ESRF	**Experiment title:** Time-resolved thermoresponse kinetics of spherical brushes on biomedical nanoparticles	**Experiment number**: SC 4067
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Report:

Summary

SAXS was used to investigate the temperature dependant collapse of a PEG shell grafted to spherical iron oxide nanoparticles (FeOx NP) in a cloud point buffer medium with a time resolution of 10ms. We were able to track changes in the conformation of the shell on minute time scales in response to temperature changes. Interestingly, the shell did not show the expected reduction of solvation on ms time scale for fast temperature (T) jumps.

Samples and Setup

The main aim of this experiment was to probe *in-situ* the kinetics and timescale of the loss of hydration of a PEG shell grafted to iron oxide nanoparticles with SAXS. The loss of hydration had already been observed in a laboratory SAXS experiment in cloud point (CP) buffer, but without resolving the time-dependence of the transition. Theoretical considerations and light scattering experimens on PNIPAM coils suggested a response time below 50 ms for PNIPAM brushes, a system thought comparable to our system.

For this purpose a stopped-flow device was set up to achieve a sub-ms temperature jump between 30 and 80°C (across the lower critical solution temperature) to follow the PEG shell collapse. In order to discriminate between short-term and long-term effects also a slow-heating setup was deviced where a temperature change was carried out in 5 minutes.

All experiments were carried out on the pinhole SAXS instrument. Energy was fixed for all the experiment at 12.46 keV using synchrotron radiation from one undulator. Scattering images were recorded using a Pilatus 300K detector set at a distance of 1.85m. Thanks to the high flux available at the beamline a total exposure and readout cycle within 10 ms could be achieved. Separate runs in USAXS settings with a sample-detector distance of 10m were carried out for a specific system to check for aggregation.

Additional experiments with water injection showed that the temperature equilibration is taking place faster than 10ms, hence the heating kinetics is sufficient for the desired time resolution. We stress the support from the beamline staff to implement this non-trivial setup.
The sample set comprised core shell nanoparticles consisting of iron oxide NPs grafted with linear PEG brush shell. Owing to the extremely high grafting density of the PEG (close to the theoretical melt density), a direct monitoring of the shell density profile is possible with SAXS. In order to trigger a temperature induced collapse a cloud point buffer system with varying ionic strength was used as solvent system.

Principal outcome

The experiments with slow heating and time resolution indeed showed a shrinkage of the shell between 50 and 80°C, as expected for loss of solvation. Additionally a reversible structure peak due to shell-shell interaction turns up at this temperature. A subsequent cooling cycle indicated the reversibility of the shell shrinkage as the shell expanded to nearly its original size. The analysis of the data was carried out on the basis of real space polymer density model (Grünewald et al. Chem Mater 2015; 27(13) 4763-4771).

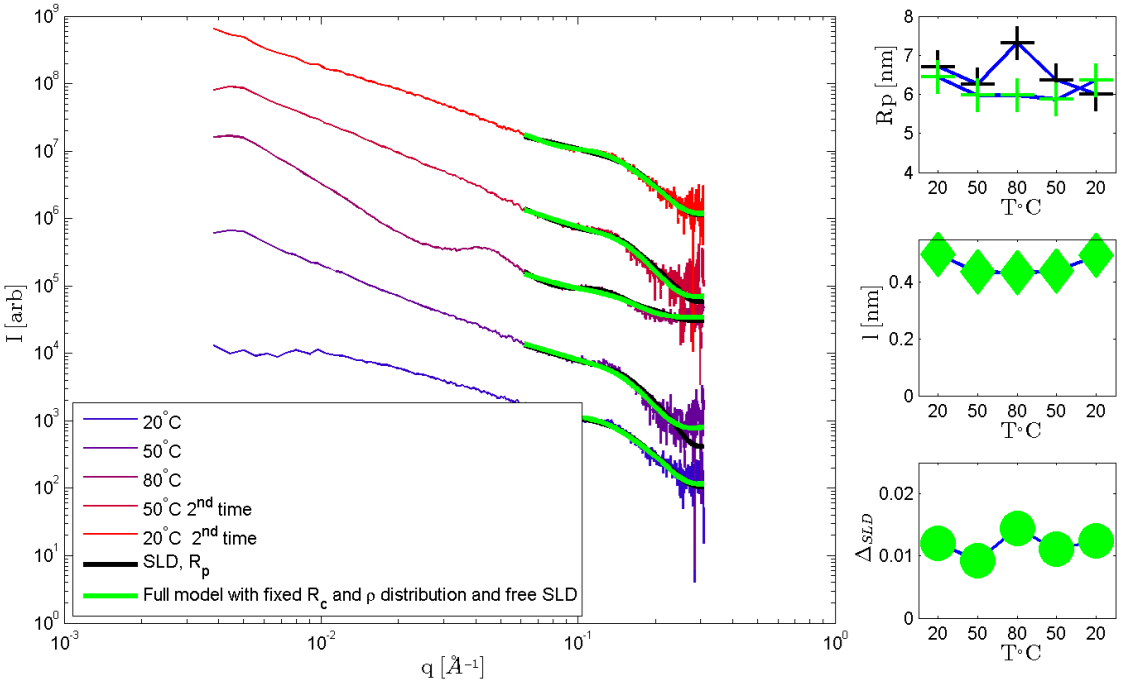

Figure 1 Fit of slow heating data showing a slight contraction of the shell (R_P)upon heating at 80° and a subsequent recovery; a behaviour as well reflected in the change of the Kuhn length l. The condensation of salts from the CP buffer can be seen in the change of the relative scattering length density contrast (ΔSLD) of the shell with respect to solvent at 80°C.

The analysis of the stopped flow data was more challenging due to the short acquisition times necessary to resolve the temperature jump behaviour. As the same injection scheme was applied repeatedly averaging of similar time frames can improve the data quality. The first analysis with our model did not show the collapse observed for the slow temperature scans, which is in contradiction to our initial hypothesis. Further investigations and modelling to interpret the unexpectedly slow transition kinetics are under way; possible causes are the unusually high polymer densities on the core-shell particles used in our study or the effect of counterions in CP buffer leading to a slow down in polymer and/or water mobility within the brush.

Conclusions and further proceedings

The analysis of the data is still ongoing and especially the data from the stopped flow injection show interesting but unexpected results (no shell collapse on short time scales). It is hence planned to extend the data evaluation to different models, carefully check the results and further discuss our findings with the beamline scientists before publication in a scientific journal.