ESRF	**Experiment title:** Structural and Dynamical transitions in dense-packed colloidal nanogels	**Experiment number**: SC-4866
Beamline: ID02	**Date of experiment**: from: 02.11.2018 to: 05.11.2018	**Date of report**: 06/12/2021
Shifts: 9	**Local contact(s)**: Thomas Zinn	*Received at ESRF:*

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Report:

We performed an X-ray Photon Correlation Spectroscopy (XPCS) experiment in ultra-small angle X-ray scattering geometry to investigate the structure and dynamics of highly concentrated core-shell silica-PNIPAm (poly(N-isopropylacrylamide)) particles. Stimuli-responsive PNIPAm microgels undergo a sharp volume phase transition at a lower critical solution temperature (LCST) in water around 32°C which results in a rapid collapse of the particle radius by increasing the temperature. Varying the temperature during the experiment we were able to study the structure and dynamics of PNIPAm in the microgel state crossing this critical temperature.

The proposed experiment is based on previous experiments at ID10 and other synchrotron radiation sources (PETRA III and APS) [1-3]. Therein, we could measure the full phase diagram of aqueous silica-PNIPAM dispersions via the sample structure and dynamics. However, using a standard SAXS geometry in such experiments, we were missing a significant part of the length scales that need to be studied. With a core radius of typically around 60 nm and PNIPAm shell sizes between 10 and 200 nm an expanded low q-regime is required. Thus, to fully understand the static changes in the underlying system and the dynamics at the relevant scattering angles the utilization of the USAXS geometry is absolutely crucial.

Therefore, the experiment was performed at beamline ID02. We used a sample-detector distance of 31 m and a beam size of 35 µm x 40 µm. To cover a wide range of relaxation times, we used the Eiger500k detector. As sample we used a silica-PNIPAm system with a silica core size of 50 nm and a shell size of about 200 nm at room temperature and 50 nm above the LCST. As the parcel with the original silica-PNIPAm sample was lost during transportation to ESRF, we used our backup sample. Instead of TMAO as co-solvent, we used different ethanol concentrations as a co-solvent to tune the LCST of the particles. Like TMAO [3], ethanol stabilizes the globular shape, so that the LCST is shifted the lower temperature. XPCS runs were performed for several particles concentrations between 0.1 wt.% and 6 wt.%. Each individual sample was measured at up 15 temperature points between 20 °C and 45 °C, both during heating and cooling.

Exemplary results are shown in Fig. 1 for the particles dispersed in ethanol (panels A and B) and water (panels C and D). The I(q) shown in panels A and C demonstrate that the particles do not undergo structural changes in

ethanol, but show the typical fingerprint of gelation in water [4]. In addition, the dynamics are slower in ethanol than in water at 30 °C, see panels B and D. Further data analysis and interpretation is ongoing.

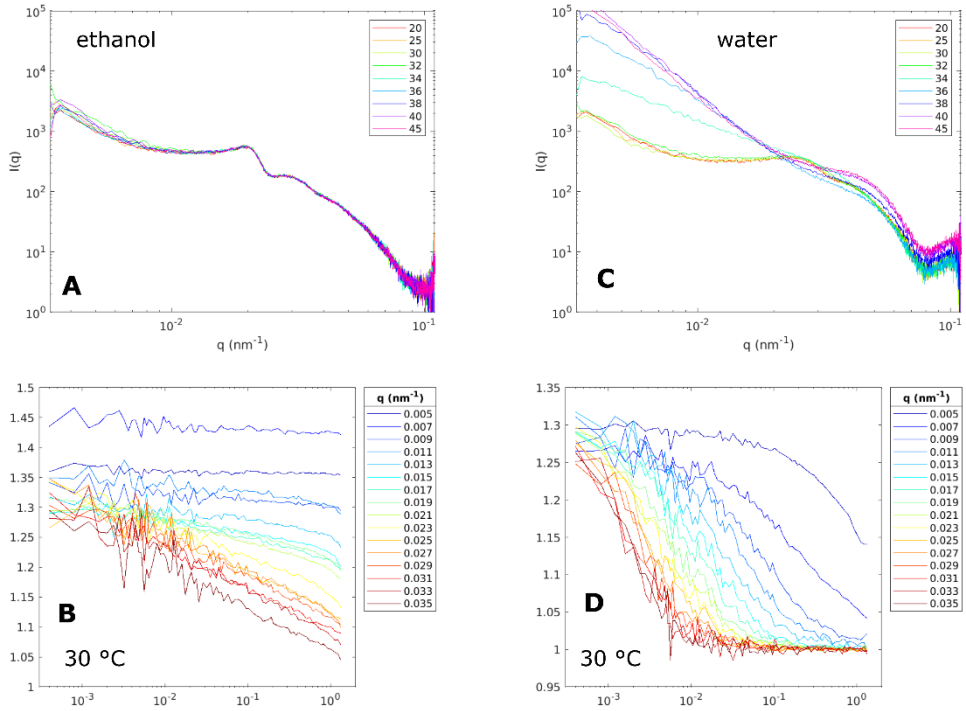

Figure 1: I(q) (A) for the silica-PNIPAm particles in ethanol at different temperatures and g_2 functions for the sample at 30°C (B). Panels C and D show the sample particles dispersed in water.

References

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[2] L. Frenzel, F. Lehmkühler, M. Koof, I. Lokteva, and G. Grübel. Soft Matter 16, 466 (2020).
[3] L. Frenzel, I. Lokteva, M. Koof, S. Narayanan, G. Grübel, and F. Lehmkühler. ChemPhysChem 21, 1318 (2020).
[4] L. Frenzel, M. Dartsch, G. Martí Balaguer, F. Westermeier, G. Grübel, and F. Lehmkühler. Phys. Rev. E 104, L012602 (2021).