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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:** Thin film structure of semiconductor donor acceptor blockcopolymers and liquid crystals	**Experiment number**:
Beamline: ID10B	**Date of experiment**: from: 21.7.2011 to: 25.7.2011	**Date of report**: 30.9.2011
Shifts: 12	**Local contact(s)**: Roberto Nervo	*Received at ESRF:*

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Report:

Experiment SC3180 was an extension of previous work performed on ID2 (SC2887). The work is part of a collaborative project investigating semiconductor donor-acceptor block copolymers for use in organic photovoltaics. These block copolymers show complex hierarchical structures consisting of a nanometre-scale phase separated structure with both phases displaing order on a molecular scale. It is generally accepted for organic semiconductors that the morphology has a strong influence on optelectronic properties and solar cell device performance.

In our experiment we intended to use a combination of GISAXS and GID to observe structures on different length scales. The samples were characterized beforehand by preliminary measurements in our home laboratory using in plane x-ray diffraction and AFM. In order to understand the complex structures arising in the copoplymers, we investigated the individual components first in order to use the resulting insight for understanding the more complex material. For that purpose the Bayreuth group synthesized in addition to the block copolymer homopolymers corresponding to the two blocks and low molecular weight model materials which resemble the chemical structures contained in the perylene side chain polymer. Fig. 1 introduces the investigated materials.

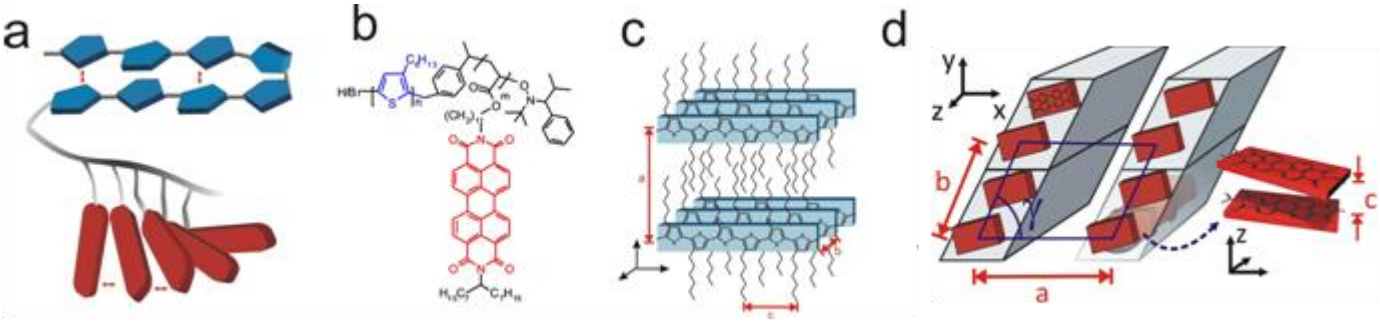

Figure 1: a) Schematic representation of the donor acceptor block copolymers with blocks of poly(3-hexylthiophene) P3HT and poly(perylene bisimide acrylate) PPerAcr. b) chemical structure of P3HT-*bl*-PPerAcr. c) crystalline structure of P3HT (lamellae), d) liquid crystalline structure of PPerAcr.

While in the previous experiment we investigated structure formation in the bulk, SC3180 was our first experiment on thin films of the materials described above. The aim of this first experiment was

a) to establish the use of thin film x-ray scattering methods for the samples under study
b) to compare structures obtained directly by spin coating with the structure formed after cooling from the melt state. The fast drying process resulting from spin coating typically leads to a non-equilibrium structure which is generally quite different from the thermodynamic equilibrium structure.

The following samples were investigated:

1. P3HT homopolymer
2. PPerAcr homopolymer
3. Low molecular weight perylene bisimide model compound
4. P3HT-b-PPErAcr block copolymer

For all samples diffraction patterns were collected in grazing incidence geometry by performing scans with the 1D detector covering the parts of reciprocal space with the most prominent Bragg reflections. Exemplary data sets are shown in Fig. 2 and Fig. 3.

