DUBBLE – EXPERIMENT REPORT

We kindly request you to answer the questions (max 2 pages) and return the form to NWO **within 2 months of the completion of the experiment** to **dubble@nwo.nl**

Beam time number: 26-02 864		**File number:**
Beamline: 26B	**Date(s) of experiment:** 11/05/2018 – 14/05/2018	**Date of report:** 14/05/2019
Shifts: 9	**Local contact(s):** Daniel Hermida Merino	

1. **Who took part in the experiments?** (Please indicate names and affiliations)
   Alexei Filippov M.Sc., Ing. Remco Fokkink, Marco Dompè MSc, Ilse van Hees MSc

2. **Were you able to execute the planned experiments?**
   YES

3. **Did you encounter experimental problems?**
   NO

4. **Was the local support adequate?**
   YES

5. **Are the obtained results at this stage in line with the expected results as mentioned on the project proposal?**
   YES

6. **Are you planning follow-up experiments at DUBBLE for this project?**
   NO

7. **Are you planning experiments at other synchrotrons in the near future?**
   NO

8. **Do you expect any scientific output from this experimental session (publication, patent, ..)**
   Yes. Data published in Advanced Materials papers in March 2019. Other publications will follow.

9. **Additional remarks**
   None.

DUBBLE Scientific report

The analysed systems are complex coacervates obtained by mixing either oppositely charged homopolymer solutions or oppositely charged grafted copolymer solutions. The graft copolymer have polyelectrolyte backbones grafted with poly(N-isopropyacrylamide) (PNIPAM) side chains. In the first experiments shown below we compared homopolymer complex coacervates prepared at 0.75 M NaCl to graft copolymer complex coacervates (with 30% mol/mol PNIPAM) prepared at the same salt concentrations.

SAXS experiments were performed on graft copolymers and homopolymers coacervates at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, at the Dutch-Belgian Beamline (BM26B, DUBBLE). A Pilatus 1M detector, a fixed energy of 12 keV and a single detector distance of 2.7 meters were used, covering a total q-range from 0.0665 nm-1 to 5.23 nm-1. The two dimensional images were radially averaged around the centre of the primary beam to obtain the isotropic SAXS profiles. The scattering pattern from Silver Behenate was used for the calibration of the q-range. Eltex was used as reference sample for the intensity calibration in absolute units (cm-1). The data have been normalized to the intensity of the incident beam to correct for primary beam intensity decay. The data were corrected for absorption and background scattering. Two ionization chambers, placed before and after the sample, were utilized for the measurement of the incident and transmitted beams. The background correction was made by subtracting from the total intensity the contribution of density fluctuations evaluated from measuring the blank (0.75 M NaCl solution).The samples were loaded into 2 mm quartz capillaries using Pasteur pipettes and stored at 4 °C before measurements. Before starting the experiment, the samples were placed in a Linkam DSC 600 furnace that allows temperature control. A temperature ramp from 10 °C to 50 °C was performed. SAXS images were recorded every 30 seconds at a fixed temperature, which was kept constant for an interval ranging from 5 to 20 minutes depending on the temperature selected. When a new temperature was selected, the heating rate was fixed to 10 °C/min. SAXS curves were recorded for both homopolymer and graft copolymer complex coacervates at several temperatures. SAXS images recorded at 10 °C, 20 °C and 50 °C are shown.

In **Figure 1** the SAXS profiles for homopolymer complex coacervates are reported.

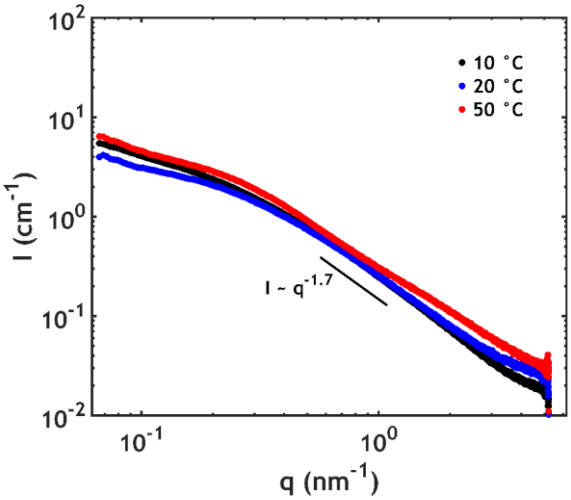

Figure 1 SAXS pattern for homopolymer complex coacervates.

When complex coacervates obtained from homopolymer solutions are analysed, no obvious difference in the scattering profiles can be observed upon an increase in temperature, as expected. At high q (0.3 – 3 nm-1) the curves show a similar slope (I ≈ q-1.7), indicating that the polymer chains attain a self-avoiding random walk conformation, behaving nearly as in a semidilute polyelectrolyte solution. At larger length scales no upturn is detected, indicating the absence of bigger domains.

