Probing the bulk heterojunction morphology in thermally annealed active layers for polymer solar cells

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Abstract

A combination of fast scanning chip calorimetry and X-ray ptychography is explored to study the effects of thermal annealing on the active layer of bulk heterojunction organic photovoltaics. The well-known P3HT/PC\textsubscript{61}BM 1:1 system is investigated as a test case. By using a custom chip calorimetry setup, it is possible to give a thermal treatment at 127 °C (400 K) to P3HT/PC\textsubscript{61}BM 1:1 thin layers, using a heating and cooling rate of 30000 K.s\textsuperscript{-1}, after which the resulting morphology is investigated with X-ray ptychography. Applying only heating and cooling, without isothermal annealing, yields a featureless morphology. This corresponds well with thermal data which indicate a mixed amorphous phase only. For increasing isothermal annealing times, a well-defined morphology appears with increasing domain size, corresponding to the formation of an endothermal melting trajectory. This melting trajectory is expected to consist of both eutectic melting and melting of coarsened crystals. In contrast to chip calorimetry results, large domain sizes are obtained for heating and cooling without isothermal annealing at a conventional rate of 20 K.min\textsuperscript{-1}. This initial morphology then develops further with increased isothermal annealing. The combination of chip calorimetry and ptychography allows separating the effects of each single thermal step on morphology development.

Keywords: Organic photovoltaics, X-ray ptychography, Chip calorimetry, P3HT, PCBM
1. Introduction

Organic photovoltaics (OPV) offer a green and sustainable way of harvesting energy directly from the sun. OPV has the potential to become a low-cost and easy-to-produce alternative to inorganic solar cells, with the added benefits of being flexible and transparent, due to their thin organic film nature [1]. The efficiency of such a thin film is greatly improved when the donor and acceptor material form a co-continuous interpenetrating morphology with optimal domain size, known as the bulk heterojunction (BHJ) morphology [2]. The optimal domain size is determined by the exciton diffusion length. As such, the morphology will play a key role in the final effectiveness of the active layer of an OPV device [3,4]. Studying how different processing conditions lead to improved morphologies is therefore important to achieve a better fundamental understanding of OPV devices.

A reference system for BHJ OPV devices is the mixture of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PC_{61}BM), which is capable of reaching efficiencies around 5% [5]. In recent years, many low bandgap donor polymers have been developed, with the aim of further improving OPV efficiencies [6,7]. By combining these optimized polymers with the C_{70} analogue of PC_{61}BM, PC_{71}BM, efficiencies exceeding 10% have been reached [8,9]. For P3HT/PC_{61}BM, but also for several more novel OPV systems, a significant increase in efficiency is seen when a post-production thermal annealing procedure is used to allow the morphology to develop [2,5,10].

The presence of a eutectic composition is important for understanding the P3HT/PC_{61}BM phase behaviour [11–16]. At the eutectic composition, both components solidify or desolidify simultaneously. This yields a fine grain morphology upon cooling, which although not a one-phase system, will desolidify at a single temperature upon heating and again form a homogeneous phase of eutectic composition. It is known that P3HT and PC_{61}BM are miscible
in the amorphous phase, while leading to separate P3HT or PC_{61}BM crystals [11,13,17,18]. Different P3HT/PC_{61}BM ratios can be found in literature for the eutectic composition, going from 40 wt% to 65 wt% P3HT, depending on the methodology and the P3HT used [13–15]. This corresponds well with the 50 wt% P3HT or 1:1 composition that is used most often for devices based on this system. In all cases, the eutectic composition and melting temperature are estimated by extrapolation, as the actual eutectic melting is not observed. Instead, the melting enthalpy decreases as the eutectic composition is being approached. This was explained by the interference of the glass transition of PC_{61}BM, which hinders crystallization [19].

An exciton diffusion length of about 10 nm is often given as the guideline value for the P3HT/PC_{61}BM system, implying that for optimal charge generation the domain size should be around this value [20,21]. As such, it can be expected that the optimal donor/acceptor interface is formed at the eutectic composition, owing to its fine grain morphology. However, according to some studies, the highest efficiencies are observed at a P3HT wt% composition slightly below the eutectic, explained by the need for a percolating network of the PC_{61}BM acceptor [13].

