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Real-Time Tracking of Polymer Crystallization Dynamics in Organic Bulk Heterojunctions by Raman Microscopy

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ABSTRACT: State-of-the-art organic photovoltaic active layers typically undergo post-treatment such as thermal or solvent vapor annealing to increase their performance by tuning the bulk heterojunction morphology. Molecular crystallinity is one of the key factors that determine the morphology. Real-time tracking of the crystallinity during the post-treatment is strongly desired for understanding the physics of the crystallization process and optimizing the post-treatment protocol. Here, we report on the cold crystallization (CC) dynamics of the polymer in the temperature range of 50−150 °C in polymer:fullerene blends based on poly(3-hexylthiophene) with various fullerene-based acceptors (C₆₀, PC₆₁BM, PC₇₁BM, bisPC₆₁BM, HBIM, AIM8, and IrC₆₀) in real-time by Raman microscopy. We also reveal how different solvents, fullerene acceptors, and temperatures affect CC during thermal annealing. We further demonstrate a correlation between the fullerene derivative weight and the polymer crystallinity for the as-cast films and also a correlation of the polymer crystallinity before and after annealing. Our findings are essential for developing efficient strategies of morphology optimization in emerging organic photovoltaic devices with real-time Raman microscopy tracking as a valuable tool.

1. INTRODUCTION

The most efficient organic photovoltaic devices (OPDs), for example, solar cells and photodetectors, are based on bulk heterojunctions (BHJs) that are phase-separated blends of donor and acceptor semiconductor materials. For efficient OPDs, organic BHJs should have a specific morphology of the donor- and acceptor-separated phases to provide efficient exciton dissociation, separation of free charges, and their transport to the device electrodes.

Polymer:fullerene blends, as the most studied BHJs, have been in the focus of research for the last 2 decades. In many cases, the charge generation and transport in such blends are disturbed by fullerene acceptor molecules. The polymer:fullerene blend morphology changes upon annealing have been probed by a number of experimental techniques: in situ atomic force microscopy, UV−vis spectroscopy, X-ray diffraction, ellipsometry, scanning electron microscopy, and ultrafast spectroscopy. For instance, as-cast poly(3-hexylthiophene) (P3HT) with [6,6]-phenyl C₆₀ butyric acid methyl ester (PC₆₁BM) blends usually show a nonoptimal morphology that results in their poor photovoltaic performance, specifically in low power conversion efficiency (PCE). Thermal or solvent annealing is commonly used to optimize the BHJ morphology. For annealing the polymer, the following two temperatures define the operational window: the glass transition temperature (the lower limit) and the melting temperature of the crystalline phase (the upper limit). Between these two temperatures, the polymer chains acquire mobility, partially crystallize, and hence become more ordered—the process known as cold crystallization (CC). In the P3HT:PC₆₁BM blends, CC results in an increase in the optical absorption at the longer wavelengths, the charge separation efficiency, and carrier mobility; these all lead to a significant boost in the PCE. For instance, differential scanning calorimetry (DSC) studies revealed that the morphology of P3HT:PC₆₁BM blend films results from a dual crystallization as the crystallization of both the donor and...
acceptor phases is hindered by the other one during thermal annealing.

Raman microscopy possesses a unique ability to distinguish crystalline and amorphous domains in the BHJ.\textsuperscript{30,31} This ability is based on the fact that the frequency of delocalized carbon−carbon stretching modes is changed upon crystallization because of interchain interactions. This approach was developed by Kim and co-workers,\textsuperscript{32} who demonstrated that the contributions of amorphous and quasicrystalline polymer phases to the Raman spectra of P3HT:PC\textsubscript{61}BM blends can be factorized.\textsuperscript{32,33} In particular, they showed that the shifts of the frequency of the Raman carbon−carbon band can be attributed to crystallization of the polymer phase in the blend films during annealing.\textsuperscript{34} Here, we refine the Raman method developed in ref 32 to track the polymer crystallinity in real-time during CC of the polymer phase and apply this technique to study thermal annealing in various P3HT:fullerene blends.

Apart from the commonly used PC\textsubscript{61}BM acceptor, other fullerene-based acceptors are actively studied to increase the OPD performance via increase of the acceptor optical absorption, reduction of the acceptor electron affinity (to increase the operating voltage of OPD), and to optimize the donor:acceptor miscibility in the blend.\textsuperscript{35−39} Although it is known that the acceptor molecules in the BHJ disturbs the ordered polymer phase,\textsuperscript{40} there is still a lack of understanding on how strong its effect is on the polymer phase crystallinity in the BHJ with non-PCBM fullerene acceptors. This understanding is important for optimization of the postdeposition treatment protocols of such blends used as the OPD active layers.