In **Figure 2** the SAXS profiles for graft copolymer complex coacervates are reported.

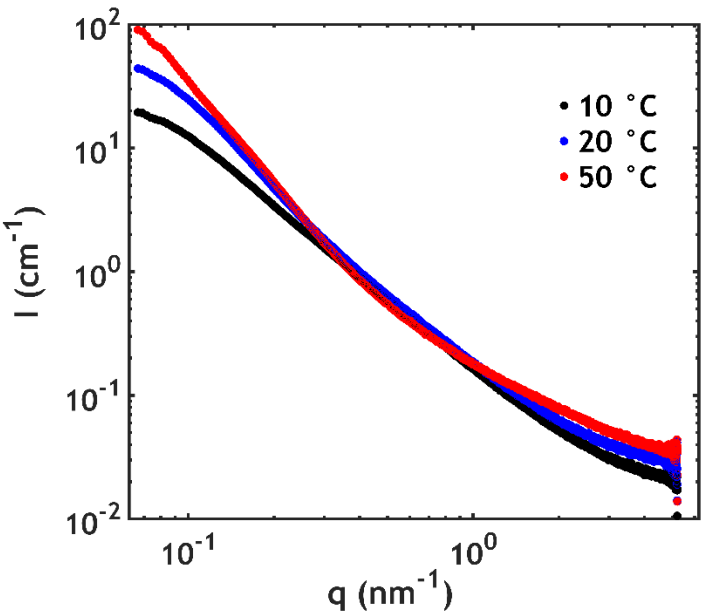

Figure 2 SAXS pattern for graft copolymer complex coacervates.

At high q (0.3 – 3 nm-1, corresponding to length scales at which the conformation of single polymer chains is detected), the curves for graft copolymer complex coacervates show a similar slope ($I \approx q^{-1.7}$) regardless of temperature: this suggests that the conformation of the individual chains is similar in both graft and homopolymer systems and does not change much as a function of temperature. More specifically, this q-dependence indicates that the polymer chains attain a self-avoiding random walk conformation, behaving nearly as in a semidilute polyelectrolyte solution. At larger length scales (q-range 0.06 – 0.3 nm-1) an upturn is detected, whose intensity increases as a function of temperature and which is not visible in complex coacervates prepared from homopolymers. This upturn is ascribed to the increased non-solubility of PNIPAM domains (with dimensions of tens of nanometers, according to the observed q-range) and the decreased compatibility between PNIPAM and the complex coacervate phase. The absence of a well-defined peak might indicate that the generated PNIPAM domains are polydisperse. The upturn is already observed at temperatures below the LCST indicating that PNIPAM chains cluster already at RT.

In addition to that, we performed the same experiments on graft copolymer complex coacervates with varying PNIPAM content (from 0% mol/mol to 40% mol/mol). In **Figure 3** SAXS measurements performed on complex coacervates prepared at 0.75 M NaCl with 0%, 20% and 40% PNIPAM content are shown.

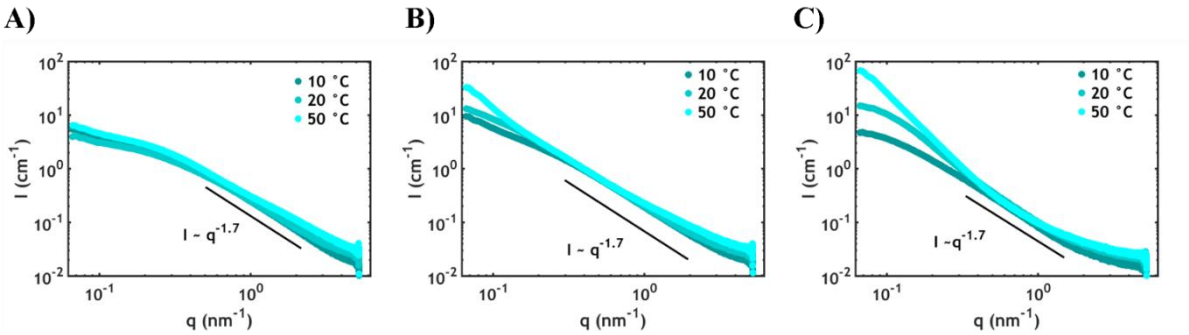

Figure 3 SAXS plots as a function of temperature for A) 0% B) 20% and C) 40% PNIPAM.

The same trend described above is observed, with the upturn becoming more and more defined as the temperature and the PNIPAM content increase.

For every PNIPAM content analysed, we measured complex coacervates prepared at three different salt concentrations (0.75, 0.5 and 0.1 M NaCl). However, only samples prepared at 0.75 M NaCl were homogeneous liquids, while the ones prepared at lower salt concentrations were heterogeneous and soft solids, making the analysis of the data too complicated. For this reason, we have focused our analysis only on well-defined samples prepared at high salt concentrations.

The time spent at ESRF was successful and useful for obtaining the required data for our samples.