



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 using the **Electronic Report Submission Application**:

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now 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.



	Experiment title: Real-time Investigation of Thermodynamic and Kinetic Factors of the Crystallization of Photovoltaic Polymer-fullerene Films from Solution	Experiment number: SI-2136
Beamline: ID10B	Date of experiment: from: 23/02/11 to: 01/03/11	Date of report: 07/11/11
Shifts: 18	Local contact(s): Alexei Vorobiev	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The goal of SI-2136 was to obtain a fundamental understanding of thermodynamic and kinetic factors that affect polymer/fullerene blend film crystallisation from the initial liquid state to the dried solid structure.

Experimental Details: A special set-up was built consisting of an evaporation channel equipped with an optical setup to monitor the thickness of the solvent-blend film coated on a substrate with an in-built motorized doctor-blade. 2D X-ray diffraction data (wavelength $\lambda=0.9305\text{\AA}$) was collected with a MAR-CCD camera from the polymer/fullerene blend from the initial instant of solvent evaporation.

Results:

The structural evolution of polymer/fullerene blend film during solvent evaporation has been described below. The polymers used were low band gap polymers poly{[4,40-bis(2-ethylhexyl)dithieno(3,2-b;20,30-d)silole]-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl} (PSBTBT), poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl]] (PCPDTBT), the widely investigated poly(3-hexylthiophene) (P3HT) and the fullerene used was [6,6]-phenyl-C₆₁(or C₇₁)-butyric acid methyl ester (PC₆₁BM or PC₇₁BM).

(i) Structural evolution of PSBTBT/PCBM

In the GIXD drying measurements (Figure 1), the first image shows freshly cast PSBTBT:PC₇₁BM film from DCB solution. At 90 s drying time and 95 wt.% solvent, PSBTBT (100) and (200) is observed indicating crystallization of PSBTBT. At the same time a powder ring is also observed evidencing the coexistence of crystallization of PSBTBT in solution. This is in contrast with our previous work on P3HT:PCBM where interface-induced crystallization was demonstrated [ACS Nano, DOI: 10.1021/nn2036279]. Subsequently PCBM aggregation occurs. Further analysis of this blend film is ongoing.

