ESRF	**Experiment title:** Investigation of nucleation process of polythiophenes by dynamic SAXS measurements	**Experiment number**: A26-2-942
Beamline: BM 26	**Date of experiment**: from: 29. 4. 2022 to: 2. 5. 2022	**Date of report**: 29. 7. 2022
Shifts: 9	**Local contact(s)**: Dr. Martin Rosenthal	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Dr. Kristof Van Hecke

Marek Beliš*

Dr. Subhrajyoti Bhandary*

XStruct – Bio-Inorganic Chemistry, Department of Chemistry, Ghent University
Krijgslaan 281-S3, 9000 Ghent, Belgium

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.

The experiments were performed as a continuation of our previous experiment no. 26-02 924, which was performed remotely due to the corona pandemic by Dr. Martin Rosenthal on 17/5/2021. During this remote experiment, one polythiophene polymer was studied. However, the data series obtained during that run were incomplete, either due to several technical issues with the stage or due to the sample behavior. This request for continuation was submitted, to fill in missing points in the data series and to extend the study to additional polymers including polymers with optical activity, incorporating obtained experience from the remote experiment in the updated experimental design.

Sample preparation

- 3 polymers were used for the current run of experiments – one identical from the previous experiment and two new polymers with different characteristics:
    - Non-chiral poly-3-hexylthiophene polymer (P3HT), synthesized without the use of an initiator (containing one defect), used also in the previous experiment.
    - Another version of P3HT polymer, synthesized with an external initiator, having no defects in the backbone structure of the polymer.
    - Chiral poly-3-(3(S),7-dimethyloctyl)thiophene polymer (P(S)DMOT), synthesized also without an initiator, therefore containing one defect.

- The polymers are dissolved in THF, with induction of the precipitation by addition of MeOH as an anti-solvent. Afterwards, the polymer can be re-dissolved by warming it up, while the nucleation and particle growth can be consecutively followed during the cooling period.
- For each polymer, 4 different concentrations of the polymer (0.5, 1, 2.5 and 5 mg/ml) were used, together with 2 different anti-solvent additions. One extra concentration of 0.05 mg/ml was prepared for the original P3HT polymer. In total, 26 polymer samples were prepared (3x4x2 and 2 extra).
- Samples were transferred in borosilicate glass capillaries of 1.5 mm diameter and flame-sealed in-house at Ghent University. All samples were done in triplicates to provide backups in case of damage during the transport, or leakage due to improper sealing.
- Blank capillaries were also prepared in the same manner, together with several capillaries with a mixture for UiO-66 and UiO-66-NH2 MOF in-situ synthesis. These MOFs are studied in a second part of our project, and would be suitable for a longer measurement without the user team present at the beamline, or if there would be extra time available.

Experiments

From the user team, Marek Beliš and Dr. Subhrajyoti Bhandary were present at the ESRF site during experiments as new users. After the introduction to the beamline by Dr. Martin Rosenthal and solving some technical issues, the experiments commenced in the afternoon on Friday 29/4/2022.

- A Linkam stage for 1.5 mm capillaries was used initially. However, due to the tolerance in the capillary diameters, it was quickly discovered that some of the capillaries were not fitting the selected Linkam stage. The stage was exchanged for a 2.0 mm Linkam, early in the evening on Friday 29/4/2022 and used for the rest of our experiments, to ensure proper fitting and identical behavior for all capillaries.
- Designed polymer experiments were performed for all samples, taking 1 – 1.5 h on average per sample. The capillaries were warmed up to 65 – 80 °C, and consecutively cooled down at 1 °C/min, doing 10 s scans with 2 s overhead (5 scans/min). Some of the measurements had to be retaken due to sample behavior (e. g. air bubbles moving in the beam), what was accounted for in the planning. Nevertheless, some of the precipitation points for the lowest concentrations of new polymers were below 0 °C, what together with the hot & humid weather caused ice formation on the Linkam stage prior to obtaining the expected data.
- The two highest concentrations of the original P3HT and the P(S)DMOT polymers were studied in more detail, by slowing down (or entirely stopping for some time) the cooling around the precipitation regions.
- Every night for 3 – 4 hours, a MOF experiment was set up during the rest period of the user team.

Results & outcome

- The obtained data from the measurements are continuously analyzed. The nucleation and 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 insight in the early stages of the particle formation. Complementary non-linear optics (NLO) measurements were also performed in July 2022 for all of our polymers, in collaboration with the group of Prof. Thierry Verbiest (KU Leuven).
- The 0.05 mg/ml polythiophene samples were included to match properties used in NLO measurements. However, in the static environment of a capillary without homogenization by stirring, these low concentrations have proven inefficient even by using synchrotron radiation.
- We would like to publish the obtained polythiophene results in a publication early this autumn. Results from one of the P3HT polymers might be included in an extra publication with Prof. Verbiest, which is focused on NLO studies of P3HT polymers of various lengths, synthetized with an initiator (‘Multimodal optical analysis of regioregular poly-3-hexylthiophenes reveals peculiar aggregation dynamics’, manuscript in preparation).
- We aim to include the UiO-66-NH2 results in a publication with the electron diffraction data we’ve obtained on this material earlier this year.