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Measuring Domain Sizes and Compositional Heterogeneities in P3HT-PCBM Bulk Heterojunction Thin Films with ¹H Spin Diffusion NMR Spectroscopy

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The application of ¹H spin diffusion nuclear magnetic resonance (NMR) is expanded to polymer-fullerene blends for bulk heterojunction (BHJ) organic photovoltaics (OPV) by developing a new experimental methodology for measuring the thin films used in poly-3-hexylthiophene-phenyl C61-butyric acid methyl ester (P3HT-PCBM) OPV devices and by creating an analysis framework for estimating domain size distributions. It is shown that variations in common P3HT-PCBM BHJ processing parameters such as spin-coating speed and thermal annealing can significantly affect domain size distributions, which in turn affect power conversion efficiency. ¹H spin diffusion NMR analysis reveals that films spin-cast at fast speeds in dichlorobenzene are primarily composed of small (<10 nm) domains of each component; these devices exhibit low power conversion efficiencies ($\eta = 0.4\%$). Fast-cast films improve substantially by thermal annealing, which causes nanometer-scale coarsening leading to higher efficiency ($\eta = 2.2\%$). Films spin-cast at slow speeds and then slowly dried exhibit larger domains and even higher efficiencies ($\eta =$ 2.6%), but do not benefit from thermal annealing. The ¹H spin diffusion NMR results show that a significant population of domains tens of nanometers in size is a common characteristic of samples with higher efficiencies.

1. Introduction

Organic photovoltaic (OPV) devices are promising candidates for low-cost solar energy conversion because their fabrication employs modern polymer processing techniques, such as rollto-roll coating, that have cost advantages over vacuum-based methods used for inorganic solar cells. Recently, much OPV research has focused on polymer/fullerene blends to create 80 to 200 nm thick bulk heterojunction (BHJ) films.^[1,2] The BHJ design attempts to reconcile the need for small domains due to the small exciton diffusion length, e.g., 6 nm to 10 nm,^[3–7] with

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the requirement for an optical path length of at least ≈80 nm for sunlight absorption.^[8] The ideal BHJ is thought to consist of pure absorber and acceptor phases, with the absorber domains having a dimension smaller than the exciton diffusion length, and with interpenetrating, bi-continuous networks of both phases in contact with the appropriate electrodes. While the record reported efficiencies for BHJ OPV devices continue to rise (currently at $\eta \approx 8.3\%$),^[9] it remains a challenge to establish robust correlations between film processing, device performance, and blend morphology. The length scales in BHJs that are relevant to exciton dissociation (e.g., exciton diffusion length) are significantly less than 100 nm and resolving such finely mixed phases with common thin-film analytical techniques such as microscopy and scattering is difficult because of the complexity of the BHJ structure and the chemical similarity of the two organic phases. Measuring the impacts of BHJ phase distribution, purity,

and domain size on device performance remains a critical need in efforts to design better OPV materials and fabrication processes.

Solid-state nuclear magnetic resonance (NMR) spectroscopy is a powerful method to measure the nanoscale structure of polymer blends and has even been utilized in characterizing OPVs.^[10-12] A particularly useful method for measuring domain sizes in polymer blends is the "spin diffusion" NMR experiment, which has been demonstrated on multiple polymer blends.^[13-16] One of the critical advantages of using ¹H spin diffusion NMR above other techniques is the enhanced spatial sensitivity since $^{1}\text{H}-^{1}\text{H}$ spin exchange occurs at the atomic ($\approx 0.1 \text{ nm}$) size scale allowing for very small domains (<5 nm) to be measured even in well-mixed regions where other techniques (microscopy) may have problems with resolution. We recently demonstrated that ¹H spin diffusion NMR measurements could be applied to polymer-fullerene BHJ blends to estimate the extent of phase separation. Our work at that time was limited to ≈100 µm thick flakes of the poly-3-hexylthiophene (P3HT) and phenyl-C61butyric acid methyl ester (PCBM) blend, due to signal-to-noise





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requirements and the lack of a suitable thin-film preparation protocol.^[17] Although our early work demonstrated the capability of solid-state NMR spin-diffusion to measure domain dimensions in P3HT-PCBM blends, it could not be confirmed whether the morphology of our thick flakes resembled the morphology in thin films.

Here, we expand the application of solid-state NMR spindiffusion measurements to the same thin films that are used in OPV devices. This critical advance is enabled primarily by a new set of essential sample preparation protocols, which we describe here. Despite the very small sample volumes of these thin films (>>0.2 mm³), we show that ¹H spin diffusion NMR curves can be obtained with adequate signal-to-noise in a reasonable amount of time (24 h). We find that the compositional heterogeneities that exist in BHJs span approximately two orders of magnitude in size, depending on processing conditions. The device efficiency is strongly correlated to the fraction of domains tens of nanometers in size regardless of processing method.