The P3HT/PC_{61}BM is mostly amorphous upon casting, which leads to low charge carrier mobilities. Upon thermal annealing, the crystallinity of the P3HT-rich phases has been demonstrated to increase significantly, while aggregation has been observed for PC_{61}BM [22,23]. This reordering of the active layer morphology, coupled with higher photon absorption and charge carrier mobility, improves the photovoltaic performance. It has been demonstrated that the steep increase in efficiency at the onset of thermal annealing can be related to P3HT crystallization, while the subsequent more gradual increase likely is the result of PC_{61}BM diffusion [24]. The resulting morphology of annealing varies significantly depending on the time and temperature chosen. Excessive annealing induces PC_{61}BM to form micrometer-size crystals, which will have a negative impact on performance as domains
become too large for efficient exciton diffusion [25,26]. One of the unresolved issues in OPV morphology studies is to understand whether the observed morphology changes are directly induced by a specific (thermal) treatment, or by more complex mechanisms involving a combination of different thermal and solution processing steps [4,5,19,27,28]. In this paper, the P3HT/PC$_{61}$BM system was chosen as a test system.

Fast scanning chip calorimetry is a thermal analysis technique based on thin membrane chips [29–32]. The combination of such a thin membrane setup together with nanogram sample masses allows for a significant increase in heating and cooling rates by reducing the mass which needs to be heated. The most recent generation of these devices has been able to reach rates above $10^6$ K.s$^{-1}$ [33]. Recently our group has used this technique in the study of thin layers of P3HT and PC$_{61}$BM, where scanning rates of 30000 K.s$^{-1}$ were used to avoid all non-isothermal effects and characterize the resulting ‘true’ isothermal structure formation [34–36]. Such a thermal methodology is exploited to apply a well-controlled isothermal annealing to the P3HT/PC$_{61}$BM 1:1 active thin layer.

The applicability of both soft and hard X-ray microscopy for weakly scattering materials has been demonstrated in several studies [37,38]. Recently, coherent diffractive imaging (CDI) techniques have been developed for high-resolution phase-contrast imaging [39–44]. In particular, X-ray ptychography (a scanning variant of CDI) [45–48] has been used to demonstrate the imaging of complex structures over large fields of view, also in situ [49–51], and at high spatial resolution below 10 nm [43,52]. Strain imaging in nanostructures has also been demonstrated using Bragg-ptychography [53,54]. X-ray ptychography is directly relevant for organic solar cells research, as it can be used to non-destructively image short-circuits in organic multilayers [55] and also to image BHJ morphologies [56]. Ptychography relies on the application of iterative reconstruction algorithms [46,57] to a series of far-field (Fraunhofer) diffraction patterns, acquired by scanning the sample in two dimensions perpendicular to a spatially coherent X-ray probe in such a way that a significant spatial
overlap between neighboring diffraction exposures is maintained. The multiple measurements
with partly overlapping illuminated regions on the sample introduce a redundancy allowing
the efficient phase reconstruction. During the process, the complex-valued projection of the
sample, i.e. both phase and amplitude, is retrieved.

In this work the combination of fast scanning chip calorimetry with X-ray ptychography is
explored for the straightforward characterization of the effect of a well-defined thermal
annealing on the BHJ morphology in a P3HT/PC61BM 1:1 thin layer.

2. Experimental section

2.1. Materials and sample preparation

Commercially available P3HT (Rieke Metals, $M_w = 10^5$ g.mol$^{-1}$, $M_w/M_n = 2.4$, regioregularity
~94 %) and PC$_{61}$BM (Solenne BV, purity 99%) were used in this study. A 1:1 (wt%) P3HT/PC$_{61}$BM
solution was produced by mixing equal amounts of P3HT and PC$_{61}$BM in chlorobenzene with
a concentration of 1 wt%. Layers of about 900 nm thickness were produced by spincoating the
obtained solution on gold foil or Si$_3$N$_4$ membranes. Au foil was used as a substrate for chip
 calorimetry measurements [34], while Si$_3$N$_4$ was used for ptychography experiments due to its
transparency for X-ray radiation.

