In Situ Studies of Solvent Additive Effects on the Morphology Development during Printing of Bulk Heterojunction Films for Organic Solar Cells

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The development of polymer morphology and crystallinity of printed bulk heterojunction (BHJ) films doped with the different solvent additives 1,8-diiodooctane (DIO) or diphenyl ether (DPE) is investigated with in situ grazing-incidence small/wide-angle X-ray scattering. The solvent additives, having different boiling points, lead to a different film drying behavior and morphology growth states in the BHJ films of the benzothiadiazole-based polymer (PPDT2FBT) and [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM). The phase demixing in the printed films is changing over time along with solvent evaporation. Polymer domains start aggregating to form larger domains in the liquid–liquid phase, while phase separation mainly occurs in the liquid–solid phase. The present work provides a profound insight into the morphology development of printed BHJ films doped with different solvent additives, which is particularly important for the large-scale fabrication of organic photovoltaics.

The power conversion efficiency (PCE) of single-junction organic solar cells (OSCs) improved up to 16% recently,[1–5] which starts to become comparable with their inorganic counterparts, e.g., silicon and hybrid solar cells. Additionally, the solution processability and flexibility of OSCs allow large-scale manufacturing of polymer-based devices by printing techniques,[6] such as slot-die coating,[7,8] doctor blading,[9] or ink jet printing.[10] Thereby, organic photovoltaics start to emerge as a very promising alternative renewable energy source for the future. For photovoltaic devices, the morphology of the bulk heterojunction (BHJ) active layer, made by a blend of donor (D) and acceptor (A) materials, plays a crucial role in the device performance.[11–14] The ideal morphology should contain sufficient interpenetrating networks between donor and acceptor materials for exciton dissociation and continuous pathways for charge transport.[15–17] Many different approaches attempt to achieve the desired morphology in the BHJ layer. The use of solvent additives in the D/A blend solution is considered to be among the simplest and fastest methods to optimize the morphology of BHJ active layers, especially in comparison with solvent vapor annealing and thermal annealing, which are undesirable for a large-scale fabrication.[18–25] 1,8-diiodooctane (DIO) (see Figure 1) is one of the most successfully used additive and suitable for a multitude of different fullerene-based BHJ devices.[26–28] DIO has a high boiling point (332.5 °C) and selectively dissolves PC71BM, which can extend the film drying process. Thus, more PC71BM molecules can integrate into the polymer network to form a D/A bicontinuous interpenetrating network, resulting in a better morphology for exciton dissociation and charge transport in the BHJ layer.[20,29,30]