A typical P3HT-PCBM BHI film is cast from a solution containing both components and can deliver up to ≈5% power conversion efficiency under optimized conditions.^[8] The efficiency of the P3HT-PCBM blend can vary significantly depending on processing conditions. For example, solvent,^[8,18] casting recipe, and post-casting treatment have all been shown to affect power conversion efficiency.^[8,18–23] The variability in power conversion efficiency is generally attributed to morphological changes in the active layer, despite the general lack of consistent and direct correlations between power conversion efficiency and morphology.^[8,18-23] Here we will compare two popular processing approaches that are both thought to result in a near-optimal efficiency and morphology: 1) improvement of a less-optimal film by thermal annealing after casting and 2) slow solidification using a low spin-coating rotational speed followed by covered drying.^[24–25] We evaluate the effects of both approaches on the sizes of the donor and acceptor domains via ¹H spin diffusion NMR.

2. Results

2.1. Thin-Film Preparation

BHJ films were prepared using two casting recipes, either with or without a subsequent thermal annealing step, resulting in the four distinct film preparations in **Table 1**. The effect of thermal annealing was evaluated by first preparing a less-optimal film by

spin-casting at a high rotational speed of $2000 \times 2\pi/60$ rad s⁻¹ (2000 rpm) from a solution at 30 mg mL⁻¹ in 1,2-dichlorobenzene, which we will refer to as a "fast-cast as-cast" film. Fast solidification of the BHJ generally produces poor power conversion efficiency in devices.^[22,26–29] Heating the fast-cast, ascast film for 30 min at 140 °C produced a "fast-cast annealed" film. Thermal annealing of fast-cast BHJ films typically yields a improvement in power conversion efficiency.^[22,26-29] The effect of slow solidification was evaluated by spin-casting a film at a low rotational speed of $600 \times 2\pi/60$ rad s⁻¹ (600 rpm) from 15 mg mL⁻¹ solution, then removing the still-wet film and allowing it to dry slowly while covered, to produce a "slow-cast as-cast" film.^[25] BHJs prepared in this way generally exhibit high conversion efficiencies. For completeness, we annealed the slow-cast, as-cast film to produce a "slow-cast annealed" film, even though thermal annealing typically does not benefit slowcast films.^[27] Solution concentrations were adjusted to maintain a constant film thickness (>>100 nm). These four BHJ recipes were also used to prepare OPV devices.

Solid-state NMR experiments require the films to be removed from their substrates, and therefore careful consideration of the substrate is required. We cast our BHJ films on deuterated polystyrene sulfonic acid (d-PSS)-coated Si wafers. The d-PSS was chosen to mimic the surface of the commonly used hole-injection layer PEDOT-PSS, while exhibiting no residual ¹H NMR signal. The BHJ films were removed from their substrates by submerging the wafer in D₂O in an H₂O-free environment (<1% relative humidity (R.H.)), which dissolved the d-PSS. The free-standing films were then collected and dried in a desiccator.

2.2. ¹H CRAMPS NMR

Solid-state NMR is a valuable technique for investigating molecular-scale organization in polymers because the nuclear signal is sensitive to local environment. In fact, specific chemical moieties on a polymer can often be isolated by chemical shift in high-resolution NMR spectra. To obtain the necessary resolution in the solid state, combined rotation and multiple pulse spectroscopy (CRAMPS)^[30] is often employed, producing spectra where resonance positions are determined primarily by the isotropic chemical shifts of protons. Spectra collected by ¹H CRAMPS on solid-state samples may have linewidths and resonance positions that are affected by secondary static^[31] and dynamic effects.^[32] The linewidth is often diagnostic of polymer chain conformation: narrow ¹H CRAMPS resonances are generally associated with rigid, ordered polymer chains and

 Table 1. The four recipes utilized for making thin films of P3HT-PCBM. All films were spun-cast for 60 s.

Sample	Concentration 1,2-dichlorobenzene [mg mL ⁻¹]	Spin-casting rate [rpm]	Covered drying time [min]	Thermal annealing temperature [°C]	Thermal annealing time [min]
Fast-cast as-cast	30	2000	-	-	
Fast-cast annealed	30	2000	-	140	30
Slow-cast as-cast	15	600	30	_	
Slow-cast annealed	15	600	30	140	30

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Figure 1. 1 H CRAMPS spectra of a) neat P3HT, b) neat PCBM, and c) a physical mixture (50:50 by mass).

broader lines are associated with disordered (and potentially mobile) chains. $^{\left[31\right] }$