In this paper, we report the polymer crystallization dynamics tracked by the real-time Raman microscopy technique during thermal annealing in the BHJ blends cast from different solvents and in the blends with various fullerene-based acceptors, with P3HT as an archetypical example. Casting blends from the higher-boiling-point solvent results in a larger content of the quasicrystalline phase in as-cast films. We show a correlation of the polymer crystallinity before and after the CC. We also establish how different solvents, blend compositions, and temperatures induce polymer mobility during thermal annealing. Thus, the real-time Raman microscopy technique provides an easy access to polymer crystallization dynamics of organic photovoltaic active layers during their postprocessing.

2. MATERIALS AND METHODS

2.1. Materials. Regiorgregular P3HT (RR-P3HT) was purchased from Lumtec. The weight-average (\(M_w\)) and regioregularity are \(>45\) 000 kg/mol and \(>95\%\), respectively. Regiorgregular P3HT (RRa-P3HT) was purchased from Rieke-Metals. The weight-average molecular weight (\(M_w\)) was \(>60\) 000 kg/mol. Different fullerene-based acceptors were studied (Supporting Information, Section 1): C\textsubscript{60} PC\textsubscript{61}BM, PC\textsubscript{71}BM, 1-(3,5-ditert-butyl-4-hydroxybenzyl)-3-(3-cyclopropene[1,9]-C\textsubscript{60}H\textsubscript{5})[5,6]fullerene-3-yl)-indolin-2-one (HBIM),\textsuperscript{40} 1-tetra-decyl-3-(3-cyclopropene[1,9][C\textsubscript{60}H\textsubscript{5}][5,6]fullerene-3-yl)-indolin-2-one (AIBM),\textsuperscript{41} exohedral metallocomplex (\(η_2\)-C\textsubscript{60})-IrH(CO)[(+)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis-(diphenylphosphino)butane] (IrC\textsubscript{60}),\textsuperscript{42} and [6,6]-diphenyl-C\textsubscript{62}-bis(butyl acryic acid methyl ester) (bisPC\textsubscript{60}BM).\textsuperscript{43} C\textsubscript{60} PC\textsubscript{61}BM, bisPC\textsubscript{60}BM, and PC\textsubscript{71}BM with purity of \(>99.5\%\); \(>99.5\%\); \(>99\%\), respectively, were purchased from Solenne BV. HBIM and AIB8 were obtained from the Arbusov Institute of Organic and Physical Chemistry (Russian Academy of Sciences), whereas IrC\textsubscript{60} was obtained from the Nesmeyanov Institute of Organoelement Compounds (Russian Academy of Sciences). Synthesis and characterization of HBIM, AIB8, and IrC\textsubscript{60} have been reported elsewhere.\textsuperscript{30−42} All the materials were used without additional purification.

2.2. Thin Films and Devices. Solutions for active layers were prepared by dissolving P3HT and fullerene derivatives together in orthodichlorobenzene (DCB) at a weight ratio of 1:1 and a total concentration of 20 g/L. This ratio was chosen as optimal or close to optimal for solar cells based on P3HT and the studied fullerene derivatives.\textsuperscript{27,40−44} For the P3HT:PC\textsubscript{61}BM and P3HT:PC\textsubscript{71}BM blends, chlorobenzene (CB) and chloroform (CF) solvents were also used. The solutions were stirred at a magnetic stirrer for 5 h at 75 °C and then were spin-cast at 900 rpm on a glass substrate. The resulted film thicknesses measured with an atomic force microscope (NTEGRA Spectra, NT-MDT) were in the range of 80−150 nm. The same film preparation protocol but with other substrates was used for fabrication of organic solar cells; the details are described in the Supporting Information, Section 2.