Today, most morphological studies of BHJ films are based on the spin-coating technique,[20,21,31] which is not suitable for large-area manufacturing of OSCs. To commercialize OSCs in the future, it is necessary to have a thoughtful understanding of the morphological growth of BHJ films fabricated by techniques which can be scaled-up such as printing. In the roll-to-roll (R2R) fabrication process, it is still challenging to coat large-area defect-free films with perfectly homogenous film thickness. Thus, devices, which can tolerate some thickness variations of the printed films, appear favorable.[32] As introduced by Nguyen et al. and Lee et al., poly[(2,5-bis(2-hexyldecyloxy)phenylene-alt-(5,6-difuuroo-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole)] (PPDT2FBT; see Figure 1) is a semicrystalline low bandgap
ether (DPE; see Figure 1) was especially effective in thick BHJ films. In earlier works, Woo and Heeger groups showed that diphenyl ether (DPE; see Figure 1) was chosen as donor and acceptor materials, respectively. Despite the big success of nonfullerene small molecule acceptors, fullerene derivatives such as PC71BM are highly interesting for large-scale applications. Therefore, we explore copolymer, which shows excellent photovoltaic performance (PCE ~ 9.0%) for film thicknesses between 100 and 300 nm.[13,34] Moreover, PPDT2FBT-based devices have outstanding thermal stability and the charge carrier mobility can be maintained even in an ~1 μm thick film.[13] Hence, in this work, the benzothia-diazole-based polymer PPDT2FBT and [6,6]-phenyl-C71-butyric acid methyl ester (PPDT2FBT:PC71BM; see Figure 1) are chosen as donor and acceptor materials, respectively. Despite the big success of nonfullerene small molecule acceptors, fullerene derivatives such as PC71BM are highly interesting for large-scale fabrication due to their potentially lower cost and easier synthesis. In earlier works, Woo and Heeger groups showed that diphenyl ether (DPE; see Figure 1) was especially effective in high BHJ films for realizing high PCEs,[13,35] and thus it is commonly used as solvent additive for PPDT2FBT-based solar cells.[18,33,36–39] It was reported that the devices doped with DPE (8.64%) had higher efficiencies than devices doped with DIO (6.84%), which could be induced by morphological differences.[38] Therefore, we explore and compare the impact of both solvent additives, namely, DIO and DPE, on the morphology formation of PPDT2FBT:PC71BM films. To accomplish this, in situ grazing-incidence small-angle/wide-angle X-ray scattering (GISAXS/GIWAXS) are applied to detect the evolution of the morphology and the crystallinity during the formation of BHJ films. To accomplish this, in situ grazing-incidence small-angle/wide-angle X-ray scattering (GISAXS/GIWAXS) are applied to detect the evolution of the morphology and the crystallinity during printing of PPDT2FBT:PC71BM solutions with additive.[40] The PPDT2FBT:PC71BM (1:1.5, 8 mg mL−1) blend is dissolved in chlorobenzene (CB) with 3 vol% DIO or 3 vol% DPE. An intense broad ring is found on different spots to avoid beam damage. More details are described in the Supporting Information. Figure S3 in the Supporting Information. Figure S3 in the Supporting Information displays the selected 2D GIWAXS data of the samples with DPE and DIO additive. An intense broad ring is found on the initially detected GIWAXS data at q values of 1.2–1.5 Å−1 (Figure S3, Supporting Information), which is mainly attributed to the scattering of the solvent (CB). The solvent peak in the sample with DIO additive shows a higher intensity and preserves for a longer time than that in the sample with DPE additive, which manifests that the solvent CB/DIO has a slower evaporation rate than that of CB/DPE. Over time, the (100) Bragg peak of PPDT2FBT crystallites (q ≈ 0.35 Å−1) becomes more and more distinct, and the scattering contribution from the solvent reduces. To track how PPDT2FBT crystals are forming, the temporal evolution of vertical cake cuts is extracted from the 2D GIWAXS data and plotted in Figure 2. The peak at q = 1.45 Å−1 is the scattering contribution of CB.[41,42] It is used to track the solvent content during the printing process, as shown in Figure S4 in the Supporting Information. For DPE, the intensity of the solvent peak decreases after 138 s and for DIO after 300 s, which marks the stage I, in which the printed film can be seen as a liquid. The out-of-plane (100) Bragg peak at q = 0.35 Å−1 results from an ordered chain packing of the PPDT2FBT molecules with an edge-on orientation of the PPDT2FBT crystallites. The crystallinity of the polymer is quantitatively evaluated by the evolution of this peak during the printing process. The development of PPDT2FBT crystallites is assessed by three parameters of the out-of-plane (100) Bragg peak, namely, peak position, amplitude, and full-width at half-maximum (FWHM), extracted by peak fitting via Gaussian functions.

In case of DPE additive (Figure 3a), the scattering intensity of the polymer (100) Bragg peak, indicating the relative crystallinity degree of PPDT2FBT in the sample, is increasing in stage I and remains unchanged during the further stages II–V. The FWHM value is not significantly affected by the solvent evaporation and remains constant within the error bars, which implies that the crystallite sizes do not undergo changes with time. In contrast, the peak position, related to the real space distance (d) of adjacent polymer backbones (calculated by \( d = 2 \pi q \)), increases from 0.28 ± 0.01 Å−1 (d-spacing of 22.4 ± 0.3 Å) to 0.35 ± 0.01 Å−1 (d-spacing of 17.9 ± 0.2 Å) with time in stage 1, suggesting that the chain stacking is getting more and more compact in this initial phase. In the remaining time (stages II–V) it does not change anymore, indicating that the PPDT2FBT crystallite formation and growth are complete after the rapid solvent evaporation during the first 138 s.

