

Polymer-fullerene phase separation by laboratory in-situ GISAXS and GIWAXS

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Abstract

Active layer in organic solar cells is bulk heterojunction consisting of a fullerene (acceptor) and a polymer (donor). As the diffusion length of the photon-generated exciton is very short, the size of polymer and fullerene domains has to be minimized by processing the polymer:fullerene blend in solvent vapours (solvent annealing). This is an unavoidable preparation step of the solar cell. Here, we present an in-situ real-time tracking of the phase separation between P3HT polymer and PCBM fullerene during solvent annealing by simultaneous GISAXS and GIWAXS measurements using the latest generation table-top high-brilliance X-ray source. We identify fullerene agglomeration and polymer crystallization to be the driving forces of the process. Being performed in laboratory instead at a synchrotron beamline, we demonstrate by this study also the potential of this approach to provide a handy feedback for technology development.

Introduction

Organic photovoltaics is attractive because of low cost of input materials and possibility to apply the roll-to-roll fabrication technology on flexible substrates. The active layer is a bi-continuous network of fullerene (acceptor) and polymer (donor) that is called bulk heterojunction (BHJ). As photon-generated electron-hole pair (exciton) diffusion path is very short (≈ 10 nm), the exciton must reach the polymer/fullerene interface fast to be dissociated into free hole and free electron before recombination occurs. Therefore, the size of polymer and fullerene domains in BHJ has to be very small. Refinement of BHJ morphology is achieved by processing the polymer:fullerene blend in solvent vapours (solvent annealing). To optimize this preparation step of solar cell, the underlying mechanism has to be studied in detail. In this contribution, we present an in-situ real-time tracking of the phase separation between polymer and fullerene during solvent annealing by simultaneous measurements of the grazing-incidence small-angle- and grazing-incidence wide-angle X-ray scattering (GISAXS, GIWAXS). A blend of poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) dissolved in dichlorobenzene was used.

Experimental details

The GISAXS and GIWAXS measurements were done simultaneously on a custom-designed Nanostar device (Bruker) equipped with a table-top Ga liquid metal-jet X-ray source Excillum at 0.134 nm wavelength (Fig. 1). The collimated X-ray beam of 0.5 mrad divergence exiting Montel optics (Incoatec) was shaped by a pinhole collimator to a diameter of 550 μm , the output photon flux being 3×10^8 photons/s. The incident angle of X-ray beam on the sample was set to 0.2° . The GIWAXS was measured by a one-dimensional (1D) X-ray detector Mythen (Dectris) oriented perpendicular to the sample surface with the exposure time of every pattern set to 2.5 s. The GISAXS was measured by a two-

dimensional (2D) X-ray detector Pilatus 300K (Dectris) with the exposure time of every pattern set to 10 s. The GISAXS flight tube was fully evacuated. The sample was prepared from a mixture of P3HT and PCBM in 1.5:1 wt/wt ratio dissolved in dichlorobenzene at a concentration of 2 wt%. 50 μL of the blend was spin-coated onto a pre-cleaned silicon substrate at a rate of 15 rps for a time duration of 15 s. The sample was subsequently mounted on a pre-aligned hexapod with six degrees of freedom. The solvent annealing was realized by covering the sample by a Petri dish equipped with two X-ray transparent windows. The X-ray detectors were manually triggered at the start of solvent annealing. Repeated collection of the GISAXS and GIWAXS patterns during solvent evaporation provided a "movie" of the phase separation in reciprocal space.



Figure 1. Nanostar device equipped with a table-top Ga liquid metal-jet X-ray source Excillum.

GISAXS and GIWAXS analyses

Temporal evolution of the radius of gyration R_g during solvent annealing derived from GISAXS Guinier plots shows an initial abrupt increase followed by approaching to saturation (Fig. 2) that is attributed to growth of PCBM clusters. In a particular case of spherical PCBM clusters, the cluster radius $R = \sqrt{5/3}R_g$. The clusters are detectable above 7 wt% of solid content and their growth starts to saturate above 10 wt% (Fig. 2). If we assume a constant number of the growing PCBM clusters after they emerge in GISAXS pattern, a fit of the temporal evolution of the radius of gyration based on Johnson-Mehl-Avrami (JMA) equation (Fig. 2) provides PCBM solubility limit 7.1 ± 0.1 wt% and the rate constant of PCBM cluster growth $(33 \pm 2) \times 10^{-4} \text{ s}^{-1}$.