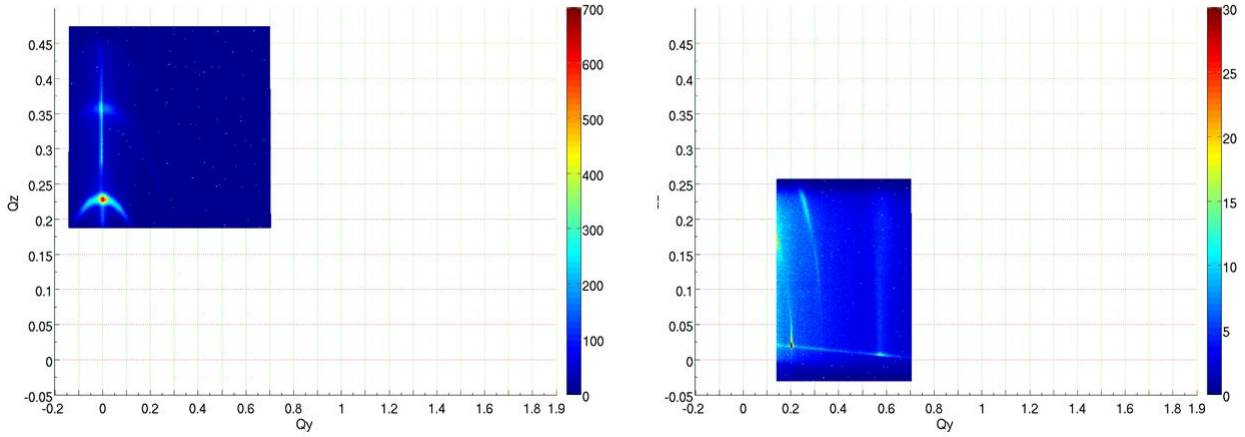

Figure 2: Grazing incidence diffraction of PPerAcr: Reciprocal space intensity maps show evidence for a strongly oriented structure after cooling from the melt. Samples measured directly after spin coating showed no reflections. Q-values are given in 1/Å.

Due to the short time available since the experiment, a full analyis of the data still has to be performed, and we can only give preliminary results at this point. As a general result,

directly after spincoating most samples were highly disordered showing no Bragg reflections. Somewhat an exception is P3HT, which showed weak reflections even directly after spin coating (Fig. 3). Samples heated to the melt state crystallized during subsequent cooling and showed strong crystalline peaks (Bragg reflections) and a strong texture. As the example of P3HT shows, the (h00) planes are oriented parallel to the substrate, in this case a known result. Similar orientation phenomena were also observed in the perylene containing side chain polymer (Fig. 2). For the PPerAcr the crystal structure in the thin film seems modified in comparison to the bulk structure. The measurements of the block copolymer inidicated a different orientation in the blocks than in the two individual homopolymers. All data sets will be analized in order to determine the crystal structure in the thin films and to work out the orientation. One aim of our work is to understand the underlying alignment process, as ideally for solar cell applications one would like to control the orientation.

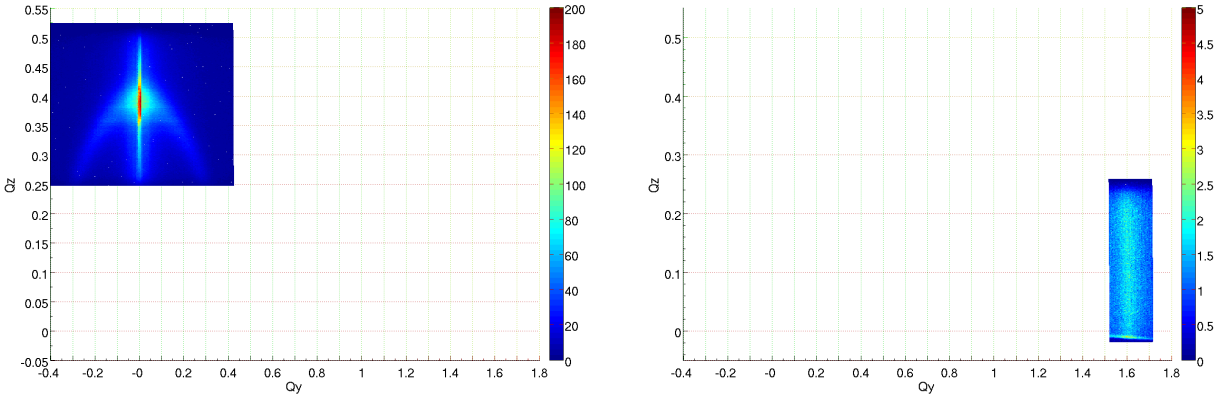

Figure 3: Grazing incidence diffraction of P3HT: Reciprocal space intensity maps show evidence for a partially ordered structure, even directly after spin coating from chloroform solution. The anisotropic intensity distribution indicates the preferred orientation of the (100) plane parallel to the silicon substrate as it was observed before by other autors. Q-values are given in 1/Å.

In a last part of the experiment we started to investigate the influence of different substrates on the orientaton of the polymers. As a first example we studied P3HT-b-PPerAcr on silicon and on PEDOT:PSS which is often used as a substrate in solar cells.

While the GID measurements worked out very well, we were not able to observe a GISAXS signal from our samples, although we know that the block copolymers show a SAXS signal in transmission and that a lateral microphase structure is visible in AFM measurements. We therefore assume that the signal from the sample was hidden below a relatively high background signal caused by slit scattering. This point has to be addressed in a next run, where we will use an additional guard slit to reduce background. The higher resolution of the upgraded beamline should also help to measure the relevant signal. For the GID measurements we would like to use mostly a 2D detector in future, in order to reduce the long exposure times necessary for scans covering a larger angular range.