In case of DIO additive (Figure 3b), the polymer crystal growth is different. Due to the high boiling point of DIO, the mixed solvent CB/DIO is supposed to have a higher boiling point
than CB/DPE, which is evidenced by the gradual decrease of the scattering intensity of CB in stage I (until 300 s in Figure S3b, Supporting Information). In this stage I, the PPDT2FBT (100) Bragg peak intensity increases slowly with time, suggesting an increasing amount of polymer crystallites in the film. In parallel, a slight decrease of the FWHM value suggests that the crystallites are growing in size in stage I. Also, we can observe a shift of the peak position at the beginning of stage I only, which can be explained that the initial peak position is attributed to the formation of solvent-swollen nuclei, and the evaporation of solvent affects the distance of chain stacking.\textsuperscript{[43,44]} Afterwards, until 400 s (stage II), the CB signal remains constant, whereas the intensity of the polymer peak exhibits a strong increase. The printed film still contains sufficient solvent molecules to enable polymer mobility and more crystallites are forming. Until 600 s (stage III), a distinct decrease of the CB scattering signal occurs, indicating that the small amount of residual solvent is evaporating slowly from the film. In stage III, the intensity of the polymer peak increases with a reduced rate due to having less and less mobility to enable further crystallization. After that (stages IV and V) show no more changes of the polymer crystallites. The FWHM values do not change within the error bars in the stages II–V. In contrast, the peak position remains almost unchanged until 400 s. In stage III, it shifts to smaller $q$ values indicating that the lattice distance of polymer crystallites becomes larger, which could be caused by stretching of alkyl chains after solvent evaporation.\textsuperscript{[45,46]} In the late stages IV and V, also the formed crystal do not undergo a further compaction.

Comparing the final state of the sample with DPE and DIO additive, a higher crystallinity degree can be found in the thin film printed with DPE additive compared to that processed with DIO additive by comparing the peak intensities in two samples. This agrees well with previous studies which showed that a competition between the formation of interpenetrating donor–acceptor networks and the growth of polymer crystallites occurs during the morphology development process.\textsuperscript{[47]} Slow solvent evaporation facilitates the formation of interpenetrating donor–acceptor networks in the BHJ film.\textsuperscript{[22,48–50]}

On the mesoscale, the morphology changes of printed films are tracked by in situ GISAXS measurements.\textsuperscript{[40,51,52]} On this scale, the initial states of liquid solution films on the solid substrate are prone to radiation damage by the intense X-ray beam. To avoid such problems, the in situ GISAXS measurements start only 200 s after the printing process with a data acquisition time optimized in radiation damage tests (see Figure S2, Supporting Information). Selected in situ 2D GISAXS data are displayed in Figure S5 in the Supporting Information. It can be seen that the intensity in the Yoneda peak range in the 2D GISAXS data becomes more and more pronounced with increasing time, which indicates that the film is forming, and the film morphology is developing. To extract changes of the lateral polymer structure, horizontal line cuts of the 2D GISAXS data are carried out at the critical angle of PPDT2FBT (0.11°), which corresponds to the strongest X-ray scattering signal. Afterward, these horizontal line cuts are modeled to obtain the temporal evolution of the polymer structures by using the effective interface approximation and the local monodisperse approximation of the distorted wave Born approximation.\textsuperscript{[53,54]} Selected horizontal line cuts and corresponding fits are shown in Figure S6 in the Supporting Information. To achieve best model fits, three lateral structures are assumed. Their corresponding radii and distances are summarized in Figure 4. Figure 4a,c shows the temporal evolution of the radii of polymer domains of the thin PPDT2FBT:PC$_{71}$BM films printed with DPE and DIO additive, respectively. The corresponding domain distances are depicted in Figure 4b,d. The initial states of liquid solution films on the solid substrate (stage I) is not probed in the GISAXS measurements.

**Figure 2.** Temporal evolution of vertical cake cuts of the 2D GIWAXS data of samples with a) DPE and b) DIO additive, respectively. The peak at $q \approx 1.45 \text{Å}^{-1}$ is the scattering contribution of CB. The position of the (100) Bragg peak of PPDT2FBT is indicated. The color code shows the time evolution as indicated.
Thus, from the five stages, on the mesoscale four stages are identified for the thin PPDT2FBT:PC71BM films.

Opposite to earlier work in other printed D/A films, we do not observe a growth of the polymer domains in the sample doped with DPE additive (Figure 4a). Such a behavior can be explained with a rapid evaporation of the solvent CB/DPE, resulting in the aggregation of polymer molecules in the first 200 s after printing. Thus, in case of DPE additive, the first 200 s comprise stages I and II. Afterward, the polymer domains decrease slowly from 200 to 600 s (stage III). The radii of the polymer domains decrease during this period in the film with DPE additive, e.g., the size of the largest structure changes from (182 ± 2) to (100 ± 2) nm. Moreover, the corresponding domain distances decrease as well. From 600 to 1000 s, the polymer domain sizes experience a slight increase, along with an increase of the corresponding domain distances (Figure 4b), suggesting that some domains are merging in this period (stage IV). After 1000 s, the film morphology remains stable on the mesoscale (stage V).