The ¹H CRAMPS spectra of neat bulk P3HT and PCBM are given in **Figure 1**; the higher signal-to-noise bulk spectra are shown for demonstration purposes. Spectra of neat P3HT and PCBM films are similar to these bulk spectra, which we present to describe the general resonance lineshapes and locations, not for quantitative comparison to the BHJ film spectra that we will describe later. The ¹H CRAMPS spectrum of P3HT is composed

of two distinct contributions: the thirteen side-chain aliphatic protons (carbons 1 through 6) resonate from 1 to 3 ppm, and the single, main-chain thiophene proton (on carbon 7) resonates near 6 to 7 ppm. The slightly downfield shoulder of the thiophene proton is presumably due to locally disordered sites in the semicrystalline solid. The PCBM ¹H CRAMPS spectrum is also composed of two distinct contributions: the aliphatic protons (on carbons 1 through 4) resonate near 3 ppm, and the aromatic protons resonate near 8 ppm. The ¹H CRAMPS spectrum of a bulk blend of the two components (50:50 by mass) is shown in Figure 1c. The blend spectrum is a weighted average of the two components in the ratio 85:15 (P3HT:PCBM), reflecting the different proton densities in the two components. In the 50:50 blend spectrum, the PCBM contribution to the resonances of the aromatic and aliphatic protons is 47% and 11%, respectively. The shape of the aromatic proton resonance is therefore more sensitive than the aliphatic resonance to the organization of PCBM, whereas the shapes of both resonances are potentially sensitive to the organization of P3HT.

The ¹H CRAMPS spectra of BHJ thin films are shown in **Figure 2**. We will confine our discussion primarily to the aromatic protons, since the breadth of the thiophene proton resonance of P3HT at ~6 ppm is closely correlated to the conformation of the P3HT backbone. The spectrum of the fast-cast as-cast sample indicates substantial conformational disorder in P3HT since the thiophene resonance exhibits no narrow feature; instead it overlaps with the upfield resonance of the PCBM phenyls and forms what appears to be a single broad peak. Upon annealing this film at 140 °C ("fast-cast anneal") the thiophene resonance narrows significantly, such that it can easily be discriminated as a separate peak from the downfield PCBM phenyl resonance. This result proves that thermal



Figure 2. ¹H CRAMPS spectra of P3HT-PCBM thin films. Spectra labels are defined in Section 2.1.

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Figure 3. 2D Grazing-incidence X-ray diffraction patterns of a) fast-cast as-cast, b) fast-cast annealed, c) slow-cast as-cast, and d) slow-cast annealed films. Indexing of (c) and (d) are identical to (a). Full pole figures showing the orientation distribution of the (100) P3HT reflection of the e) fast-cast and f) slow-cast films.

annealing increases the conformational order of the P3HT backbone, likely due to increased P3HT crystallinity.

attained either by thermally annealing a fast-cast sample or imply by using slow-cast methods.

The slow-cast as-cast films exhibited a high degree of main chain order as well, as evidenced by the clearly discriminated thiophene peak, which is somewhat narrower than that of the fast-cast annealed sample. Further annealing to create the slowcast annealed sample further increases the narrowness of the thiophene proton resonance. This spectrum, among all of the thin film ¹H CRAMPS spectra, has a thiophene proton resonance that most closely resembles that of neat P3HT in Figure 1. We note that there exist trends in the aliphatic portions of the thin film ¹H CRAMPS spectra that correlate well with the differences in the thiophene proton resonance, but in some cases these changes are complex and a complete analysis of P3HT side chain behavior is outside the scope of this manuscript. In summary, the ¹H CRAMPS spectra reveal that the effect of thermal annealing is less significant in slow-cast films than in the fast cast films. A state of thiophene proton order can be

2.3. Grazing Incidence X-Ray Diffraction (GIXD)

Although the aromatic proton features of the ¹H CRAMPS spectra are sensitive to local packing, they are not as sensitive to long-range order. We used grazing incidence X-ray diffraction (GIXD) to measure the extent of long-range order in the BHJ films. GIXD is frequently used for characterizing the crystal orientation, structure, and relative degree of crystallinity in polymer thin films and BHJs.^[33–35]

GIXD patterns of the four films are given in **Figure 3**. All four films exhibit a strong (H00) series of reflections with 3 orders of peaks due to the P3HT lamellar stacking, as well as a (020) reflection due to intermolecular π -stacking. These films also exhibit a broad halo which is due to amorphous PCBM at



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 $q \approx 1.4 \text{ Å}^{-1}$. In the fast-cast as-cast BHJ film, the P3HT crystallites are oriented with the (020) spacing predominantly parallel to the film plane (solid line in Figure 3e), indicating that the polymer chains are primarily oriented with the thiophene ring edge-on with respect to the substrate with a small fraction of chains that are oriented plane-on. When the fast-cast film is annealed, the orientation distribution of the ordered regions becomes more pronouncedly bimodal (dashed line, Figure 3b), with the growth of a significant fraction that is oriented plane-on ((020) spacing perpendicular to the substrate) as evidenced by the increased intensity >60° (and $< -60^{\circ}$) in Figure 3e (dashed curve). In addition, the overall (100) signal becomes significantly more intense upon annealing (as quantified in the Supporting Information), showing increased polymer crystallinity. The coherence length of crystallites oriented plane-on increased from 7 nm to 17 nm making it difficult to assign the increased crystallinity to either the growth of new crystallites or ripening of pre-existing crystallites from the GIXD data alone. In both the slow-cast films (Figure 3c,d,f), the ordered P3HT appears to be predominantly oriented edge-on with the (020) direction parallel to the substrate, and no significant change in orientation upon annealing. The increase in intensity upon annealing combined with the sharpening of the peaks is consistent with a ripening of crystallites.

