

## 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.



<b>ESRF</b>	<b>Experiment title:</b> In situ X-ray study of the drying kinetics of donor/acceptor polymer blends	<b>Experiment number:</b> SC-2700
	<b>Beamline:</b> ID10B	<b>Date of experiment:</b> from:08/04/09 to:13/04/09
	<b>Shifts:</b>	<b>Date of report:</b> 05/08/09
<b>Local contact(s):</b> Alexei Vorobiev		<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b>  <b>Esther Barrena*, Monamie Sanyal*, Carmen Munuera*,</b> Max-Planck-Institut für Metallforschung, 70569 Stuttgart, Germany  <b>Felix Buss*, Benjamin Schmidt-Hansberg*</b> University of Karlsruhe, Inst. of Thermal Process Engineering, 76128 Karlsruhe		

## Report:

The goal of SC-2700 was to get an insight into the drying process of P3HT-PCBM blend films from the initial liquid state to the dried solid structure and to investigate the effects of the substrate and of the blend ratio.

## Experimental details

For this experiment a special set-up was built consisting in a evaporation channel equipped with a optical set-up to monitor the thickness of the solvent-blend film and a doctor-blade to spread the solvent-polymer blend on the substrate with spatial uniformity. The doctor blade was motorized and could be controlled from the control hutch. This allowed us to collect x-ray diffraction data from the initial instant of the solvent evaporation. We begin by monitoring in real time the drying kinetics of P3HT-PCBM blends (1:0.8 by weight) dissolved in solvent ortho-dichlorobenzene (97% by weight). The structural evolution of the film was studied with X-rays of wavelength  $\lambda=0.934\text{\AA}$ . 2D Grazing Incidence X-ray Diffraction data of the film was taken with a MAR-CCD camera. The angle between the sample and the incident beam was  $0.12^\circ$ . The range of  $q_z$  measured was  $0.002\text{\AA}^{-1}$  to  $2.4\text{\AA}^{-1}$  covering angles between  $0.015^\circ$  to  $20.76^\circ$  and the range of  $q_x$  measured was  $1.8\text{\AA}^{-1}$  to  $-2.0\text{\AA}^{-1}$  covering angles  $-17.7^\circ$  to  $15.6^\circ$  in the MAR-CCD. The window of the drying channel was made of aluminum foil. 2D images of the drying film was taken in intervals of 50 seconds.

## Results

Fig 1 shows selected 2D diffraction maps from the drying. In the initial stages of drying, the 2D diffraction maps show two diffraction rings assigned to the solvent ortho-dichlorobenzene (Fig 2(a)-arcs 1 and 2) which correspond to a lattice spacing of  $3.78\text{\AA}$  and  $5.61\text{\AA}$ . The first Bragg peak of P3HT appeared after approximately 200 seconds. The optical data simultaneously recorded by the interferometer confirmed that at this stage the most of the solvent has been evaporated. The second and third Bragg peaks appeared at 300

seconds (Fig 2(d)-arc 4). The Bragg peaks have arcing in  $q_x$  direction indicating that the P3HT crystallites in the blended films are not perfectly ordered along the  $q_z$  direction, showing an angular mosaicity range. The mosaicity increases with drying time. The ring corresponding to amorphous PCBM appeared in the image at 400 seconds.