In contrast, the polymer domains in the sample with DIO additive show a different growth behavior in the same time scale. First, a rapid increase of the polymer domains occurs from 200 to 600 s, accompanied by a significant increase of the corresponding domain distances (Figure 4d). Besides, initially, there are only two characteristic structures in the film with DIO additive. In principle, the solvent evaporation rate is determined by the vapor pressure. However, since the environmental conditions are the same, the boiling point can be used to indicate the evaporation rate. Because the boiling point of DIO is higher than that of DPE, a slower release rate of the CB/DIO solvent occurs. Along with the evaporation of the solvent, the polymer molecules slowly reach saturation in the solution and small structures aggregate to form larger structures, which is in agreement with increasing domain distances. Thus, this period of domain growth is marked as stage II+III. Then, the polymer domains experience a slow change (stage IV). A reduction of polymer domain sizes follows, accompanying with a decrease of the corresponding domain distances, which is caused by phase separation (stage IV). Finally, a stable film morphology is achieved (stage V) after around 1000 s.

In conclusion, in situ GISAXS and GIWAXS measurements provide insights into the polymer morphology and crystallinity formation process of printed PPDT2FBT:PC71BM films with...
different solvent additives, namely, DPE and DIO. A sketch of the polymer domain and polymer crystallinity evolution is shown in Figure 5. In both cases, the film formation starts from a solution state (stage I). It has been demonstrated that liquid–liquid (L–L), liquid–solid (L–S), and solid–solid (S–S) demixing occur with time during the drying process of a solution containing two components, like a blend of a donor polymer and a fullerene acceptor.[48] Due to the low boiling point of CB/DPE, the solvents evaporate rapidly from the film. Therefore, we do not observe the L–L phase (stage II) (marked with a dashed rectangular in Figure 5a) via GISAXS measurements during the solvent evaporation, in which polymer aggregation forms large domains. However, according to the GIWAXS investigations, crystallite growth starts from the L–L state (stage II). Then, L–S demixing (stage III) quickly takes place in the sample along with a phase separation, leading to a decrease of the polymer domain sizes based on the GISAXS observations. The phase separation is driven by the Flory–Huggins interaction parameter ($\chi_{DA}$) between donor and acceptor.[20,55] Subsequently, the film morphology undergoes a S–S phase (stage IV), in which polymer domain sizes present a slight increase. At last, the morphology and polymer crystallinity stabilize in stage V. In contrast, the solvents in the sample processed with DIO evaporate slowly. It has been reported by Lee et al. that the donor polymer tends to aggregate in a solution if doped with DIO additive.[56] Thus, the polymer molecules start to aggregate

Figure 4. Temporal evolution of structure parameters obtained from modeling the horizontal line cuts of the 2D GISAXS data in terms of polymer domain radii of the sample with a) DPE and c) DIO solvent additive as well as polymer domain distances of the sample with b) DPE and d) DIO solvent additive. The five stages of the film formation process are indicated.

Figure 5. Schematic of the morphological evolution of the films doped with a) DPE (yellow) and b) DIO (orange) over time based on the GISAXS/GIWAXS measurements performed in situ during printing of PPDT2FBT (red) and PC$_{71}$BM (black) from CB (green). The five stages of the film formation process are indicated as explained in the text.
even from the dissolved stage (stage I), which agrees with the GISAXS observations that two characteristic structures are present around 260 s (stage I) after printing. With the initial slow evaporation of the solvent, the polymer crystallinity and crystallite sizes increase gradually with time. In the next stage, along with the fast evaporation of the solvent, proofed by the intensity evolution of the solvent scattering, an L–L demixing state (stage II) is dominant in the film, and the polymer domains enlarge further. In parallel, a sharp increase of the X-ray scattering intensity of the polymer (100) Bragg peak is observed, indicating more crystallites forming during the L–L stage. Afterwards, as the solvent further evaporates, a L–S demixing (stage III) is shown in the film, in which the growth rate of polymer domains increases rapidly, whereas that of the polymer crystallinity is slightly slowing down. Then, a S–S demixing is observed in the film, and phase separation occurs during this period, presenting a decrease of the polymer domain sizes together with an unchanged polymer crystallinity in this stage (stage IV). Finally, the film morphology shows no obvious further changes in the last stage (stage V). Overall, this work presents a detailed investigation of the polymer morphology and crystallinity development during printing with different solvent additives, providing basic knowledge for further optimization of the morphology and crystallinity of BHJ films, which are indispensable for large-scale fabrication and marketability of organic photovoltaics.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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