2.4. ¹H Spin Diffusion NMR

¹H spin diffusion NMR is an established method for measuring the degree of miscibility of two-component blends.^[13–16] Our spin-diffusion experiment consists of two basic steps: 1) establishing a chemical-shiftbased magnetization gradient between the

two components and 2) measuring the magnitude of that gradient as a function of mixing time $t_{\rm m}$. We have previously shown that that it is possible to establish a clean average-magnetization gradient between P3HT and PCBM, even though they have significant spectral overlap, due to the different aliphatic to aromatic proton ratios in P3HT (large ratio) and PCBM (small ratio).^[17] The initial rate of decay of this magnetization gradient is related to the ratio of interfacial surface area to volume in the sample, which is in turn related to domain size. The domain size or distribution of sizes can be determined if the spin diffusion constants are known and a general morphology for the blend (e.g., lamella, rod/matrix) is either known or assumed.^[13,36]

To measure the decay of the magnetization gradient, its magnitude must first be quantified at each $t_{\rm m}$, which can be

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Figure 4. ¹H NMR spectra of P3HT-PCBM: a) CRAMPS spectrum of the physical mixture (50:50 by mass); b) CRAMPS spectra of the neat components (PCBM is inverted) demonstrating the component breakdown of c) the spin diffusion spectrum of the physical mixture ($t_m = 2$ ms); d) CRAMPS spectrum of the slow-spin unannealed thin film blend, e) the spin diffusion spectrum of the physical mixture ($t_m = 2$ ms), and f–i) spin diffusion spectra of the slow-spin unannealed thin film blend for $t_m = 2$ ms (f), 30 ms (g), 60 ms (h), and 240 ms (i).

achieved by comparing the experimental intensity to that of a physical mixture at the same composition. Alternatively, the blend spectrum can be separated into contributions of the neat components, as demonstrated in **Figure 4**a–c, which show: a) the CRAMPS spectrum of the physical mixture, b) the contributions of the positive P3HT and negative PCBM polarizations, and c) the spin diffusion spectrum ($t_m = 2$ ms), which appears as a sum of the neat component spectra. We typically quantify the magnitude of the magnetization gradient by comparison to a physical mixture, though both comparison and separation methods provide similar results. These methods ignore the variations in spectral lineshapes caused by differences in molecular order as discussed in Section 2.2. These spectral variations have an insignificant effect on the quantification of the magnetization gradient magnitude compared to the more

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significant artifact of pulse amplitude variability and so can be ignored. The magnitude of the magnetization gradient cannot be quantified for mixing times less than 2 ms because intramolecular spin equilibration is incomplete.^[14–16] All intracomponent magnetization gradients are >97% equilibrated after 2 ms as evidenced by an invariant lineshape, so any decay after that time can be attributed solely to intercomponent exchange, also called "spin diffusion."

Typical ¹H spin diffusion NMR spectra of the P3HT-PCBM thin films are given below in Figure 4f-i. Figure 4e shows the spectrum of a physical mixture where there is essentially no spin diffusion for comparison. After 2 ms of mixing (Figure 4f) the intensity of the spectrum is significantly decreased relative to Figure 4e due to spin diffusion. Further decreases in intensity are observed after 30 ms (Figure 4g), and 60 ms (Figure 4h). The magnetization gradient approaches zero at long mixing times (240 ms, Figure 4i), when the magnetization has come to equilibrium. It is possible that these results are influenced by the decay of magnetization via longitudinal relaxation, which occurs on a significantly longer time scale, $T_1 \approx 680$ to 800 ms, where T_1 is the longitudinal relaxation time, and we correct the magnitude of the magnetization gradient accordingly when analyzing the decay.^[17] Typically T_1 also sets an upper limit for $t_{\rm m}$, i.e., $t_{\rm m} < T_1$.