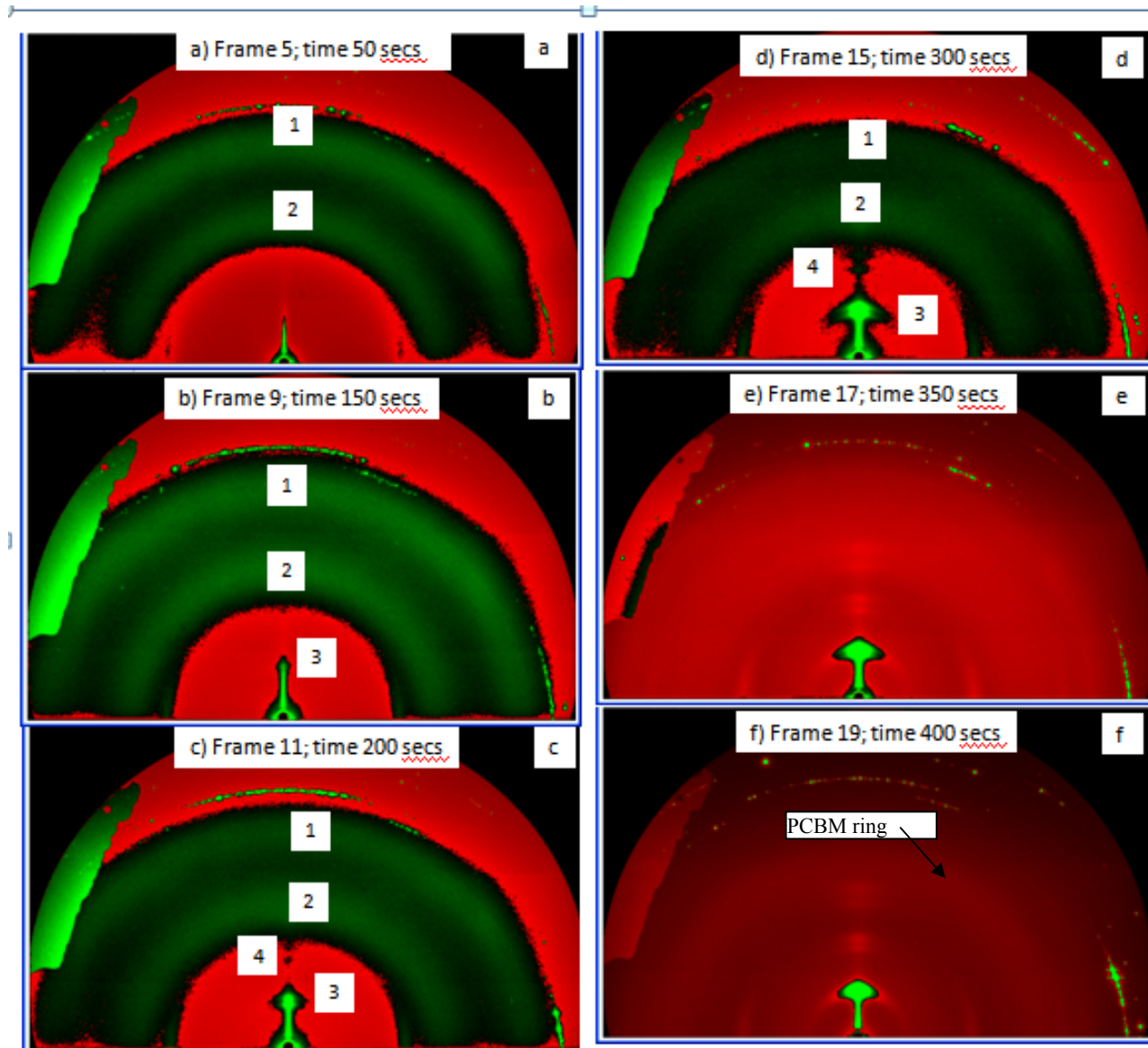


Fig 1. MAR CCD images taken during evaporation of the solvent a) arcs 1 and 2 are the solvent rings b) emergence of the 1<sup>st</sup> Bragg peak (arc 3) c) Emergence of 2<sup>nd</sup> and 3<sup>rd</sup> Bragg peak (arcs 4) d) Intensity and arcing of the Bragg peaks are increasing. Solvent arcs present. e) Solvent arcs have disappeared. f) PCBM ring appears.

Evolution of maximum intensity and width of the 1<sup>st</sup> Bragg peak with drying time of solvent is shown in Fig 2. Fig 2 suggests that after the solvent has evaporated out of the film, the P3HT film attains a more crystalline structure. In the final dry state, there exists order correlation along  $z$  for about 7 monolayers. In the initial stages of drying, the values of width obtained shouldn't be taken seriously as the crystalline domains might not have formed. We note that the intensity gradually decreases at the end. This may be due to the increase of mosaicity with time and the consequent distribution of the total intensity in a wider angular arc. It is observed that the width of the peak (along  $q_z$ ) increases versus time which indicates a reduction of mean size of the crystallites.