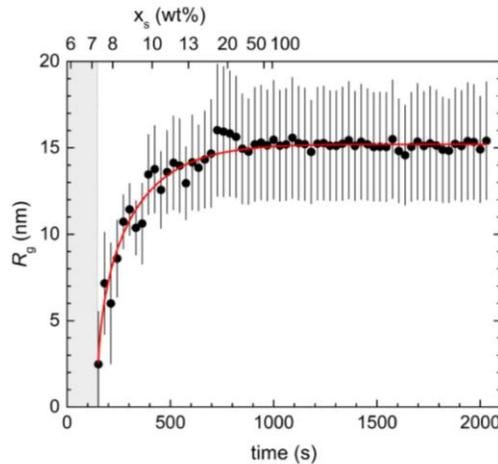


Figure 2. Temporal evolution of the PCBM cluster growth and its JMA fit. The upper horizontal axis refers to the increasing concentration of solid content in the blend due to the solvent evaporation during solvent annealing.

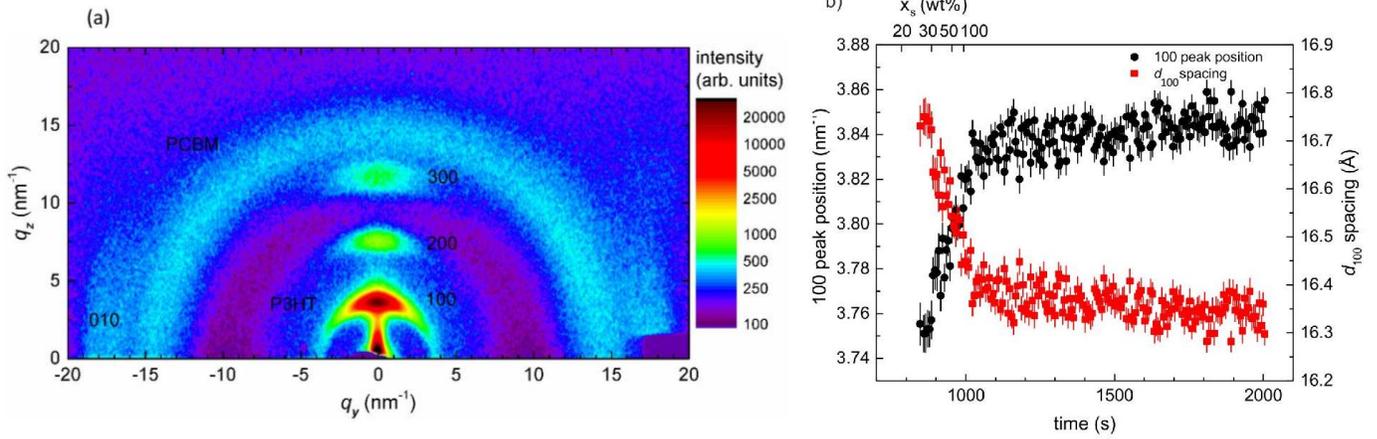


Figure 3. (a) GIWAXS pattern of P3HT:PCBM blend taken ex-situ on solvent annealing and (b) temporal evolution of the position of 100 diffraction peak of P3HT along q_z axis and the corresponding interplanar spacing derived from the in-situ measured GIWAXS patterns during solvent annealing.

The final GIWAXS pattern of the dried P3HT:PCBM blend on solvent annealing confirms presence of the crystalline P3HT lamellar phase with the edge-on lamellae orientation in P3HT domains (Fig. 3a). Temporal evolution of the area under P3HT 100 diffraction peak along q_z axis during solvent annealing, that is proportional to the growing volume of P3HT crystalline phase, was analyzed within JMA formalism, revealing two rate constants. The first stage of P3HT crystal growth is completed by solvent evaporation, the rate constant being $(10 \pm 2) \times 10^{-3} \text{ s}^{-1}$. The Avrami exponent close to 2 indicates heterogeneous nucleation with 2D crystallite growth [1]. The second stage is characterized by a much smaller rate constant $(20 \pm 7) \times 10^{-4} \text{ s}^{-1}$, being dominated by a gradual slow release of residual solvent molecules. Both stages are manifested also in d_{100} lattice spacing evolution (Fig. 3b). GIWAXS cannot provide any information on PCBM as its diffraction ring is overlaid by a strong diffraction of the solvent.