The decay of the magnetization gradient is most directly analyzed by plotting the normalized change of magnetization, ΔM , versus the square root of the mixing time, $t_{\rm m}^{1/2}$. ΔM is proportional to the average magnetization gradient between the two components, corrected for longitudinal relaxation. ΔM is normalized such that $\Delta M = 1$ at $t_m = 0$ and $\Delta M = 0$ upon sample-wide equilibration. In situations where there is no spin diffusion between components (e.g., in a physical mixture), $\Delta M = 1$ for all $t_{\rm m}$. Typically, two-component blends that are mixed on the molecular level (i.e., ≈1 nm) exhibit decays that approach zero very rapidly ($\approx 2 \text{ ms}^{1/2}$), whereas phase-separated systems exhibit decays of ΔM over a longer timescale where ΔM may not approach zero during the time window of the experiment; recall $t_m < T_1$. A more thorough description of this type of spin diffusion plot has been given in earlier studies.[36]

Spin diffusion plots of the four thin film samples are shown in Figure 5. The fast-cast as-cast sample shows the fastest decay, coming close to equilibrium over the short time scale of >>6 ms^{1/2}. The fast-cast sample is therefore well mixed, with domain sizes less than 10 nm (quantification will be further discussed below). After annealing, the spin diffusion curve exhibits a significantly slower decay, indicating increased phase separation that appears with the increased P3HT order detected by both the CRAMPS resonance lineshape analysis and our GIXD measurement. The slow-cast, as-cast film exhibits a slower decay than the fast-cast, as-cast film, demonstrating that spincoating speed affects the degree of mixing. Upon annealing, the slow-cast film shows little change in its spin diffusion curve, suggesting little to no change in the degree of phase separation of the two components. Interestingly, the component interfaceto-volume ratio is the highest for the fast-cast film and becomes the lowest after thermal annealing. The slow-cast film exhibits an intermediate component interface-to-volume ratio that does not change significantly after annealing. This demonstrates



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Figure 5. ¹H spin diffusion NMR curves of thin P3HT-PCBM films spuncast for different recipes. The last two 600 rpm (no anneal) data points (open squares) are covered by the 600 rpm (anneal) data points (black squares).

that the initial state of the film determines the degree of phase mixing for a given annealing protocol.

3. Discussion: Domain Size Distribution, Morphology Formation, and Correlation to BHJ Operation

3.1. Analysis Framework for ¹H Spin Diffusion NMR

Domain sizes can often be determined from the characteristic decay of the spin diffusion. For well-behaved two-component systems with a narrow domain size distribution, such as block copolymers of similar proton densities, the domain size can be determined from the initial decay slope. A straight line is fit to the early mixing time data, and the *x*-intercept of that line, $t_{1/2}$ * (ms^{1/2}) can be used to calculate the domain size, *x* (nm), of the minority phase, *a*, using Equation 1

$$x = \frac{\varepsilon}{f_{\rm b}} \sqrt{\frac{4 \, D_{\rm eff}}{\pi}} t_{1/2^*} \tag{1}$$

where ε is the dimensionality of the morphology (1 for lamella, 2 for rods-in-a-matrix, 3 for spheres-in-a-matrix), f_b is the volume fraction of the major phase, *b*, and D_{eff} is the effective spin diffusion coefficient (nm² ms⁻¹), which is the geometric mean of the spin diffusion coefficients in phases *a* and *b*.^[36]

We found that the analysis described above could not be applied to the spin diffusion curves for the BHJ samples (Figure 5) because the early time slopes were typically not linear. The non-linearity results from a broad distribution of domain sizes. An alternative approach to the analysis in Equation 1 is



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to model the spin diffusion curve over the measured $t_{\rm m}$ range, and to fit the measured spin diffusion data to the model by varying the model parameter for the domain size of phase separation.

The construction of a model for spin diffusion rests on several assumptions. First, we must assume that the ¹H spin diffusion process is isotropic and Fickian in both phases, and that both domains are relatively pure. Recall that ¹H spin diffusion NMR probes size scales on the order of the PCBM molecule or P3HT monomer (<1 nm), so the presence of a mixed $\mathsf{phase}^{[37-39]}$ does not a priori compromise this assumption. Secondly, we must assume a morphology. We considered simple geometric model morphologies with regular domain size and shape and regular spacing between domains. These included: 1) a lamellar morphology and 2) a rods-in-a-hexagonal-matrix morphology. A spheres-in-a-matrix morphology was intentionally omitted since it is more typical of minor phases whose fractions are below 0.10.

The most important parameter of the model is the spin diffusion constant (D_{eff}). We determined the spin diffusion constant experimentally by performing a ¹H spin diffusion measurement on a bilayer of 28 nm thick P3HT and 51 nm thick PCBM that was prepared by evaporating PCBM onto a neat P3HT layer. The film thicknesses were determined via both X-ray and neutron reflectivities (data not shown) and varied by no more than 1 nm. The ¹H spin diffusion NMR is

given in **Figure 6** (black circles). The "effective" spin diffusion constant of this bilayer (e.g., including diffusion within P3HT and PCBM) was found to be $\approx 0.4 \text{ nm}^2 \text{ ms}^{-1}$ by way of comparison to simulated curves for multiple spin diffusion coefficients (black lines). The slight non-linearity at early times is likely due to interface roughness. This result is surprisingly close to that predicted for neat P3HT from well-known empirical relations,^[13,40] indicating that the spin diffusion constant of PCBM is likely $\approx 0.4 \text{ nm}^2 \text{ ms}^{-1}$ as well.