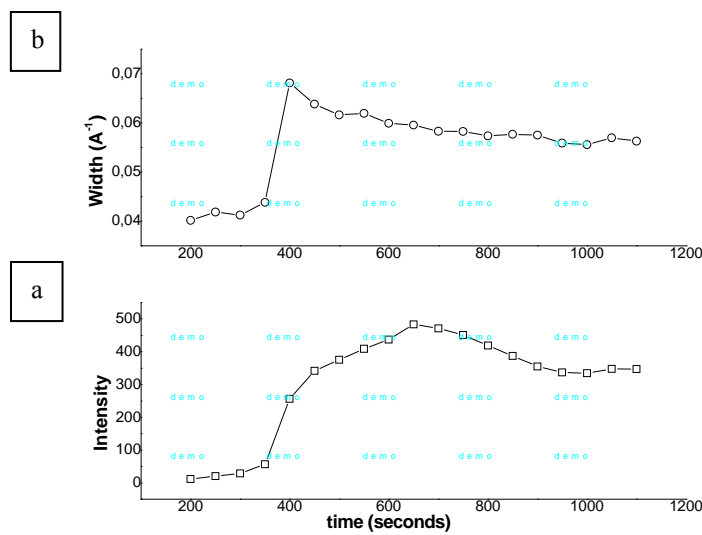


Fig 2. Evolution of a) integrated intensity and b) width of the first Bragg peak

The effect of the substrate and blend ratio has in detail been investigated. Fig 3 and Fig 4 depict 2D diffractograms for the dried P3HT:PCBM films for two different blend ratios and on two different substrates, respectively. Visual inspection shows that an increase of PCBM leads to a worse alignment of the P3HT crystallites (higher mosaicity). The substrate is observed to have an important influence on the crystallization as well. Analysis is in progress to quantify the evolution of the structure versus drying time on the various substrates (ITO,  $\text{SiO}_2$ , glass, PEDOT/ITO, PEDOT/ $\text{SiO}_2$ , PEDOT/glass) and for different blend ratios.

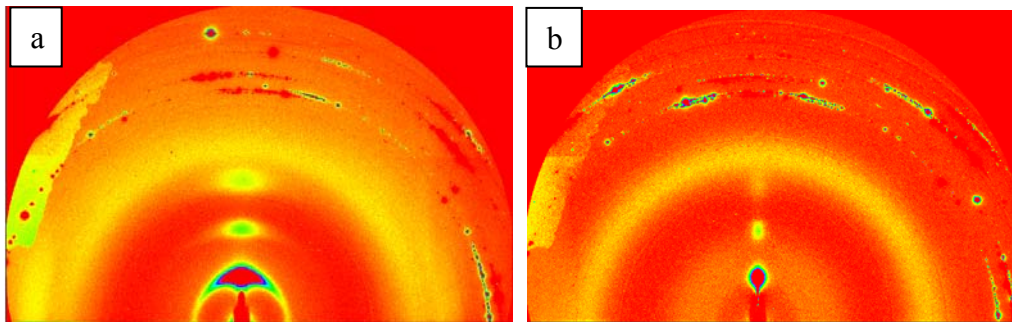


Fig 3. 2D GIXRD images of P3HT-PCBM blend on PEDOT-glass having blend ratios a) 1:2 b) 2:1

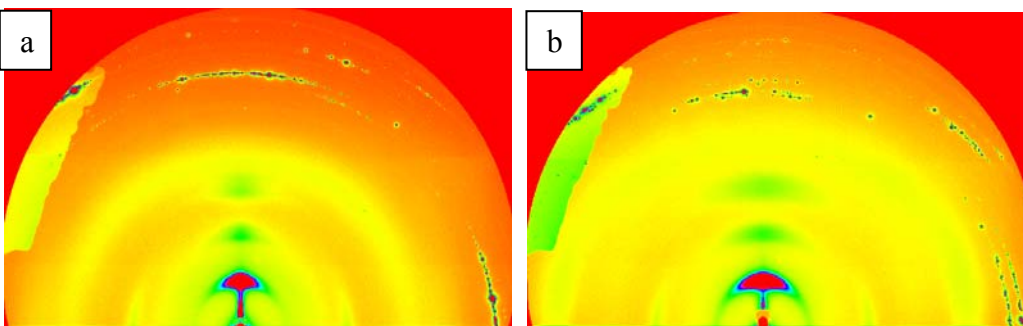


Fig 4. 2D GIXRD images of P3HT-PCBM blend (1:0.8 by weight) on a) pure glass b) PEDOT-glass

## Conclusions

The experiment was very successful. By in-situ x-ray diffraction we monitored the real-time crystallization process of P3HT-PCBM blends as the solvent evaporates. We have measured the effect that the substrate and blend ratio have on the drying process. Analysis is in progress to quantify the changes of microstructure occurring in the P3HT:PCBM blend during drying and to correlate these data with theoretical modeling of the drying kinetics. These results are of paramount importance to provide a microscopic understanding on how the different processing parameters of drying affect the nanomorphology and structure of the polymer blend.