2.2. Thermal annealing treatments

Isothermal treatment studies were performed using a fast scanning chip calorimeter developed
at Rostock University [32,58] in combination with Xensor Integration 39391 nanocalorimeter
chips. The XEN-39391 chips possess an active area of 60 µm x 60 µm with a 6-couple
thermopile for temperature detection and two heaters. A custom setup was designed which
allowed the TO-5 chip housing, as used in the standard setup, to be replaced by a ceramic
chip housing. Both the ceramic housing and the XEN-39391 chip can be seen in
Figure 1. Such housing allows for X-ray measurements in transmission due to the chip membrane being accessible from both sides, instrumental for the combination with X-ray ptychography.

Figure 1. A XEN-39391 chip mounted on a ceramic holder (left), the chip itself (center, active area indicated by arrow) and a detailed picture of the membrane with the 60 µm x 60 µm active area (right, active area indicated by arrow). The center and right image were reproduced from the Xensor Integration product catalogue.

Figure 2. Scheme of the two different isothermal annealing pathways. For isothermal annealing from the glass (right) the sample is cooled below Tg before the isothermal segment, where this is not the case for the isothermal annealing from the molten state (left). Analysis is performed in subsequent heatings. An indication of the annealing temperature of 127 °C (400 K), well above the Tg, is given. Adapted from [34].

Thin layer samples on Au foil were placed on the active area with the aid of silicone oil and heated and cooled at a rate of 30000 K.s⁻¹. In analogy with earlier work, isothermal treatments were performed through two pathways, a molten state and a glassy state pathway (see Figure 2), where the glassy state pathway is more sensitive to non-isothermal effects [34]. A random order of the isothermal segments was used. For comparison, thin layer samples on Si₃N₄ membranes for isothermal treatments, achieved by a more conventional scanning rate of 20 K.min⁻¹, were prepared using a Mettler Toledo DSC822e as furnace.
2.3 Two-dimensional (2D) X-ray ptychography

The 2D X-ray ptychography experiments were carried out at X12SA (cSAXS) beamline of Swiss Light Source (Paul Scherrer Institut, Villigen, Switzerland). The coherent X-ray beam with an energy of 6.2 keV ($\lambda = 2$ Å), selected through a double-crystal Si(111) monochromator, was passed through a pinhole aperture of approximately 3.0 µm diameter, placed at a distance of 4 mm in front of the sample. A helium-filled flight tube was positioned between the sample and detector separated by the distance of 7.36 m for all measurements, in order to reduce absorption and scattering by air. The standard sample holder with chip membranes having a ceramic housing was fitted directly onto a XYZ nPoint piezoelectric nanopositioning stage. During the measurement, the sample was scanned laterally across the beam using the piezo stage in a Fermat spiral pattern [59], with an average step size of 0.2 µm and counting time of 1.0 s for each of the 100 exposures per scan. The diffraction patterns were recorded with a pixelated hybrid Pilatus 2M detector with 172 µm x 172 µm pixel size [60]. Each scan covered a field of view of 5 µm x 5 µm.

To summarize the phase reconstruction briefly, the complex valued two-dimensional exit wave at each scanning position $j$ on the sample corresponds to the $j^{th}$ diffraction pattern and is described as $\Psi_j(r) = P(r - r_j) \cdot O(r)$, where $P(r - r_j)$ is the “probe” wave field and $O(r)$ is the sample transmission function with $r \equiv (x, y)$ being the transverse Cartesian coordinate and $r_j$ the position vector for the $j^{th}$ exit wave. On the condition that there is sufficient overlap between neighboring illuminated regions of the sample, both $P(r)$ and $O(r)$ can be reconstructed simultaneously from the far field intensity measurements of all the exit waves.

For ptychographic reconstructions, a nonlinear optimization algorithm with 300 iterations on the central 192 x 192 detector pixels for diffraction patterns was implemented [46,57]. Linear phase gradients in the reconstructed ptychography images were removed by considering the
probed region outside the sample corresponds to zero phase change. For cases where several scans were jointly reconstructed in order to effectively stitch a larger field of view, we used the reconstruction approach detailed in [61] where the algorithm reconstructs the scans simultaneously using a shared object and probe.