The most important variable of the model is the domain size. The regular model morphologies considered here have a domain size that depends on two parameters: the morphology pitch *d* and the volume fraction of the respective components φ_i . In the lamellar morphology, the pitch is the thickness of a P3HT:PCBM layer pair, and the PCBM slab thickness is therefore $d\varphi_{\text{PCBM}}$. In the rods-in-a-hexagonal-matrix morphology, the pitch *d* is the distance between nearest rod centers, and the rod diameter is $1.05d(\varphi_{\text{PCBM}})^{0.5}$.^[41] We assume in all cases that $\varphi_{\text{P3HT}} = 60\%$ and $\varphi_{\text{PCBM}} = 40\%$, given the formulation ratio of 1:1 by mass and the pure component densities.

We simulated the spin diffusion process for these two morphologies at a variety of domain sizes, with results shown in **Figure 7**. The simulation reveals that there is a significant



Figure 6. a) ¹H spin diffusion NMR curve (black circles) of a thin P3HT-PCBM bilayer film (51 nm PCBM, 28 nm P3HT), simulated curves using various spin diffusion coefficients (black lines), and the best fit line (red line). b) The simulated magnetization profile of the P3HT-PCBM bilayer assuming a spin diffusion coefficient of 0.4 nm² ms⁻¹.

morphology dependence to spin diffusion behavior. As we expected based on our appraisal of the initial decay slope, the experimental spin diffusion curves in Figure 5 do not resemble any single simulated curve in Figure 7, indicating that the true sample structure possesses a distribution of domain sizes.

We incorporated this notion of a distribution into our data fitting by considering the simulated curves in Figure 7 as representative of spin diffusion in a certain domain size range. We then fit the experimental data to a linear combination of these simulated curves. The domain size distribution is then represented by the relative contributions of the simulated curves. In our analysis, we "bin" the domain distribution into the seven size categories corresponding to each curve in Figure 7. An eighth curve representing domains too large to observe any measurable decay was added as well ($\Delta M = 1$ for all $t^{1/2}$ _m). The data fit was performed using a linear least-squares fit of the data in the program $R^{[42]}$ using the bootstrap method.^[43] The fit included significant constraints on the coefficients (all coefficients sum to one, are positive, and range from zero to one). Although the assumptions of this fit (e.g., pure domains, no long-range compositional heterogeneities) may not be necessarily representative of the actual morphology, we use this framework as a first approximation for analyzing the rather www.afm-journal.de

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Figure 7. Model spin diffusion curves of various domain sizes assuming both lamellar (a) and rods-in-a-matrix (b) morphologies. The size associated with each curve is of the depleted phase (e.g., PCBM).

complex morphologies typically observed in BHJs and address particular shortcomings of the model below.

The coefficients generated from the fit were used to describe the estimated domain size distributions for both morphologies as given in **Figure 8**. The uncertainty of each fraction includes the experimental error of ΔM and the statistical quality of the fit. In general, this framework delivers domain size distributions with significant differences that are beyond the method uncertainty. It is notable that the distributions are of similar shape regardless of the assumed morphology. The experimental data in Figure 5 are represented quite well by this method, as shown



Figure 8. Estimated domain size distributions of thin P3HT-PCBM films assuming both lamellar (a–d), and rods-in-a-matrix (e–h) morphologies for different casting recipes. a,e) Spin-cast from solution at $2000 \times 2\pi/60$ rad s⁻¹ (2000 rpm) for 60 s. b,f) Spin-cast from solution at $2000 \times 2\pi/60$ rad s⁻¹ for 60 s and annealed at 140 °C for 30 min. c,g) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for 60 s. d,h) Spin-cast from solution at $600 \times 2\pi/60$ rad s⁻¹ for $60 \times 2\pi/60$ rad s⁻¹ for 60



The fast-cast as-cast sample exhibits a domain size distribution of almost solely (>80%) small domains (<10 nm, Figure 8a,e). Upon annealing, this film coarsens, exhibiting a very broad distribution of domains ranging to sizes greater than 100 nm (Figure 8 b,f). The slow-spun films exhibit a domain size distribution different from the fast-cast samples (Figure 8 c,d,g,h). The fraction of smaller domains is intermediate between the as-cast and annealed fast-cast

films. At the other extreme the fraction of large-scale domains is less than that of the fast-cast annealed sample.

It is notable that our analysis shows a significant population of domain sizes greater than 100 nm in the fast-cast annealed film in spite of the fact that the film thickness was about 100 nm. The implication is that there is some in-plane compositional heterogeneity on distance scales greater than 100 nm. In this connection, we looked into the possibility that such compositional variations could be due to the formation of large PCBM crystallites during annealing. Such crystallites have been shown to deplete the PCBM concentration surrounding the growing

crystallite,^[38,44] hence, creating a long range compositional heterogeneity that would produce a slow decaying component like what is observed in Figure 5 (solid circles). We looked for such crystallites using optical microscopy (data not shown) and concluded that less than 1% of the PCBM was in the form of (1 to 10) µm crystallites. Furthermore, since there was no significant crystalline PCBM signature in the GIXD data, it seems unlikely that such long range compositional heterogeneities are due to PCBM crystallization.

