EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Investigation of the polymerization process in a novel two-dimensional polymer using diffuse scattering	**Experiment number**: 01-02 1082
Beamline: BM01a	**Date of experiment**: from: 18.11.15 to: 21.11.15	**Date of report**: 19.09.16
Shifts: 9	**Local contact(s)**: MIKHEYKIN Alexey	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

***Gregor Hofer[1+, 2], *Thomas Weber[1+], A. Dieter Schlüter[2]**

[1]X-Ray Platform D-MATL, Vladimir-Prelog-Weg 5-10, 8093 Zurich, Switzerland

[2]Laboratory of Polymer Chemistry, Vladimir-Prelog-Weg 5-10, 8093 Zurich, Switzerland

[+]formerly Laboratory of Crystallography

Report:

We are investigating photon induced polymerization and depolymerization propagation in two-dimensional polymer crystals [1]. Of particular interest is the real crystal structure on the local scale, which is analyzed using diffuse scattering [2], to better understand the polymerization mechanism and the stability of the polymers. Trifunctional monomer molecules suitable for two-dimensional polymerization were crystalized. These molecules form new bonds between them when irradiated with blue light. This process can be reversed by heat treatment.

We collected Bragg and diffuse datasets at 100 K using a wavelength of 0.6935 Å and a Pilatus 2M detector. The Bragg datasets were measured as single 360° φ-scans with fine slicing of 0.1° and exposure time of 0.1 s per frame. The diffuse scattering datasets were collected by four repetitive 360° φ-scans with fine slicing of 0.1° and exposure time of 1.0 s per frame. The repetitive scans as well as the increased exposure time were required to collect the weak diffuse scattering with sufficient intensity. A welcomed side effect of repetitive scans is that potential beam damage could be identified. Fortunately, none of the crystals showed any signs of beam damage.

We encountered two major problems during the measurements. First, during our preliminary on-site data evaluation, we found an unwanted, regular spiking of the R_{int} value. Thanks to the staff at the beamline, including Alexey Mikheykin and Dmitry Chernyshov, we were able to identify the problem as a malfunction of the used cryostat. The cryostat was exchanged and thus the problem solved. The beamline's staff showed us how to use established software to correct for these problems in our Bragg datasets. For our diffuse scattering datasets, symmetry averaging and outlier rejection is the best approach to correct for this problem.

Second, we noticed a drop in beam intensity after the first couple of experiments. A re-alignment of the monochromator crystal solved this problem. It was probably caused by a warming up of the monochromator crystal after the beam down-time. We encountered no further obstacles.
The raw data looks very promising. The Bragg datasets are used to monitor and quantify the cell parameters, the polymerization conversion and the reorientation of the trapped and partially disordered solvent molecules. In the beginning of the polymerization reaction, the peaks are intense, sharp and scatter to high 2θ angles. After the reaction had finished, we observed a very fine, but still unexplained, reflection splitting, which we could not see with our in-house diffractometer. The reflection intensities are reduced and fewer reflections are observed along the c^* direction. Upon polymerization, the unit cell slightly expands, but upon depolymerization, the *c*-axis first abruptly decreases and then steadily increases again and reaches the original unit cell dimensions prior to polymerization. The 2-cyanopyridine solvent molecules are responsible for the crystals electric dipole momentum. The solvent molecules partially reorient themselves upon polymerization, and we calculated the accompanying change in electric dipole momentum.
The recorded diffuse scattering shows a rich variety of features. We were able to observe cloud- and streak-like features and diffuse maxima at systematically extinct Bragg positions. During the first qualitative assessment, we were already able to attribute some of these features to different structural changes during polymerization and depolymerization. For example, the diffuse scattering maxima at systematically extinct Bragg positions appear after the polymerization has started and disappear upon full conversion. Since the unpolymerized and fully polymerized states are fully ordered, this type of diffuse scattering is likely caused by the distribution of bonded and non-bonded monomer molecules. Interestingly, the diffuse scattering is different for the polymerization and depolymerization reaction.
Data evaluation is well under way. The Bragg datasets pose no particular challenge in processing and interpreting, with exception of the reflection splitting. We are currently completing the evaluation and preparing a manuscript which focuses on the findings from the Bragg datasets, such as the hysteresis of the cell parameters. In the processing of the diffuse scattering datasets, we are faced with typical problems, namely background treatment and Bragg reflection masking. Unlike Bragg scattering, diffuse scattering data evaluation is in general very challanging and standard software is not available. Therefore, custom made algorithms and computer programs are necessary for further data processing. A powerful algorithm for Bragg peak masking has already been established and the background correction algorithm is currently under development.
Some of the obtained results were already presented during the *Meeting of the German Crystallographic Society 2016* in Germany as an oral and poster contribution, at the *Two-Dimensional Synthetic Polymer Conference 2016* in Japan as an oral contribution and during the *European Crystallographic Meeting 2016* in Switzerland as a poster contribution.

Thanks to the beamline staff and their instrumentation, we were able to collect data of very high quality which also finds recognition in the scientific community.

[1] Welberry, T. R. & Weber, T. (2016). Crystallogr Rev. **22**, 2–78.
[2] Payamyar, P., King, B. T., Öttinger, H. C. & Schlüter, A. D. (2016). Chem Commun (Camb). **52**, 18–34.