2.3. Raman Spectra. Raman spectra were recorded using a Renishaw inVia Raman microscope (50×, NA = 0.5 Nikon large working distance objective) in the confocal configuration. The excitation laser wavelength was set at 488 nm (Ar\textsuperscript{+} laser line). It has been shown that this (resonant) excitation wavelength provides high Raman sensitivity to P3HT crystallization.\textsuperscript{45} The excitation beam power on the sample was 0.25 mW to ensure a linear excitation regime (Supporting Information, Section 3.1); the acquisition time of one Raman spectrum with \(\sim 1\) cm\textsuperscript{-1} resolution was \(\sim 1\) s. To avoid laser-induced changes of the sample (e.g., photodegradation and laser heating) under long-time exposure, the Raman spectra were collected by scanning over the sample area of \(\sim 100 \times 100\) \(\mu\)m\textsuperscript{2} and then averaged (see Supporting Information, Section 4, for details). The sample temperature was controlled by a Linkam stage (THMS6000) with nitrogen gas purging. Following ref 32, the Raman spectra were recorded and analyzed in the spectral region from 1350 to 1500 cm\textsuperscript{-1} containing the in-plane ring vibrations of P3HT:symmetric C=C stretch mode at 1450 cm\textsuperscript{-1} and C=C intraring stretch mode at 1380 cm\textsuperscript{-1} (assigned in ref 45), which are highly sensitive to the crystallization of polymer chains in resonant Raman conditions.

2.4. Annealing Protocols. Raman probing of polymer crystallization during thermal annealing was performed using two thermal annealing protocols: the fast and slow ones. In the fast protocol, annealing was performed under a constant elevated temperature to simulate common annealing protocols normally used to enhance the OPD performance.\textsuperscript{46} The polymer:fullerene blend was first heated fast at the maximum heating rate (100 °C/min) up to a preset temperature (75, 90, 105, 120 °C) and then annealed at this temperature. The Raman spectra of the sample were recorded during the constant temperature phase of the experiment. This experiment was performed in real-time to obtain the crystallization rate in situ, that is, during annealing. In the slow annealing protocol, the heating rate was set at a much lower value, 5 °C/ min, to achieve quasiatic annealing,\textsuperscript{47} in the temperature range of 20−170 °C.
The polymer crystallinity was calculated by fitting the Raman spectrum of the sample with a linear combination of the “amorphous” and “crystalline” reference spectra as was proposed by Tsoi et al. (Supporting Information, Section 3.4). However, an important difference of this study is that the spectral decomposition was performed in real-time at the current temperature of the sample (i.e., without having it cooled before the Raman measurements). This approach required to obtain reference Raman spectra at all temperatures used (see below). Raman spectra of the annealed pristine RR-P3HT and RRa-P3HT:PC61BM (4:1 weight ratio to quench the polymer fluorescence) samples were used as the references for the quasicrystalline and amorphous phases, respectively (Supporting Information, Section 3.4). RRa-P3HT does not crystallize, whereas pristine RR-P3HT shows the highest degree of crystallinity. The pristine P3HT samples were prepared as described in ref 32 to facilitate direct comparison of the results.

The polymer crystallinity in blend films was quantified by the “index of polymer crystallinity” (IPC). The IPC value was defined as a fraction of the RR-P3HT spectrum in the fit to the blend film spectrum, where the fit is constructed from a superposition of both reference spectra

\[
IPC(T) = \frac{P_{RR}(T)}{P_{RR}(T) \times \frac{\sigma_{RR}}{\sigma_{RRa}} + P_{RR}(T)}
\]

where \(P_{RR}\) and \(P_{RRa}\) are the fitting coefficients obtained as shares of the RR- and RRa-P3HT reference spectra in the Raman spectrum of the blend (Supporting Information, Section 3.2); \(T\) is the temperature, \(\sigma_{RR}/\sigma_{RRa} = 1.2 \pm 0.2\) is the ratio of Raman cross sections of the reference samples (Supporting Information, Section 3.2). This ratio was obtained from Raman and Fourier-transform infrared (FTIR) absorption spectroscopies (see Supporting Information, Section 3.2). Unlike the approach based on comparing visible absorption spectra proposed in ref 32, the method applied here benefits from direct measurement of the chromophore density in the sample and hence should be more accurate for calculation of the relative Raman cross sections. IPC = 1 corresponds to the annealed pristine RR-P3HT film, whereas IPC = 0 corresponds to the amorphous polymer.

The Raman spectra of conjugated polymers depend on temperature (Figure S3a). Therefore, we measured the reference Raman spectra at all temperatures with a 1 °C step and used the corresponding spectra for calculation of the IPC according to eq 1. Note that the ratio of Raman cross sections of the reference samples does not show any temperature dependence (Figure S3b).

