



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://www.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.



	Experiment title: Structure and thermal behavior in ordered one-dimensional conjugated polymer nanoarrays	Experiment number: SC-3637
Beamline: ID02	Date of experiment: from: 08 March 2013 to: 11 March 2013	Date of report: 4 June 2014
Shifts: 9	Local contact(s): Peter Boesecke	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Mari Cruz García-Gutiérrez ^{1*} Tiberio A. Ezquerro ^{1*} Michelina Soccio ^{1*} Inés Puente-Orench ^{2,3*} Alejandro Sanz ^{1*} ¹ Instituto de Estructura de la Materia, CSIC, C/ Serrano 121, 28006 Madrid, Spain ² Instituto de Ciencia de Materiales de Aragón, CSIC, C/ Pedro Cerbuna 12, 50009 Zaragoza, Spain ³ Institut Laue-Langevin, BP 156-38042 Grenoble Cedex 9, France		

Report:

One of the main objectives of creating new systems by mixing up two or more components is to improve or modify the structure-properties relationships. Nowadays, science and technology demand the preparation and manipulation of structures with highly controlled morphologies at the nanoscale. In 1995 it was observed that the mixing of two conjugated polymers formed a three-dimensional heterojunction leading to efficient charge generation within the whole film. Since then, solar cells based on blends of methanofullerenes with derivatives of conjugated polymers have been under investigation [1]. Organic photovoltaics (OPVs), based on conjugated polymers, are usually created by blending electron-donors with electron-acceptors polymers. It is established that the performance of OPVs devices strongly depends on the morphology adopted by the polymer blend. Therefore, nanoscale phase separation in photovoltaic blends plays a crucial role on the effectiveness of the exciton generation and further carrier transport. With these ideas in mind, we have prepared ordered polymer nanoarrays by template wetting, using porous anodic aluminum oxide (AAO) templates [2], consisting of vertically aligned conjugated polymer nanorods as the donor phase in a potential ordered bicontinuous heterojunction. To fully understand the structure-property or

structure-performance relationships in these systems, morphological and structural investigation in-situ during thermal treatment is required. Here we report on the structural analysis of a series of pure and biphasic nanoarrays based on photoconductive polymers by means of in situ wide angle X ray scattering (WAXS) measurements at ID02 beamline.

The following table summarizes the organic components used to prepare the nanoarrays:

Organic component	Bulk Tg / °C	Bulk Tm / °C	Mw / Kgmol ⁻¹	Role
PBTTT	100	230	82.8	Donor
[70]PCBM	-	300	1.03	Acceptor
P3HT	-	225	34.1	Donor
PCDTBT	130	-	35.4	Donor/Acceptor

Photoconductive nanoarrays with diameters of 25, 40, 180 and 400 nm respectively, were examined by two dimensional WAXS as a function of temperature, paying special attention to the effect of thermal annealing on the structure at the nanoscale. Measurements were performed using the following

setup: $\lambda = 0.063$ nm; Sample-detector distance = 0.831359 m; Type of detector: Frelon.

The majority of the samples showed some kind of order reflected in well defined crystalline peaks, with the exception of nanoarrays formed by PCDTBT which turned to be essentially amorphous. Given that PBTTT has been less explored as a donor system in OPV devices, in this report we mainly focus on the structural implications of blending PBTTT with PCBM at the nanometre scale. 2D images were recorded in two

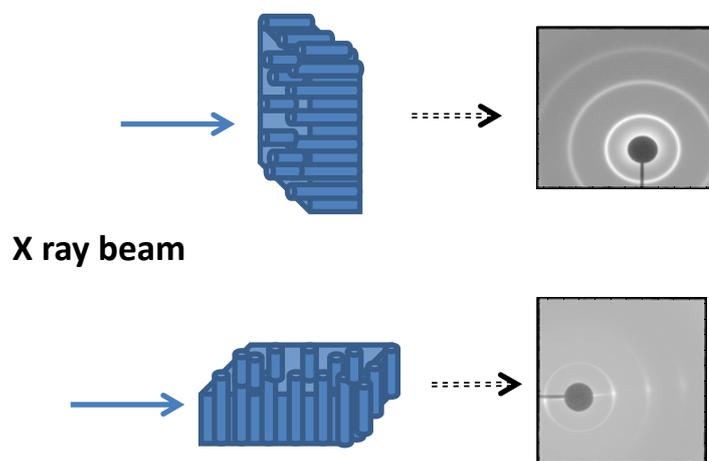


Figure 1. 2D WAXS images for 400 nm nanoarrays of neat PBTTT, recorded with the X ray beam either parallel or perpendicular to the long axis of nanopores.

different geometries, aligning the beam either perpendicular or parallel to the polymer nanoarrays as illustrated in Fig. 1. Here we see the X ray patterns for pure PBTTT confined in AOO porest with 400 nm diameter.

Data confirm the crystalline character of the PBTTT domains and a high level of anisotropy for the corresponding crystallites. The main peak corresponds to the (100) reflection that is associated to the regular packing of the main backbone. Successive higher-order reflections are also observed. We find a d-spacing for this lamellar packing of approximately 2.4 nm for a PBTTT sample confined in nanopores of 400 nm.