Since no pure, large domains were observed, we must instead carefully consider what information we can unambiguously extract from the spin diffusion plots (Figure 5), which are single profiles recording the overall rate at which composition-based polarization gradients disappear via spin diffusion. Even in a two-component system, the problem of mapping the spin diffusion profile into a detailed morphological picture is strongly underdetermined, especially if the thermodynamics and/or the kinetics introduce heterogeneity in domain size as well as local concentration. In the simpler case of immiscible glassy di-block copolymers, for example, a smaller set of variables influence the spin diffusion because one can expect uniform composition and domain size. In our case, a) the components are not tethered, b) one (or both) of the components crystallizes, c) there is some degree of miscibility between



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noncrystalline P3HT and PCBM,^[17,37–39,45], and d) there is likely some influence on the morphology from the presence and rate of escape of the solvent. Indeed, there are numerous reasons why spatial compositional heterogeneity would be expected in the P3HT-PCBM blend.

Returning to what we can learn from the domain size distributions (Figure 8) we note that these distributions should more correctly be understood as the length scale over which compositional variations occur (see Supporting Information). The caveat is that, if phases have mixed composition, the mass fraction of domains of a given size in Figure 8 would tend to overemphasize the fraction of smaller domains and correspondingly underestimate the fraction of larger domains. In BHJs, the distinctiveness of "domains" as a boundary between regions of well defined composition may only hold for the boundaries between crystalline P3HT and the mixed matrix material and is admittedly an ill-defined parameter in such a heterogeneous system. Regardless, this concept explains how a significant population of domains with size greater than 100 nm is found in our films; it can be attributed to lateral compositional heterogeneity on that length scale.

3.2. Mechanism of Morphology Formation

We turn again to the domain size distribution of the fast-cast annealed film (Figure 8b,f), which has a clear prevalence for long range spatial heterogeneity as opposed to the slow-cast films (Figure 8c,d,g,h). Considering how differently P3HT crystallites could form in these three films, such a finding is quite reasonable. In the case of the slow-cast film, it is likely that the rate of crystallization is comparatively slow and controlled by the concentration of solvent molecules with solidification occurring much closer to equilibrium. Annealing this relatively ordered film causes ripening of the P3HT crystallites without a significant change in the degree of compositional heterogeneity, suggesting that few or no crystallites are formed from the mixed phase.

P3HT crystallites that form from thermally annealing a more disordered, highly mixed film, such as the fast-cast film, will likely do so in a different manner from those discussed above. Annealing the fast-cast film increases the P3HT crystallinity, modifies the orientation distribution of crystallites, and introduces significant long-range compositional heterogeneity, suggesting that crystallites are formed from the mixed phase. The growth of these crystallites is likely to depend on local PCBM concentration and may not necessarily be confined to the preexisting crystallites. Furthermore, since the fast-cast as-cast film exhibited the lowest degree of P3HT order via GIXD and NMR, it represents the most probable candidate for melting and recrystallization of smaller and/or less ordered crystallites.^[46] It is likely then that the long range compositional heterogeneity that is observed after annealing the fast-cast film has its origins in the kinetics of crystallization from the mixed phase and/or from melting/recrystallization of P3HT, both of which could impart some degree of spatial heterogeneity to the distribution of P3HT crystallites.

This concept of spatial heterogeneity of P3HT crystallites can also explain why the fast-cast annealed film exhibited a

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significantly smaller mixed-phase fraction (1–3 nm domains, Figure 8b,f) than the slow-cast films, despite nominally similar P3HT crystallinities and a known miscibility of PCBM in noncrystalline P3HT.^[17,37–39,45] One potential cause for depleting the mixed phase is kinetic trapping of P3HT; if the molecular mobility of P3HT in the mixed phase is limited (i.e., tie-chains between crystals) and the fraction of free P3HT chains is low, then the probability of creating larger, purer PCBM aggregates would increase with heterogeneity. Such a scenario is possible for a high molecular weight, semicrystalline polymer such as P3HT, but remains somewhat speculative at this point.