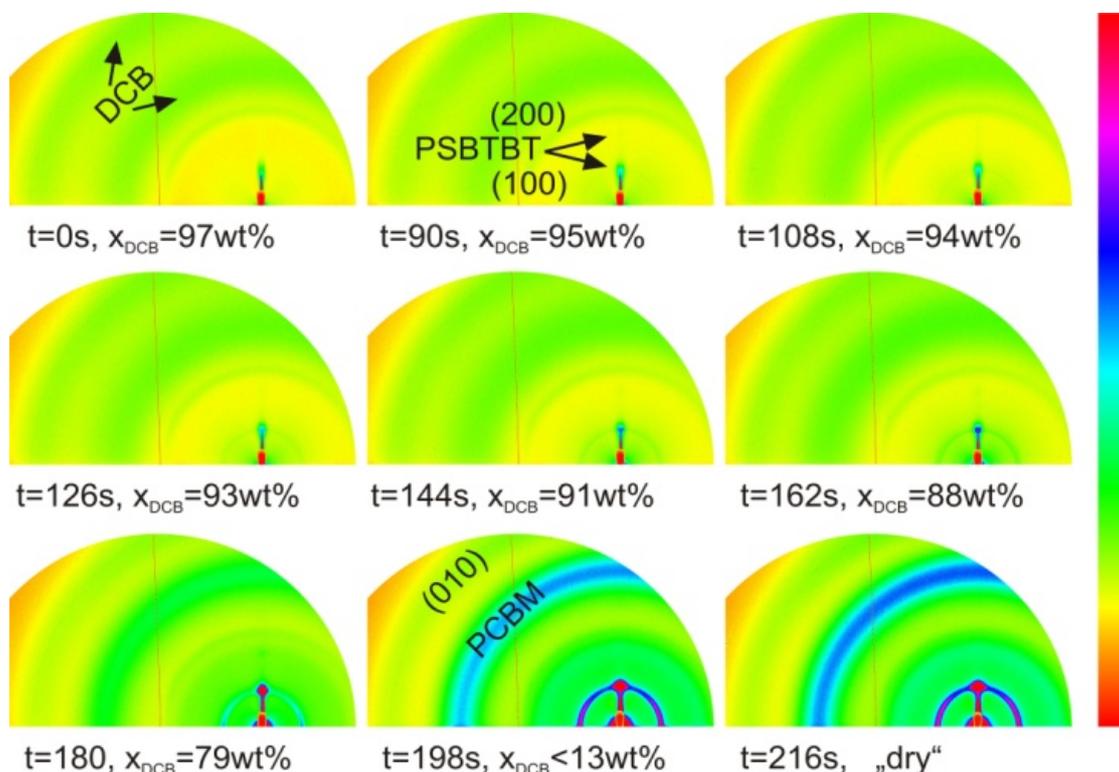


Figure 1. Evolution of GIXD patterns during the drying of PSBTBT:PC₇₁BM (1:2) film cast from DCB solution by doctor blade at 40°C on native silicon substrate. First image is of the freshly coated film. Second image shows the first indication of crystallinity. Subsequent images show the evolution of film during drying and crystallization. The drying time and actual solvent fraction is mentioned beneath each image.

(i) Structural evolution of PCPDTBT/PCBM

The incorporation of 1,8-octanedithiol (ODT) additive changes the structural evolution of (PCPDTBT)/PCBM blend film during its drying from solution as seen in Figure 2, aiding the structural ordering of PCDTBT, evidenced by the emergence of the PCPDTBT Bragg peak in the bottom row of Figure 2. Further analysis of this blend film is ongoing.

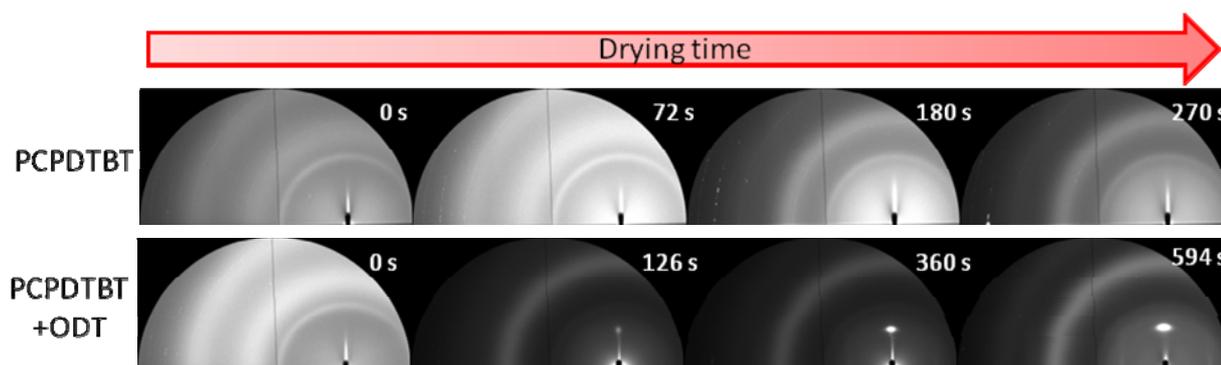


Figure 2. 2D MAR-CCD frames of PCPDTBT/PCBM blends drying without (top row) and with (bottom row) additive ODT.

Conclusions:

In this experiment, we successfully used in-situ x-ray diffraction to monitor the real-time crystallization of polymer/fullerene blend films as solvent evaporates. Further analysis is in progress to quantify and correlate these data with theoretical modeling of the drying kinetics. These results provide a microscopic understanding of the different processing parameters impacting the nanomorphology and structure of the polymer blend.