3. RESULTS AND DISCUSSION

3.1. Real-Time Tracking of Polymer Crystallinity. Figure 1 shows the polymer crystallization dynamics of the P3HT:PC61BM and P3HT:PC71BM films for different annealing temperatures for the fast annealing protocol. At high temperatures (105, 120 °C), the IPC reaches 90% of its final value faster than in 5 min and then levels off. At low temperatures (75, 90 °C), the IPC dynamics exhibit different behavior: the initial crystallization rate is significantly lower, which is assigned to lower mobility of the polymer chains so that the IPC does not reach the maximum achieved at higher temperatures. Note that IPC = 1 does not imply that all RR-P3HT is in the crystalline state, but only the fraction that can crystallize; the share of this fraction was estimated as ∼10% from the DSC data.

As follows from Figure 1, the higher annealing temperature results in faster IPC rising at the initial annealing stage for both PCBM. However, the polymer crystallization dynamics are somewhat different: the IPC rising amplitude during the first 2 min is lower for PC61BM (panel a) than for PC71BM (panel b), that is, from ∼0.43 to ∼0.65 versus from ∼0.49 to ∼0.8. This difference is explained by the effect of PC61BM and PC71BM on the polymer packing and will be discussed in detail in Section 3.3.

The OPD performance based on the P3HT:PC61BM blend depends strongly on the polymer crystallinity. Polymer crystallization results in the higher external quantum efficiency of the OPD and in the red shift of the absorption spectrum, which altogether lead to a significant PCE increase. To investigate the effect of crystallinity on the PCE, the photovoltaic performance of the solar cell samples was examined (Supporting Information, Section 5). The PCE showed excellent correlation with the IPC for both P3HT:PC61BM and P3HT:PC71BM blends (Figure 1, insets). Thermal annealing optimizes the BHJ morphology by increasing the crystallinity of the conjugated polymer chains in the active layer. This increases the charge mobility and reduces the energy of the lowest electronic states, thereby broadening the absorption spectrum. All this leads to an
increase in the short-circuit current and the PCE,52 which is fully consistent with our results. Moreover, the obtained correlation between the IPC and the PCE is in line with the previous studies probing the blend morphology and photovoltaic performance. Direct structural studies on P3HT:PC61BM and P3HT:PC71BM blends indicate that thermal annealing improves the polymer crystallinity, resulting in the PCE increase.36,53,54 Furthermore, such a directly measured morphological parameter as the crystal domain purity, which is closely related to the IPC, clearly correlates with the PCE for a wide range of OPD including high-efficiency solar cells.55

3.2. Solvent Effect. To unravel the slow polymer crystallization dynamics, an annealing protocol with a significantly slower (quasistatic) temperature increase is required. As was established previously for the P3HT:PC61BM blends,54 the dynamics of the C=C Raman band shift of P3HT during annealing was similar for the heating rates of 5 and 10 °C/min, indicating a quasistatic process. Therefore, for the slow annealing protocol, we chose a heating rate of 5 °C/min (Section 2), which allowed us to quantitatively describe the impact of the solvent and various fullerene derivatives (Section 3.3) on the polymer crystallization.

Figure 2 shows the IPC dynamics at the slow annealing protocol for P3HT:PC61BM and P3HT:PC71BM blend films prepared from different solvents. The data in both panels are subdivided into three areas: no evident IPC change at a temperature below ~50 °C; efficient polymer crystallization with a steep IPC increase in the range of 50–110 °C; IPC leveling off at temperatures above ~110 °C. According to the DSC data in ref 29, the glass transition temperature, \( T_g \), in the P3HT:PC61BM 1:1 blend is about 50 °C; therefore, \( T_g \) is well correlated with the beginning of efficient annealing (IPC increase).

Annealing significantly increases the IPC of the P3HT:PC61BM blend cast from CB, from 0.31 ± 0.04 to 0.74 ± 0.04. The IPC values before and after annealing are similar to those reported in ref 32: 0.42 to 0.94 (annealed at 140 °C for 30 min), respectively (the IPC are recalculated from the crystalline molar fraction reported in ref 32). The difference in the IPC most probably originates from different approaches to evaluate the \( \sigma_{RR}/\sigma_{RRa} \) ratio, which in ref 32 was reported as 0.6 (see the Supporting Information in ref 32). Using this value, we would obtain the IPC ranging from 0.45 ± 0.04 to 0.88 ± 0.04 before and after annealing, respectively, which is in better agreement with the values in ref 32.

