



<b>Experiment title:</b> Investigation of nucleation process of polythiophenes by dynamic SAXS measurements	<b>Experiment number:</b> 26-02 924	
<b>Beamline:</b> BM26-DUBBLE I	<b>Date of experiment:</b> from: 17/5/2021 to: 13/6/2021	<b>Date of report:</b> 24/8/2021
<b>Shifts:</b> 3	<b>Local contact(s):</b> Dr. Martin Rosenthal Dr. Daniel Hermida Merino	<i>Received at ESRF:</i>
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## Report:

While nucleation is having major impact on the outcome of crystallization, this initial moment is still rather unexplored. In our project, we are studying the nucleation by SAXS, in collaboration with complementary research in non-linear optics (NLO). As part of the project, also these measurements at ESRF BM26 beamline were performed, which are focusing on the nucleation and particle growth of organic polymers, namely polythiophenes.

Due to the corona pandemic, the experiments were performed completely remotely, without the presence of the user team at the ESRF site. The user team had prepared the samples in-house at Ghent University, and shipped them to ESRF, where these were measured by local contact (Dr. Martin Rosenthal) according to the instructions obtained from the user team.

## Sample preparation

- Non-chiral poly-3-hexylthiophene polymer (P3HT) was used in the experiments.
  - The polymer is dissolved and precipitation is induced by addition of an anti-solvent. The polymer can be re-dissolved by warming it up, while the nucleation and particle growth can be consecutively followed during the cooling period.
  - 2 series of different anti-solvent amounts were prepared, each containing 3 different concentrations of the polymer (6 samples in total), while flame-sealed in borosilicate capillaries in-house at Ghent University.
  - Capillaries were prepared in triplicates to provide backups, in case of damage during the transport, or leakage due to improper sealing.

- The package contained also blank capillaries, and capillaries with a mixture for UiO-66 MOF in-situ synthesis, which is studied in a second part of our project, and would be suitable for a longer measurement without local contact present on site.

## Experiments

- The major bulk of experiments was performed on 17/5/2021 by Dr. Martin Rosenthal.
  - Capillary stage had to be exchanged due to malfunction after initial four measurements, also minor adjustment had to be done to the top temperature for the most concentrated samples.
  - In total, 12 measurements were done, out of which 3 provided useful and reliable data for further processing (0.5 mg/ml and 5 mg/ml concentrations with 20% anti-solvent addition, and 1 mg/ml with 15% addition). Rest of the measurements were either affected by stage malfunction, or by sample behavior, where air bubbles probably moved in the beam.
- Another trial was performed by Dr. Martin Rosenthal on 13/6/2021, where one unsuccessful measurement of P3HT polythiophene polymer was executed, and where one long overnight measurement of UiO-66 MOF in-situ synthesis took place as well.

## Results & outcome

- The obtained data from the P3HT polythiophene measurements are continuously analyzed. The growth of particles is clearly observed with good time resolution (5 scans/min), what is greatly superior to our in-house capabilities with 10 min scans. This combination of fast dynamic measurements from the synchrotron beamline, together with equilibrium in-house measurements provides now insight in the early stages of the particle formation. Complementary NLO measurements are currently scheduled in-house at the end of September.
- However, as not all goals/samples have been fulfilled, including missing data for completing at least one series of samples, we are intending to apply for continuation of the project for the period 3/2022 – 8/2022. In this continuation, we would like to fill in missing data, utilize our knowledge from the current run together with insight provided by NLO and extend it also to a second set of samples of polythiophene polymer showing optical activity. All results would be summarized in a manuscript submitted after the 2<sup>nd</sup> run of experiments from eventual continuation, to provide the full story where various observations and comparisons can be stated.