EUROPEAN SYNCHROTRON RADIATION FACILITY
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	Experiment title: Revealing in-situ defect formation and annealing in soft colloidal crystals	**Experiment number**: 26-02-923
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Report:

The objective of the present study was to investigate defect behavior in soft colloidal crystals by inducing the formation and annealing of defects with temperature changes in a system of thermorepsonsive colloids. Four different colloidal particles were prepared for the experiment. One batch of non-responsive colloids consisting of fluorinated polymer and three thermoresponsive colloids possessing a poly-N-isopropyl acrylamide (PNIPAM) shell and a fluorinated polymer or gold core. For all particles samples with a broad range of concentrations were prepared. The samples were investigated with the microradian setup employing an x-ray energy of 13 keV and a sample to detector distance of 7.9 m. We employed a CCD camera from Photonic Science with 4008 by 2671 pixels of 9 μm and high sensitivity purchased by the Utrecht group.

We found that not all samples showed the formation of colloidal crystals with large single crystalline domains as expected from previous studies. Figure 1 shows examples of the SAXS patterns of the four different colloidal systems at high concentrations. We only could observe distinct Bragg peaks in on eof the the core-shell systems with a polymer core Fig (1C) and the system with a gold nanoparticle core (Fig. 1D). We further found that unfortunately the typical distance between the particles in two of the systems were too large to be properly visualized with the provided resolution of the microradian-setup (Fig.1A and 1B) and that the scattering from the core was much lower than for the gold system.

For the core-shell particles with a polymer core and PNIPAM shell, we investigated the response of the crystalline system when heating. The measurements were performed with two different types of heating/cooling stages provided by DUBBLE.

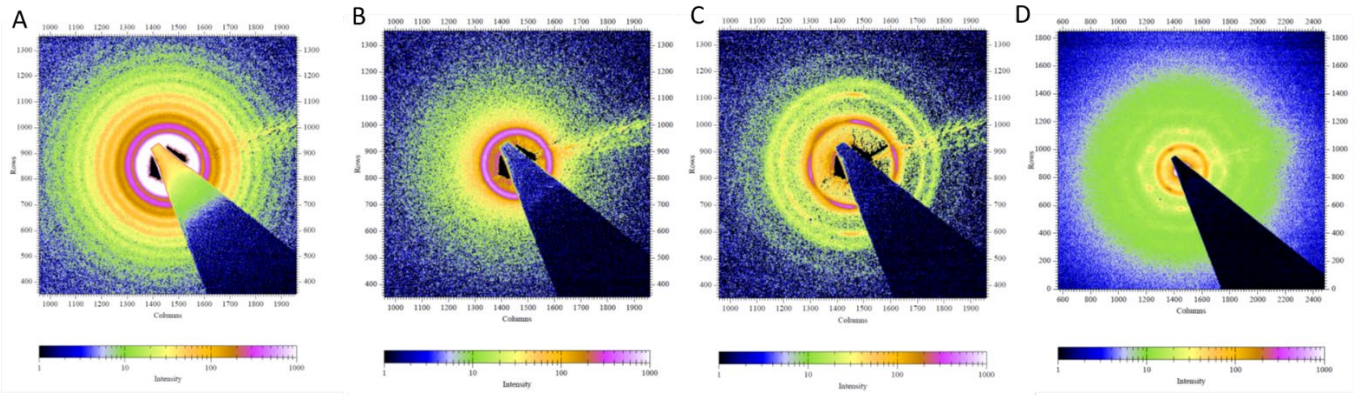

Figure 1. Microradian X-ray diffraction patterns of the four different colloidal particles at high concentrations. A) non-responsive core-shell particles of fluorinated polymer. B,C) Core-shell particles with fluorinated polymer core and PNIPAM shell of different total size. D) Core-shell particles with gold nanoparticle core and PNIPAM shell.

Figure 2 shows the evolution of the scattering patterns for core-shell colloids with PNIPAM shell and polymer core in response to a temperature increase from 20C to 50C. In the patterns the disappearance of the Bragg peaks can be observed indicating the melting of the crystal in response to temperature as expected. Unfortunately, the low scattering contrast required us to use to large sample volumes, reducing the sharpness of the Bragg peaks. In addition, the low sensitivity of the detector led to high background noise.

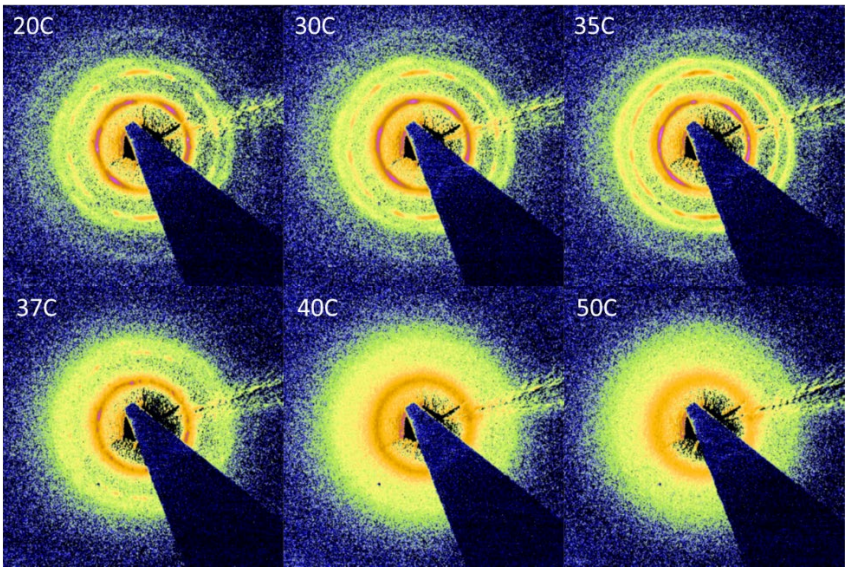

Figure 2. Microradian X-ray diffraction patterns measured for core-shell colloids with PNIPAM shell and polymer core at different temperatures.

We would like to note that we did face some setbacks due to COVID-19 in our experimental preparation as well as the experiment execution at the ESRF. First of all, due to delays and restrictions in lab access we were unfortunately not able to synthesize all the required particles and samples and systems for the proposed experiments. In addition, due to lack of access to microscopy setups we could not test our systems well and we failed to bring our own heating stage with which we were planning to do more detailed temperature studies. Second, we noticed that due to vibrations somewhere upstream from the experiment hutch the beam position fluctuated on the sample leading to smearing of the Bragg peaks over short exposure times. Also we found that the Photonics camera operating software did not function on windows 10 and we were restricted to the use of a windows XP computer with no access to the ESRF network and required us to make back-ups of the data manually. We hope that in the future the ESRF will provide support for the use of Photonics detectors. Overall the experiments showed that the core shell systems can be investigated with microradian SAXS but that the samples as well as the sample stage and detection require more optimization.

We would like to thank the DUBBLE team and especially Daniel Hermida Merino for the excellent support throughout the experiment.