3. Results and discussion

3.1 Thermal properties of P3HT/PC$_{61}$BM thin layers studied by fast scanning chip calorimetry

It is generally accepted that by mixing P3HT and PC$_{61}$BM, these two components hinder each other during crystallization, slowing the crystallization kinetics [24,62]. Based on a previous study, a scanning rate of 30000 K.s$^{-1}$ was proven to be sufficient for avoiding non-isothermal effects when investigating P3HT, which is the fastest crystallizing component [34]. A 30000 K.s$^{-1}$ heating and cooling rate is therefore expected to be sufficient to avoid non-isothermal effects in the mixture (see below). Furthermore, using the same scanning rate as for the constituting components will facilitate comparisons. An interesting property of the P3HT/PC$_{61}$BM 1:1 mixture is that the $T_g$ step can be clearly observed in chip calorimetry (see Figure 3), in contrast to that of P3HT [35]. From rapid heat-cool calorimetry (RHC) a $T_g$ of 38 °C has been observed for this mixture [19]. In chip calorimetry, the $T_g$ is observed to shift significantly to slightly below 100 °C, due to the increased scanning rates combined with substrate effects [36,63]. The lower and upper limits of the glass transition are observed to be ca. 70 °C and 130 °C, respectively. For comparison, the $T_g$ of PC$_{61}$BM at ca. 200 °C, with a lower and upper limit at 180 °C and 220 °C, respectively, is also shown in Figure 2 [35]. For similar reasons it is also shifted ca. 60 °C upward with respect to the RHC value of 139 °C [19].
Figure 3. Comparison of $T_g$ of P3HT/PC$_{61}$BM 1:1 and PC$_{61}$BM as obtained from chip calorimetry (thin layer) at 30000 K.s$^{-1}$. The upper and lower limits of the transitions are indicated with vertical lines.

The effects of thermal annealing were studied at 127 °C (400 K), the upper limit of $T_g$ of the 1:1 mixture. When isothermal annealing treatments of varying time are carried out at $T = 127$ °C, a double endothermic peak is observed. The resulting heating trace after isothermal treatments can be seen in Figure 4. This endothermic peak has the form of a major, lower-temperature maximum, and a smaller shoulder at higher temperatures. These can be attributed to eutectic melting (lower peak), and delayed melting of coarsened crystals with increasing annealing time (upper shoulder), respectively. As the annealing time is increased, the endothermic peaks are growing at the expense of the amorphous P3HT/PC$_{61}$BM mixed phase (indicated by arrows in Figure 4). It is interesting to note that the onset of the melting trajectory corresponds to the lower limit of the PC$_{61}$BM $T_g$. Similar observations were also made for P3HT/PC$_{61}$BM mixtures in bulk, where this was explained by the effect of the PC$_{61}$BM vitrification on the initial formation of the eutectic [19].
Figure 4. Endothermic peak evolution seen for the P3HT/PC_{61}BM 1:1 mixture during heatings at 30000 K.s^{-1}, following isothermal treatments at 127 °C (400 K) using the molten state (top) and glassy state (bottom) pathways. Results are shown for isothermal treatments of 0 s, 2.6 s, 10.5 s, 68.7 s, 176 s, 721 s, 2952 s, and 7556 s. The results for isothermal treatments investigated by ptychography are indicated in color. Arrows have been drawn to clarify observed trends in the thermal transitions.
Figure 5. Evolution of P3HT/PC_{61}BM 1:1 melting enthalpy by isothermal crystallization at 127 °C (400 K) obtained at scanning rate of 30000 K.s^{-1}, with results from molten (filled symbols) and glassy state (open symbols). Red lines indicate the isothermal times for the samples studied by ptychography (0 s not shown). Note the logarithmic time on x-axis.

As expected, similar results are obtained for annealing treatments performed directly from the molten state or from the glassy state. This can also be seen in Figure 5, where the obtained melting enthalpies at all treatment times for both pathways are compared. This similarity indicates that all effects during cooling and heating were avoided. For this reason, only treatments utilizing the molten state pathway will be considered from this point on.