Figure 3 shows a schematic representation of the observed crystallization behavior of a polymer:fullerene blend at quasi-equilibrium heating (i.e., slow annealing protocol). The crystallization dynamics represented by the black curve is similar to the measured IPC dynamics for the P3HT:PC61BM blend film shown in the Supporting Information, Figure S12a. According to the CC theory,56 CC occurs above the glass transition temperature at which the amorphous phase in a polymer system can acquire mobility. In the temperature range between \( T_g \) and \( T_m \) that is, during the CC process, the polymer chains from the amorphous phase of the blend tend to crystallize. The polymer crystallization dynamics are irreversible in the temperature range of 50–110 °C in Figure 2 (Figure S11). This temperature range is very similar to that reported for the P3HT:PC61BM blend by Demir et al.,23 who obtained \( T_m = 36 \) °C and the CC temperature region of ~70–150 °C from the rapid-scanning DSC. In our experiments, CC occurs at somewhat lower temperatures, in the range of 50–110 °C. The apparent difference in the CC temperatures can be assigned to different rates at which the sample was heated.24 In the present experiments, the heating rate was a factor of 100 slower than in the rapid-scanning DSC, so that the slow annealing protocol used herein is much closer to the...
thermodynamic equilibrium in the blend. Another reason for the mentioned difference could be assigned to the fact that the CC temperature depends on the film thickness.

The real-time Raman microscopy technique allowed us to identify and quantify polymer crystallization in the form of temperature dependence similar to that recorded in a DSC scan. Indeed, the slow heating protocol is similar to the one routinely used in DSC. However, in contrast to DSC, the Raman technique benefits from chemical selectivity of the Raman spectrum. Therefore, the IPC curves report crystallization dynamics of the polymer chains in the blend, whereas the DSC curves encompass the features of all the components in the blend including, for example, fullerene crystallization/melting. Moreover, the real-time Raman microscopy technique can be applied directly to the OPD active layer at standard OPD post-treatment conditions—this is important as $T_g$ and the CC temperature range depend on the film thickness.

Finally, the data collection on the thin films needs a few micrograms of material (i.e., the amount needed for film preparation), whereas DSC usually requires special nonequilibrium conditions and several milligrams of material.

To quantify the characteristic parameters of the blend film under annealing, we define the following quantities: (1) the IPC of the as-cast blend film, IPC$_{ac}$, that is an average value of the IPC below 50 °C; (2) IPC of the annealed blend film, IPC$_{ann}$, that is an average value of the IPC within a 10° window around the IPC maximum; (3) the initial IPC value which is provisionally defined as the latest value above the 5% uncertainty margin of the IPC$_{ac}$ value: IPC$_i$ = IPC$_{ac}$ + (IPC$_{an}$ − IPC$_{ac}$)$\times$0.05, and a temperature corresponding to the initial IPC, $T_{CCi}$, at which CC starts; (4) a temperature at which CC ends, $T_{CCe}$, corresponding to the final IPC, IPC$_f$ = IPC$_{ac}$ + (IPC$_{an}$ − IPC$_{ac}$)$\times$0.95. This temperature corresponds to the upper limit of CC: all the polymer chains that could crystallize have been crystallized. These four parameters are presented in Figure 2 as the coordinates of the rectangles’ corners (the parameter values are presented in Table S2).

As follows from Figure 2, the initial IPC values depend on the type of solvent. Increasing the solvent boiling temperature in series of CF, CB, and DCB (boiling temperatures are 61, 131, and 181 °C, respectively) increases the solidification time of the liquid spin-cast films, which is determined by the solvent evaporation time, and results in longer time available for mobility of the polymer chains. This mobility fosters the initial crystallization during the film solidification and results in a clear correlation between the IPC$_i$ and the solvent boiling temperature (Table S2). Note that P3HT solubilities are very close in CF, CB, and DCB (14–16 g/L), whereas PC$_{61}$BM solubilities in these solvents are different (29, 60, and 42 g/L, respectively) and do not correlate with the IPC (Figure 2a). This could be explained by the fact that the acceptor solubility largely affects the aggregated acceptor phase but not the mixed polymer:fullerene phase and hence the IPC.