A concept of Porod invariant [2, 3] was applied to evaluate intermediate stage of phase separation between the initial PCBM agglomeration and final P3HT crystallization. In particular, the temporal evolution of a quantity

$$\Phi(t) = \frac{\int_{Q1} q^2 I(q) dq}{\int_{Q2} q^2 I(q) dq} \quad (1)$$

was evaluated from the in-situ measured GISAXS patterns. Here, $I(q)$ is a lateral cut of GISAXS pattern at the critical angle that exhibits an interference peak from ≈ 900 s of solvent annealing, $q^2 I(q)$ is Kratky plot and the integration in numerator and denominator of eq. (1) runs over a selected Q1 range around the expected or already present interference peak and over the total Q2 recorded range, respectively. Therefore, $\Phi(t)$ provides information on a fraction of the sample volume coherently scattering into the selected Q1 range of reciprocal space at a given moment t of solvent annealing, being independent of a continuously changing electron density in the irradiated volume due to solvent evaporation. It is a true fingerprint of the phase separation between P3HT and PCBM that controls the final BHJ morphology.

Discussion and conclusions

Putting together GISAXS and GIWAXS results, scenario of solvent annealing can be divided into 5 principal stages (Fig. 4). At stage I, P3HT and PCBM molecules are randomly distributed in the solution and no phase separation proceeds, $\Phi(t)$ being constant. The phase separation driven by agglomeration of

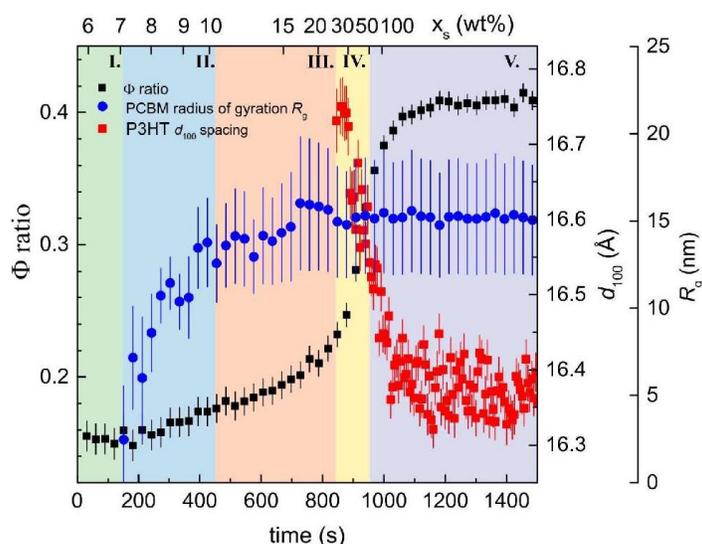


Figure 4. Scenario of solvent annealing based on GISAXS and GIWAXS results.

PCBM molecules into fast-growing clusters, as evidenced by increasing radius of gyration R_g , is observed at stage II when $\Phi(t)$ steadily increases. At stage III, the cluster growth is slowed-down but the increase of $\Phi(t)$ ratio continues without a visible slope change. Presumably, P3HT molecular chains are stretching and ordering during solvent evaporation. This facilitates release of PCBM molecules from P3HT-rich domains and prepares P3HT crystallization that is observed from stage IV. Being longer than two previous ones, stage III is the most important for formation of a fine and thermodynamically stable BHJ morphology. Stage IV is dominated by an abrupt decrease of d_{100} spacing as a marker of P3HT crystallization that is well correlated with a steep increase of $\Phi(t)$. Hence, P3HT crystallization is the driving force of phase separation at stage IV. Stage V is characterized by a slow saturation of $\Phi(t)$ ratio suggesting the end of phase separation that is controlled by a slow release of residual solvent molecules.

Summarizing, we presented an in-situ comprehensive study comprising all relevant stages of phase separation during solvent annealing of a prototypical P3HT:PCBM blend that is used as active layer in organic solar cells. The solvent annealing was done in the same way as that used for standard preparation of organic solar cells. The latest generation table-top high-brilliance X-ray source allowed simultaneous GISAXS and GIWAXS measurements of the process in real time. Hence, our work demonstrates a general possibility of such in-situ GISAXS and GIWAXS laboratory studies of organic and hybrid solar cells as viable pre-screening techniques for everyday use before more sophisticated X-ray scattering experiments at synchrotron beamlines are undertaken.

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