3.2 Visualization of BHJ morphology using X-ray ptychography

To get an overview of the developed morphology in the active layers, four samples with different annealing treatments prepared by chip calorimetry (0 s (quenched), 60 s, 721 s and 7556 s; indicated by red lines in Figure 5), were chosen for 2D X-ray ptychographic imaging. This innovative technique was chosen over more conventional imaging techniques used in BHJ research, such as atomic force microscopy (AFM) and transmission electron microscopy (TEM). Due to measuring by X-ray transmission, it is possible to investigate the whole thin layer, instead of just the surface as by AFM. Furthermore, unlike in TEM, the thin layer can be kept on the chip after the annealing treatment and no extra sampling steps are required.
Figure 6 shows the reconstructed phase contrast 2D projections of the active layers at room temperature. The (quenched) sample at 30000 K.s⁻¹, not exposed to isothermal annealing treatment (Figure 6a), shows a presumably purely amorphous P3HT/PC₆₁BM mixed phase, in agreement with the chip calorimetry study performed in section 3.1, where only a glass transition was visible, but no endothermic peak (Figure 4, 0 s). The samples exposed to isothermal annealing show the well-developed BHJ morphology starting already at a treatment of 60 s (Figure 6b). With the further increase of isothermal time for annealing treatments to 721 s and 7556 s (Figure 6c-d), the well-defined morphology is developed and further enhanced in relation to the domain sizes to an extent where the domains can be clearly resolved. The size of these domains is in the range of 250-400 nm. Since the electron density ($\rho_e$) of PC₆₁BM (~ 0.7 e⁻.Å⁻³) is greater than that of P3HT (~ 0.4 e⁻.Å⁻³), the darker and the lighter regions represent PC₆₁BM-rich and P3HT-rich domains [64].
Figure 6. The reconstructed high-resolution phase-contrast images of P3HT/PC_{61}BM 1:1 active layer at room temperature showing the co-continuous morphology development. a) After non-isothermal (quenched) annealing treatment, b-d) after isothermal annealing treatment with increasing annealing time: 60 s, 721 s and 7556 s. The values on the colorbar represent the relative phase shift (Δϕ) where the darker regions in the images are PC_{61}BM-rich domains and lighter regions are P3HT-rich domains.

The increase of the domain sizes, for increasing isothermal annealing times, as seen in the phase contrast images, are in agreement with the endotherms obtained from the chip calorimetry. The systematic increase in the melting enthalpy indicates enhanced crystallinity, while the peak maxima of both the main endothermic peak as well as the shoulder are found to shift to higher temperatures, which corresponds to coarsening of the morphology. It can be seen that for the three annealing times probed here, the higher temperature shoulder of the melting endotherm is already present. As the appearance of this shoulder can be linked to the formation of coarsened crystals, this explains the clear domains and their sizes seen in the phase contrast images.

Note that the spatial resolution of about 100 nm obtained in the present study is not sufficient to resolve the initial finely grained morphology, formed at the shortest annealing times. However, with the new developments in coherent X-ray imaging, a resolution of 10 nm might be expected in near future also for soft materials, provided that ways are found to circumvent the problems of radiation damage [52,65]. To this end, the on-going developments of diffraction-limited sources [66,67], which will significantly increase the coherent flux, will be crucial. Through the use of fast scanning chip calorimetry, the formation of such morphology was detected thermally, despite the inherent thermodynamical instability of such nanosized structures. More conventional thermal analysis techniques are unsuited for this, as they do not allow for sufficiently high scanning rates to (i) freeze in such an unstable morphology at short annealing times and (ii) measure it after formation.
3.3 Comparison to annealing treatments using conventional cooling and heating rates

Samples of a thin layer of P3HT/PC$_{61}$BM 1:1 mixture on Si$_3$N$_4$ membrane were thermally annealed in the furnace of a standard DSC and also investigated by X-ray ptychography. As here a more conventional heating and cooling rate of 20 K.min$^{-1}$ was used, such a comparison elucidates the importance of the scanning rate. In analogy with the chip calorimetry treatments, comparable isothermal DSC annealings of 0 s up to 7500 s at 127 °C were investigated [56].

