

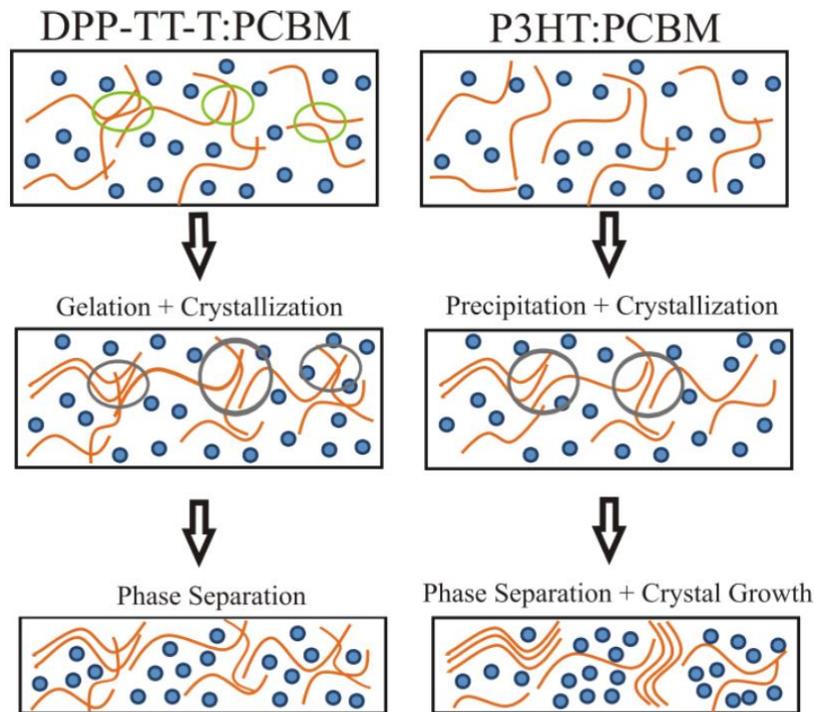


	<b>Experiment title:</b> In-situ study of the intercalation of fullerenes between the side chains of semiconducting polymers	<b>Experiment number:</b> MA-2464
<b>Beamline:</b> ID10	<b>Date of experiment:</b> from: 12 Sep 2014 to: 15 Sep 2014	<b>Date of report:</b> 29.07.2015
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## Papers published by the proposers as a result of last beam time at the ESRF

[1] N. S. Güldal, T. Kassar, M. Berlinghof, T. Ameri, A. Osvet, R. Pacios, G. Destri, T. Unruh, C. J. Brabec, "Real-Time Evaluation of Thin Film Drying Kinetics by an Advanced, Portable and Atmosphere-Controlled Setup", Manuscript submitted for publication (2015).

**Abstract:** We presented a flexible and portable in situ drying chamber, which is a powerful tool to completely characterize film formation of any organic, inorganic or hybrid thin film coating, without any need for additional extraneous measurements. The results presented on P3HT:PCBM and DPP-TT-T:PCBM blends represent the direct observation of the competition between thermodynamics and kinetics, including phase separation, gelation and crystallization, and give deep insight into drying and microstructure formation mechanisms (cf. Fig.1). In situ PL measurements, which have not been reported in previous drying studies, are proved to be especially powerful, as we were able to investigate the different thermodynamic/kinetic evolutions for two different systems. Using our novel in situ drying chamber, we will systematically investigate the drying mechanisms of multiple systems under several drying conditions to build a roadmap for morphology control in printed electronics, which can be directly adapted to large-scale processing.

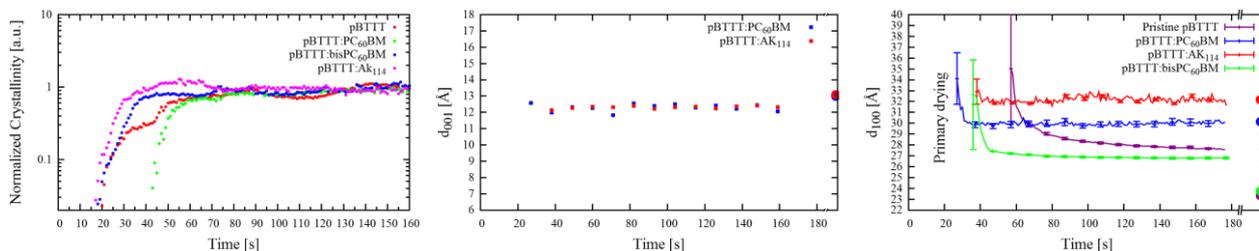


**Fig. 1:** Proposed model describing film formation during the drying process. Small blue circles and orange lines represent PCBM and the polymer, respectively. The DPP-TT-T:PCBM solution contains loose aggregates, indicated with large open circles in the top left panel. Crystallization mechanism for each solution is relatively different as DPP-TT-T:PCBM undergoes gelation instead of precipitation. Gelation causes cross-linking of DPP-TT-T chains, indicated with large gray circles in the middle left panel. Large gray circles in the middle right panel indicate the ordering of P3HT chains. As the drying continues, P3HT chains order even more, while DPP-TT-T ordering is hindered by the cross-linking (bottom panels). Nevertheless, phase separation takes place in both cases, which causes the light scattering.

[2] T. Kassar, N. S. Güldal, M. Berlinghof, T. Ameri, A. Kratzer, B. C. Schroeder, G. Destri, A. Hirsch, M. Heeney, I. McCulloch, C. J. Brabec, and T. Unruh, “Study on structure formation of printed polymer:fullerene bulk hetero-junction thin films”, Manuscript submitted for publication (2015).

**Abstract:** The complex intermixing morphology is critical for the performance of the nanostructured polymer:fullerene bulk hetero-junction (BHJ) solar cells. Here, time resolved in-situ grazing incidence X-ray diffraction (GIXD) and grazing incidence small angle X-ray scattering (GISAXS) are used to track the structure formation of BHJ thin films formed from the donor polymer Poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene) with different fullerene derivative acceptors. We have investigated the formation of stable bimolecular crystals through the intercalation of fullerene molecules between the side-chains of polymer crystallites. Such systems exhibit more efficient exciton dissociation but lower photo-conductance and faster decay of charges. On the basis of the experimental observations, intercalation obviously takes place before or with the formation of the crystalline polymer domains. It results in more stable structures whose volume remains constant upon further drying (cf. Fig. 2). We observed three distinct stages of drying:

Primary drying of the liquid layer whose thickness diminishes from about 10  $\mu\text{m}$  at the beginning to about 1  $\mu\text{m}$  at the end of this period. The thickness of the formed film continues to decrease during the next drying period to about 100 nm. During this secondary drying period the pure polymer or intercalated (bimolecular) crystallites start to nucleate and grow, respectively. This period is characterized by the highest solvent evaporation rate. The development of uni-dimensional fullerene channels along the  $\pi$ -stacking direction of the polymer crystallites was confirmed. Intercalation seems to speed up the drying process resulting in stable morphologies in less than one minute.



**Fig. 2:** Normalized polymer crystallinity as a function of the drying time derived from the integrated intensity of the  $pBTTT(100)$  peak of real time GISAXS measurements (left). Temporal change of the lamellar spacing of  $pBTTT$  crystallites (right) and the  $d_{001}$  spacing of fullerene sub lattice in the bimolecular crystals (center) during drying as derived from the time resolved GIXD measurements. The open circles on the right hand side represent the corresponding values of the films after extensive drying in vacuum.