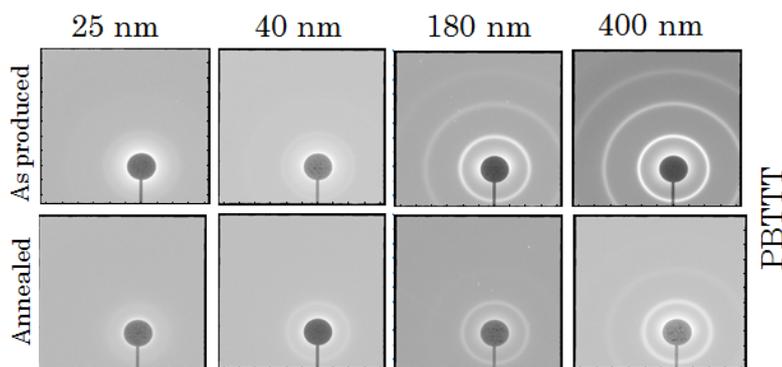


Figure 2. 2D WAXS images for PBTTT nanoarrays with different pore diameter at 25 °C. Data are showed for fresh and annealed samples at 180 °C.

The influence of the pore dimension on the PBTTT structure is illustrated in Fig. 2. The intensity of the reflections clearly decreases with the pore size, suggesting that the crystallization of the PBTTT chains takes place under confining conditions that preclude an optimum folding of PBTTT into crystals. We have also explored the effect of thermal annealing within the rubbery region by in situ time resolved measurements. The annealing treatment was performed after the corresponding destruction of the ordered arrangement through warming up to high temperatures. A detailed data analysis of the integrated 1D patterns is currently underway. At the moment, as a result of the mentioned data analysis, Fig. 3 shows the temporal evolution of the intensity and location of the main (100) reflection during isothermal annealing at 180 °C. We

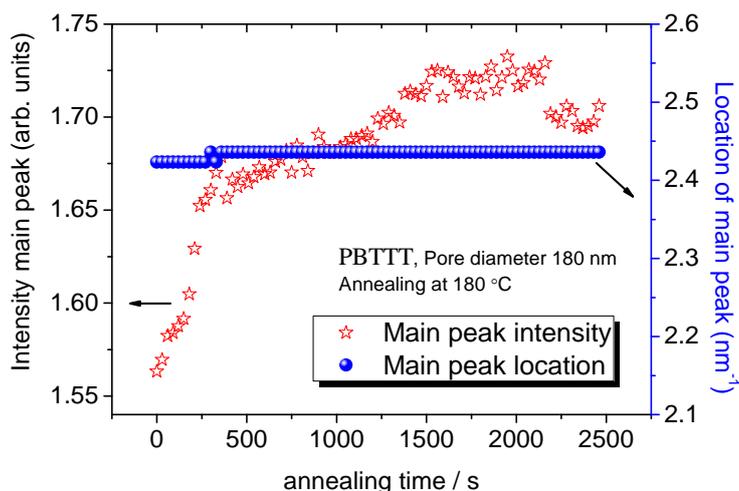


Figure 3. Effect of thermal annealing on position and intensity of the (100) reflection for PBTTT nanoarray. Sample was previously melted.

potentially act as the photoactive layer in OPV devices.

Incorporating PCMB into the PBTTT matrix has an impact on the obtained results, as showed in Fig. 4. In comparison to the neat PBTTT nanoarray, the blend is characterized by less intense peaks, high order reflections poorly developed and displacement of the main (100) peak towards lower values of Q. We have encountered similar results for the rest of pore diameters explored.

In summary, we have successfully investigated the structural implications of forming photocunductive polymer nanowires with different diameter, and also how these structure is altered by blending with the corresponding component in order to create potential photoactive systems.

we see a modest increase of the amplitude of the (100) peak with annealing. On the contrary the peak position remains almost unchanged. As a general trend, the fraction of crystalline phase, d-spacing and crystalline coherence length are not recovered after the sucesive melting and thermal annealing treatments for the whole pore diameter range.

As previously mentioned, we have also studied 50:50 blends of PBTTT with fullerene derivative PCBM. This blend could

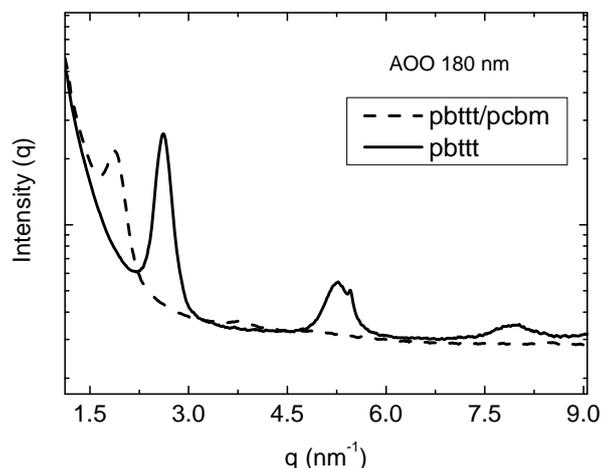


Figure 4. 1D WAXS patterns for nanoarrays based on PBTTT and PBTTT-PCBM blend (50:50) at 25 °C.

¹ J. J. M. Halls et al. Nature. 376, 498-500 (1995)

² Steinhart M., Wehrspohn R.B., Gösele U., Wendorff J.H., Angew. Chem. Int. 43, 1334 (2004).