Figure 2 indicates that the higher boiling solvent DCB as compared to CF results in an increase of the CC temperature range (the horizontal size of the rectangles) from 50–100 °C to 55–115 °C and from 45–100 °C to 60–120 °C for P3HT:PC$_{61}$BM and P3HT:PC$_{71}$BM, respectively. However, the CB-cast films show the same IPC$_i$ as those prepared from DCB. Meanwhile, the CF-cast film exhibits the lowest IPC that does not achieve the maximum after annealing as was observed for the other solvents. Even though the initial IPC of the CF-cast and CB-cast films are very close, the IPC in the annealed CF-cast film is significantly lower (Figure 2). This indicates that the maximal IPC value critically depends on the solvent type, and the fullerene acceptor solubility might be an essential factor. Therefore, the particular solvent used for blend preparation can increase both IPC$_i$ and IPC$_f$. However, casting blends from some solvents (e.g., CF) might negatively affect the polymer phase crystallinity, not allowing the highest IPC value even after thermal annealing of the blend films. As the films prepared from DCB showed the highest crystallinity, we decided to choose DCB as a solvent for the further study of blends of P3HT with different fullerene acceptors.

3.3. Various Fullerene-Based Acceptors. In the Raman technique, the IPC exclusively accounts for the properties of the polymer (donor) component in BHJ. As the acceptor component could affect both amorphous and crystalline phases of the blend, we studied how various fullerene derivatives influence the polymer crystallization dynamics during annealing.

Figure 4 shows slow annealing dynamics for P3HT:fullerene 1:1 blends spin-cast from DCB. All the blends demonstrate the
According to the published data, the fullerenes blended with the amorphous polymer blends, this ratio highly depends on the portion of the crystalline and the other blend components that are unable to intercalate into the polymer crystalline phase between the nearest polymer side-chains in poly(terthiophene):PC61BM. Nevertheless, there is an insusceptible difference in the ratio between the weights of the polymer species that can crystallize and the other blend components that are unable to contribute to the crystalline phase. In the case of P3HT:fullerene blends, this ratio highly depends on the portion of the fullerene acceptor blended with the amorphous polymer phase. According to the published data, PC60BM can intercalate into the polymer crystalline phase between the nearest polymer side-chains in poly(terthiophene):PC60BM and poly(2-methoxy-5-(3,7-dimethyloxy)-p-phenylene vinylene):PC60BM. Nevertheless, there is an insufficient space between the side-chains of the ordered RR-P3HT to allow the fullerene intercalation. Meanwhile, all the investigated fullerene derivatives are miscible with P3HT, which might result in the amorphous P3HT:fullerene phase. Above the amorphous phase gains mobility, allowing CC to commence, and the IPC starts to grow. Therefore, the CC temperature range \( T_{\text{CC}} \) is determined by the amorphous phase composition, namely, the polymer:fullerene weight ratio and the fullerene derivative type.

To understand whether the chemical composition of the fullerene addend affects the polymer phase crystallinity in the blend films, in Figure 5a we plot the IPC as a function of the fullerene acceptor molar volume (the IPC vs the fullerene weight is given in Figure S14a). The molar volumes for P3HT and C60, PC60BM, PC71BM, and bis-PC60BM were taken from ref 14, and, for the other fullerene derivatives, they were calculated as a sum of the van der Waals volumes of the fullerene cage and the corresponding addend as described in ref 59 (ref 60 for an Ir atom). The approximately linear correlation between the IPC in the blend and the fullerene acceptor molar volume might be attributed to the P3HT:fullerene miscibility in the polymer amorphous phase, that is, the less fullerene acceptor volume affects more the polymer phase, leading to the lower IPC in as-cast blends. However, the initial IPC does not show any clear correlation with the fullerene acceptor solubility (Figure S13). This is in line with the data from ref 61, which show that the fullerene acceptor solubility, albeit important, is not directly correlated with the PCE. Similar to the fullerene acceptor solubility, the PCE generally increases with increase of the IPC upon annealing, but this trend is not universal (Table S2).

Figure 5b plots the IPC versus the IPC for all the P3HT:fullerene blends studied. These IPCs show a positive correlation, indicating that the lower limit of the IPC is determined by its initial value (IPC). Note the apparent similarity between CC and solid film formation from the solution (e.g., by spin-casting): the mobility of the polymer chains at temperatures higher than \( T_g \) is akin to the polymer fluidity in the liquid film formed upon film-casting. As a result, polymer crystallization occurs both during film drying and thermal annealing of the P3HT:fullerene blends. However, the room for the increase of polymer crystallinity is limited: the fullerene acceptor disturbs the polymer crystallinity during film drying (leading to lower IPC), the lower the IPC, the more the fullerene acceptor solubility (Figure S13). This is in line with the CC theory of polymers.