A clear difference with the mixture treated by chip calorimetry can already be seen from the ptychography image taken for no annealing treatment (0 s). While this yielded an essentially featureless image for the treatment by chip calorimetry, a clear micron-sized phase separation can now be observed (see Figure 7). For longer annealing times this morphology can be seen to develop further into bigger discrete domains, leading eventually to massive phase separation on the scale of tens of micrometers after an annealing of 7500 s (see [56]). This final evolution is reminiscent of what has been reported in literature for excessively annealed P3HT/PC$_{61}$BM mixtures, where large PC$_{61}$BM crystals were observed, surrounded by a depletion zone [25,26,68].
Figure 7. The reconstructed high-resolution phase-contrast projection for P3HT/PC_{61}BM 1:1 thin film after non-isothermal annealing by conventional DSC, measured at room temperature. a) 20 µm x 50 µm field of view (FOV) obtained after stitching 3 x 9 scans together with an overlapped field of view of 5 µm. Each scan covered a FOV of 10 µm x 10 µm with using a time of 0.5 s for each of the ca.100 exposures per scan and an average step size of 1 µm. b) The reconstructed phase-contrast image corresponding to the marked area in (a) with 5 µm x 5 µm FOV.

This striking difference seen for the same mixture, given the same isothermal treatment, only differing in the heating and cooling rates clearly illustrates the importance of the whole thermal history of the samples. It is evident that during the cooling from the molten state to the isothermal annealing temperature, structure formation already takes place (nucleation effect), which is then further enhanced upon annealing. In the absence of this non-isothermal structure formation, a completely different morphology will be formed (see 3.2). This may be explained by the much faster crystallization kinetics at elevated temperatures, suppressed by the much shorter residence time at such temperatures when the scanning rate is increased using chip calorimetry. Note again that the suppression of non-isothermal effects of crystal nucleation and growth can only be realized by ultrafast heating/cooling rates as implemented in chip calorimetry.

It can be expected that in actual OPV active layers the initial structure formation or nucleation, leading to large-scale effects during annealing, will be caused by the preparation of the active layer from a solvent. The effect of different solution processing methodologies on the crystals formed in P3HT/PC_{61}BM mixtures has been documented before [17,19,28,69], and the present study represents an important step towards a fundamental understanding of these observations.

4. Conclusions

An isothermal annealing study at 127 °C (400 K) was performed on a P3HT/PC_{61}BM 1:1 mixture using chip calorimetry, and the resulting morphologies were imaged using X-ray ptychography. The results show that true isothermal structure formation can be observed,
without any influence of non-isothermal effects. The initial structure formation, observed as an endothermic transition, primarily corresponds to eutectic melting. For longer treatment times the delayed melting of coarsened crystals also contributes to the observed endothermic transition.

While chip calorimetry allowed for scanning rates which completely avoid non-isothermal effects, X-ray ptychography has made it possible to directly investigate the morphology of samples given such a treatment. The ptychography results confirm the absence of any non-isothermal structure formation, and indicate that a well-defined morphology is formed when isothermal annealing is performed at 127 °C (400 K). However, the current spatial resolution does not allow the imaging of the initial finely grained morphology expected at the shortest annealing times. The annealing treatments visualized by ptychography all correspond to times where coarsened crystals are seen to melt by chip calorimetry.

When X-ray ptychography is used to visualize the same P3HT/PC_{61}BM 1:1 system, only annealed using conventional cooling and heating rates, a striking difference is seen [56]. Much more pronounced domains are visible, which are already present in a mixture given no isothermal treatment. Isothermal annealing leads to the further development of this initial structure formation, leading to large-scale PC_{61}BM crystals as seen in literature for excessive annealing. Based on these results it can be concluded that to thoroughly understand the effect of a thermal annealing on morphology development, not only the isothermal annealing itself but also the preceding thermal pathway should be investigated. The latter will be largely influenced by the solvent processing methodology in actual OPV devices. Fast scanning chip calorimetry in combination with X-ray ptychography is proven to be an excellent analytical tool to unravel the effect of each single thermal step on morphology. In future this approach could contribute to characterize the effects of isothermal and non-isothermal pathways, in combination with the role of solution processing, on the BHJ morphology of thin OPV layers.
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