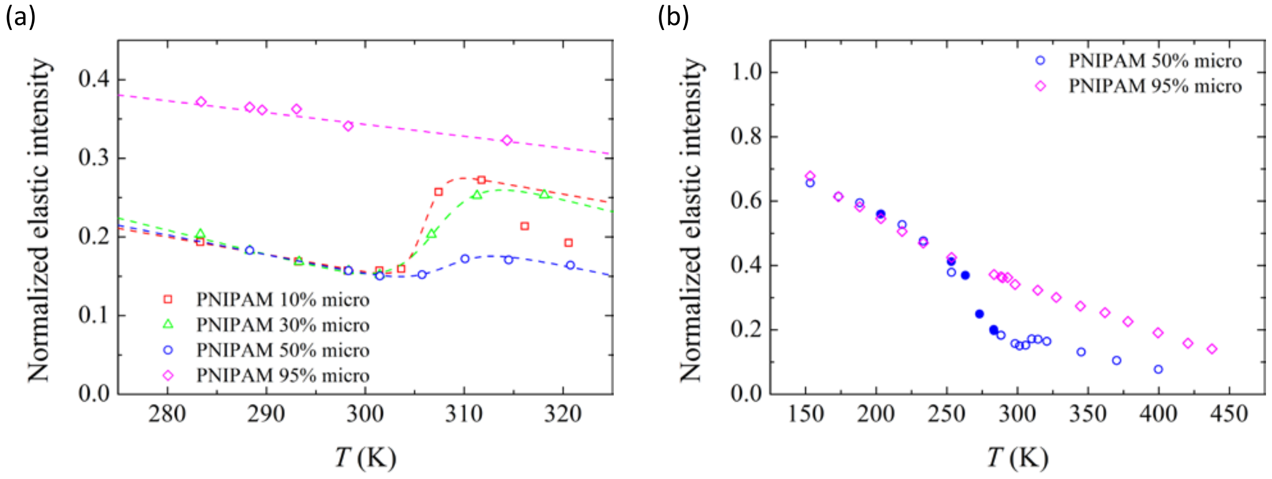

Figure 1. (a) EINS intensity close to the volume-phase transition for all the samples. Dashed lines are guides for the eyes. (b) Comparison between PNIPAM 50% (blue circles and dots) and PNIPAM 95% (pink diamonds). Blue dots represent the measurements on PNIPAM 50% upon re-heating.

Fig.1(a) shows the EINS intensity behaviour close to room temperature. For the hydrated samples, the **signature of the volume-phase transition (VPT) is clearly visible** at about 305 K. By increasing the particle weight concentration, the VPT slightly shifts to higher temperatures and becomes softer, eventually vanishing in the dry sample.

Fig.1 (b) shows the comparison between PNIPAM 95% and PNIPAM 50%, in the whole *T*-range explored. The **50% sample shows a sharp increase of the elastic intensity at about 250 K**, which suggests a transition into a solid phase. On the other hand, an inspection of the *Q*-dependence of the elastic intensity shows no evidence of water crystallisation. The absence of D_2O crystallization is also confirmed by differential scanning calorimetry (DCS) measurements performed in our home laboratory on the same sample. This increase of EINS intensity is almost fully reversible upon re-heating of the samples (blue dots). Such findings are certainly promising and deserve further investigations, in particular to clarify whether water crystallisation can actually take place and at which concentration.

The proposal aimed at exploring the connection of the short-time atomic mean-squared displacements (MSD), within the cage of close neighbours, with the long-time structural relaxation [1]. For a first and quick analysis, the MSD can be extracted from the EISN intensity by using the simple Gaussian approximation to fit the Q-dependence of the elastic intensity. A typical result is reported in Fig. 2 and shows that such an approximation is not adequate to fit our data above 2 Å^{-1}, where the measured scattering intensity displays a systematic overshoot with respect to the fitting curve. This might be due either to the presence of anharmonic relaxation processes, which would obviously break the Gaussian approximation, or to a residual coherent contribution from the D_2O static structure factor. To gain insight on the specific nature of the microscopic motions involved in the observed overshoot, **all the samples should be also probed by quasielastic neutron scattering (QENS)**.

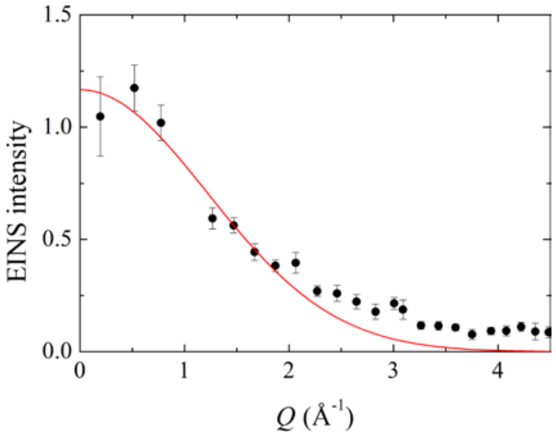

Figure 2. EINS intensity at T = 311 K for the PNIPAM 30% microgel. Experimental data (black dots) were fitted with a Gaussian function (red line).

References

[1] L. Larini, A. Ottochian, C. De Michele, and D. Leporini, Nature Physics **4**, 42 (2008).