EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: Grazing Incidence Scattering for the Morphological Investigation of Block-copolymer Containing Bulk Heterojunctions	**Experiment number**: MA 1856
Beamline: BM26B	**Date of experiment**: from: 11 April 2013 to: 15 April 2013	**Date of report**:
Shifts: 12	**Local contact(s)**: Dr. G. Portale	*Received at ESRF:*

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Report:

A publication in *Macromolecules* came out of this experiment:

- "Crystallization-driven Enhancement in Organic Photovoltaic Performance through Rod-coil Block Copolymer Incorporation into P3HT:PCBM Blends"
  D. Deribew, E. Pavlopoulou, G. Fleury*, C. Nicolet, C. Renaud, S.-J. Mougnier, L. Vignau, E. Cloutet, C. Brochon, F. Cousin, G. Portale, M. Geoghegan, G. Hadziioannou*
  Macromolecules **46** (8), 3015-3024 (2013).

Abstract:
We report the increased crystallization of poly(3-hexylthiophene) (P3HT) in the donor acceptor mixture of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) with P3HT by the addition of a block copolymer, P3HT-*b*-PI, where PI refers to polyisoprene. The photovoltaic performance of devices created using this blend is markedly improved by the addition of the diblock copolymer. We have characterized the structure of thin films of the P3HT-*b*-PI containing mixtures using optical microscopy, scanning force microscopy, UV-vis absorption spectroscopy, neutron reflectometry, and grazing incidence X-ray diffraction (GIXD). The GIXD data provide the information on the crystallinity of the films, the absorption data were used to confirm that the addition of the diblock was responsible for the increase in crystallization, neutron reflectometry data reveal a PCBM-rich region near the hole injection layer, and the two microscopy techniques revealed the structural effect of the crystallization at the surface of the films.

Additionally, we took advantage of this beam time to perform preliminary measurements on two systems that are particularly important for our research. The success of these tests encourages us to submit two new proposals for beam time on the March 2014 call.

A) Ferroelectric:semiconducting polymer blends: Polyvinylidene fluoride-*co*-trifluoroethylene, PVDF-*co*-TrFE, and poly(3-hexylthiophene), P3HT, have been blended in equal masses and spin-cast on an ITO-coated glass substrate. The 2-D GIWAXS pattern was collected at an angle of incidence angle 0.13^{o} and is presented in Figure 1a, along with the corresponding 1D pattern (Figure 1b) that was derived by the radial integration of the 2D image. The quality of the image and the appearance of all diffraction peaks expected for P3HT and for the ferroelectric β-phase of PVDF-*co*-TrFE, provide clear evidence on the feasibility of GIWAXS experiments on this system at BM26B.

B) Directed self-assembly: A polystyrene-*b*-polyethylene oxide (PS-*b*-PEO) copolymer was self-assembled to a well-ordered array of spheres and the GISAXS image was collected (Figure 2a). The corresponding 1D pattern (Figure 2b) allows to estimate a domain size of 31.5nm, almost equal to the 32nm size we have estimated from AFM data. The good quality of the image recorded suggest that we can perform this kind of measurements at BM26B

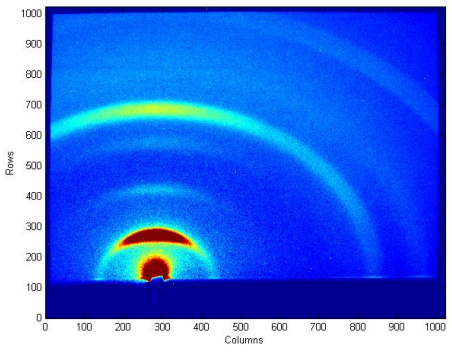

Figure 1a

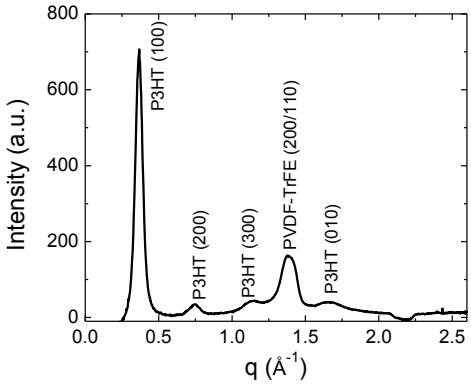

Figure1b

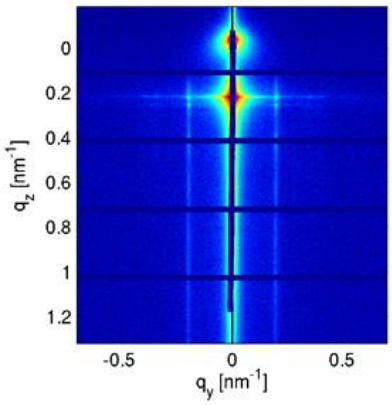

Figure 2a

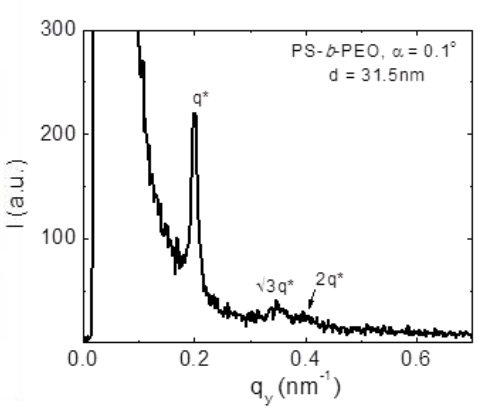

Figure 2b