Experimental report

16/09/2019

Proposal:	**9-11-1866**	**Council:**	4/2018

Title: Low-temperature dynamical transition in polymeric aqueous environments

Research area: Physics

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	6	19/09/2018	25/09/2018
IN5	4	0		

Abstract:

The occurrence of a dynamical transition at low-temperature has been reported in a large number of different proteins and even in hydrated amino acids mixture. However, we recently observed a "protein-like" dynamical transition also in a non-biological aqueous environment made by poly-N-isopropylacrylamide (PNIPAM) microgels. By means of elastic incoherent neutron scattering and quasielastic neutron scattering we aim to exploit PNIPAM-based systems to investigate the nature of such a transition. In particular, we want to ascertain whether this phenomenon is intimately related to the complex internal architecture of microgels or if it can be generalized to other polymeric architectures, such as hydrogels, i.e. macroscopic gels, and/or suspensions of individual chains. These results can extend the concept of a low temperature dynamical transition and shed new light to this widely debated phenomenon.

We measured the temperature evolution of the elastic incoherent neutron scattering (EINS) intensity *I*(*Q*,0) on two set of PNIPAM based samples:

- hydrogenated PNIPAM linear chains suspensions in D_2O at different PNIPAM weight concentration, to study the polymer dynamics.
- deuterated PNIPAM microgels suspensions in H_2O at different PNIPAM weight concentration, to highlight the dynamic contribution of the water with respect to the gelator network.

Samples were measured upon cooling and heating. Sample concentrations and explored temperature ranges are reported in Table 1.

	T range
PNIPAM linear chains in D_2O 50%	283 K – 320 K
PNIPAM linear chains in D_2O 60%	283 K – 318 K
PNIPAM linear chains in D_2O 95%	153 K – 400 K
D-PNIPAM microgels in H_2O 45%	283 K – 320 K
D-PNIPAM microgels in H_2O 50%	283 K – 318 K
D-PNIPAM microgels in H_2O 60%	153 K – 400 K

Table 1. Samples measured during Exp. 09-11-1866.

Samples were loaded in Al slab cells and sealed with a In o-ring. The thickness of each sample was fixed to get a transmission of about 90%. To correctly analyse data, a vanadium standard and the empty cell were also measured.

Fig. 1 shows the temperature evolution integrated 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 integrated EINS intensities were normalized to 1 for T = 0 K, by linearly extrapolating their low-*T* behaviour.

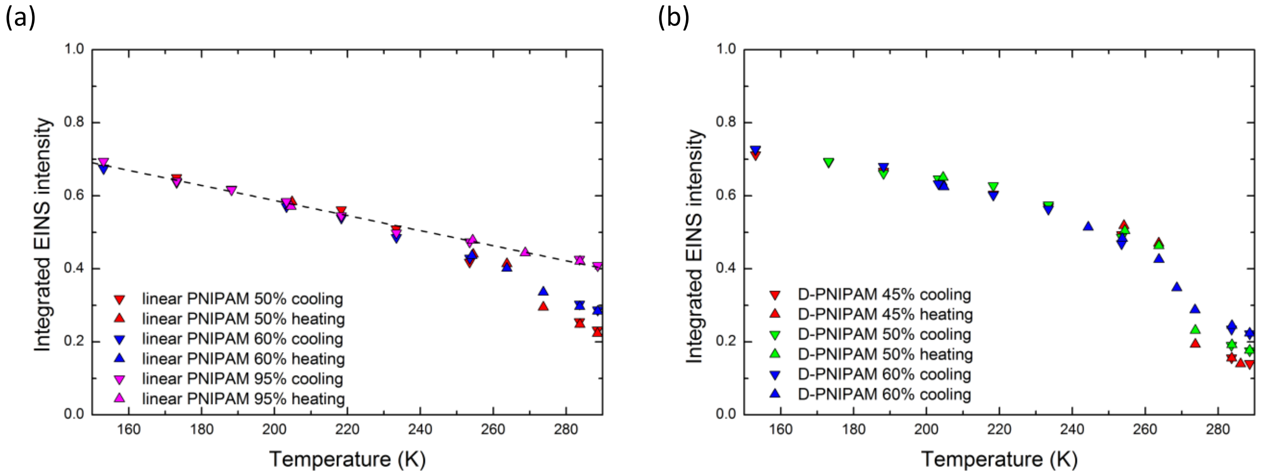

Figure 1. Integrated EINS intensity for (a) PNIPAM linear chains samples and (b) deuterated PNIPAM microgels. The black dashed line in Fig. 1(a) represents the behaviour of the dry (95%) sample. Symbols are reported in the legend.

Integrated EINS data clearly show the same protein-like dynamical transition previously observed in hydrogenated PNIPAM samples, see Ref. [1]. Measurements on PNIPAM linear chains show the fundamental role of the complex macromolecular architecture, irrespectively to specific structural arrangements [1]. Measurements on deuterated samples and their comparison with hydrogenated ones confirm the driving role of water [2].

Following our analysis of hydrogenated PNIPAM microgels, see [1], present data will be fitted using the double-well model to determine the mean square displacement (MSD) and then the transition temperature T_c.

References

[1] M. Zanatta et al., Sci. Adv. **4**, eaat5895 (2018).
[2] L. Tavagnacco et al., J. Phys. Chem. Lett. **10**, 870-876 (2019).