4. Conclusions

In summary, we have demonstrated Raman microscopy to be a powerful tool to probe polymer CC dynamics in real-time during thermal annealing. The CC of polymer chains is shown to operate within the temperature range of 50–150 °C in various P3HT:fullerene blends. The IPCs of P3HT:PC60BM and P3HT:PC71BM annealed blends show excellent correlation with the PCE of organic solar cells based on the blends. The refined Raman microscopy technique has allowed us to monitor the dynamics of CC of P3HT:fullerene blend films in real-time at subsecond timescales right during temperature annealing. This technique is similar to DSC but, in contrast, can be applied directly to the solar cells’ active layer and benefit from high chemical selectivity and spatial resolution. The results show that the parameters important for polymer crystallization in the BHJ are the annealing temperature, solvent, and acceptor type. Specifically, the casting blend from the higher boiling solvent results in a larger quasicrystalline phase in as-cast films. Furthermore, we found a correlation between the fullerene addend weight and the polymer...
crystallinity for as-cast films, and also a correlation of the polymer crystallinity at the start and end of the CC. The real-time Raman microscopy technique might be easily extended to an in situ study of CC dynamics during another popular annealing technique, solvent vapor annealing.

As Raman microscopy is chemically selective, it has the ability to clearly distinguish the donor and acceptor species in the blend and hence a high potential to probe crystallization of either the donor or the acceptor component in BHJs separately. From this point of view, it will be interesting to study the crystallization of the acceptor component (be it a fullerene derivative or another polymer or a small-molecule acceptor), which could also contribute to charge photogeneration in organic solar cells.

The spatial resolution of standard Raman microscopy as used herein does not suffice to probe the nanomorphology that is of key importance for the OPD performance. A radical increase of the spatial resolution to directly distinguish the donor/acceptor domains of a few tens of nanometers in size could be achieved with the tip-enhanced Raman microscopy. Indirect morphology retrieving by time-resolved Raman microscopy is also in the horizon similar to the early-reported pump-probe approaches. This together with the ability of Raman microscopy to distinguish crystalline and amorphous phases in vivo (as demonstrated in this paper) of the donor and acceptor components makes it a powerful tool for optimization of the morphology in real-time, which is hardly accessible to other structural methods.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b03136.

Chemical structures of the fullerene derivatives studied; fabrication of organic solar cells; tracking polymer crystallinility; excitation assisted laser annealing; correlation between the PCE and IPC; supporting data of the slow annealing protocol; IPC and $T_{CC}$ charts for P3HT blends with various fullerene acceptors (PDF)

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**Author Contributions**

V.V.B. conceived the project; A.A.M. participated in its further development. A.A.M. performed the preparation of polymer-fullerene films and their Raman microscopy study. A.A.M. and V.V.B. developed the real-time protocol. E.V.F. performed the Raman study under the fast annealing protocol. V.A.T. fabricated the solar cells and evaluated their PCEs. D.Y.P. and M.S.P. supervised the development of the project. A.A.M., V.V.B., M.S.P., and D.Y.P. wrote the article.

**Notes**

The authors declare no competing financial interest.

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**ABBREVIATIONS**

OPD, organic photovoltaic device; CC, cold crystallization; IPC, index of polymer crystallinity; DCB, orthodichlorobenzene; CB, chlorobenzene; CF, chloroform; PCE, power conversion efficiency; P3HT, poly(3-ethylthiophene); PC$_{61}$/BM, [6,6]-phenyl C$_{61}$/benzyl butyric acid methyl ester; HBIM, 1,3-(5-dimet-butyl-4-hydroxybenzyl)-3-(3-cyclopropane[1,9][C$_{60}$]h$_{1}$[6,5]-fullerene-3-yl)-indolin-2-one; AIM8, 1-tetracyclic-3-(3-cyclopropane[1,9][C$_{60}$]h$_{1}$[5,6]-fullerene-3-yl)-indolin-2-one; IrC$_{60}$ exohedral metallocomplex ($\eta_2$-C$_{60}$)IrH(CO)[(+)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane]; bisPC$_{61}$BM, [6,6]-di-phenyl-C$_{60}$/bis(butyric acid methyl ester)

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