3.3. Correlation to Photoluminescence Quenching

The photoluminescence (PL) quenching of a BHJ is related to its ability to harvest excitons, which is strongly dependent on the domain size. The PL of P3HT will be quenched if PCBM is located within an exciton diffusion length of exciton formation, so PL quenching can be used as a diagnostic of degree of mixing and photoinduced charge separation efficiency.[47] We performed PL quenching experiments on the four films studied, with spectra given in the Supporting Information. As shown in Table 2, the fast-cast as-cast film exhibits very low PL intensity $(I_{BHI}/I_{P3HT} = 0.04)$, indicating good mixing in agreement with the domain size distribution for that film, which is weighted toward small domains. The coarsening that occurs in the fast-cast annealed film is also confirmed, with an increase of the PL intensity ($I_{BHI}/I_{P3HT} = 0.2$). Interestingly, however, the PL quenching of both slow-cast films (as-cast and annealed) are approximately the same as the fast-cast annealed film. This result indicates that the fast-cast annealed film cannot have a significantly larger fraction of large, pure P3HT domains, i.e., crystallites, as would be suggested by Figure 8, assuming that the component interface (and hence exciton splitting efficiency) of the fast-cast annealed film is nominally similar to the slowcast films. The consideration discussed above permits us to instead interpret the large domain sizes in Figure 8 in terms of spatial heterogeneity: the fast-cast annealed film may have a greater extent of spatial heterogeneity than either slow-cast film.

3.4. Correlation to OPV Device Operation

The power conversion efficiency of an OPV device is its ultimate figure of merit, and it is important to determine how our

Table 2. Device (columns 2-5) and photoluminescence (column 6) characteristics of the four films studied.

	J _{sc} [mA cm ⁻²]	V _{oc} [V]	η [%]	FF	I _{BHJ} /I _{P3HT}
Fast cast, as-cast	1.6	0.65	0.4	0.39	0.04
Fast cast, annealed	6.1	0.61	2.2	0.59	0.2
Slow cast, as-cast	6.9	0.56	2.6	0.65	0.2
Slow cast, annealed	6.3	0.58	2.2	0.59	0.2

morphological measurements correlate to this. The device characteristics (short circuit current, $J_{\rm sc}$; open circuit voltage, $V_{\rm oc}$; efficiency, η ; fill factor, FF) of our four P3HT:PCBM films are shown in Table 2. It is clear that the worst device, the fast-cast as-cast film, represents the most highly mixed case, as seen from our ¹H spin diffusion NMR, with >80% of the domains being <10 nm in size. Such high interfacial area would be beneficial from an exciton dissociation perspective, which is exactly what we observe from our PL measurements. We can thus assign the rather poor device efficiency that is observed to the lack of charge harvesting, which could be due to either low mobility or excess recombination. The large fraction of noncrystalline P3HT present in this sample would lead to low hole mobility. Furthermore, molecularly dispersed PCBM would serve to obstruct charge if the domains were isolated.

The higher efficiencies of the other three devices seem to be roughly correlated to increased P3HT crystallinity, which is linked to the increased fraction of domains that are tens of nanometers in size. The best device, the slow-cast, as-cast film exhibits high power conversion efficiency without an annealing step. The decrease in power conversion efficiency after annealing the slow-cast film is curious, as the domain size distribution does not change significantly. Furthermore, the ¹H CRAMPS NMR and GIXD data indicate that order is gained in the polymer upon annealing (Figure 2c,d). Thermal annealing was done before the Ca/Ag metal was evaporated, so it is not due to metal penetration or oxidation. It is possible that annealing the slow-cast film causes a fraction of crystallites to ripen to sizes greater than the exciton diffusion length, or produces more resistive grain boundaries during growth.

We posit that thermal annealing is less optimal than slow solvent casting as a means to achieve the desired degree of phase separation in polymer–fullerene BHJ films. It is possible that the better efficiency of the slow-cast, as-cast film over the fast-cast, annealed film is due to the greater spatial homogeneity. Thermal annealing of the fast-cast film appears to result in greater spatially heterogeneity of domains, with large-scale compositional fluctuations on the >100 nm length scale. One might expect the formation of an efficient percolative charge transport network to be less favored in a film in which the domains are not uniformly distributed.

4. Conclusions

With appropriate experimental protocols and a well-developed analysis framework, ¹H spin diffusion NMR can be used to measure the domain size distributions in the same BHJ thin films that are used in OPV devices. Higher power conversion efficiency in our BHJ films correlates most closely to a significant fraction of domains in the tens of nanometers size range. There may also be a correlation of higher efficiency to a greater spatial homogeneity of domains. These results explain why thermal annealing is less optimal than slow solvent casting as a means to achieve the desired degree of phase separation in polymer-fullerene BHJ films.

Our analysis framework for ¹H spin diffusion could be improved by combination with other analytical techniques sensitive to local composition such as small angle scattering and



transmission electron microscopy. These techniques could be used to inform our morphological models, making discrimination of domain size versus spatial heterogeneity less ambiguous. ¹H spin diffusion NMR proves to be a valuable technique that provides information relevant to the BHJ active layer morphology and well-correlated to its operation in real OPV devices.

5. Experimental Section

Materials: P3HT (Plexcore 2100, Plextronics Inc., Pittsburgh, PA) and PCBM (99.5%, NanoC Inc., Westwood, MA) were used as received. PEDOT:PSS (Clevios P VP Al 4083, H. C. Starck Inc., Newton, MA) and d-PSS (Polymer Source, p/n P4123) were filtered through glass syringe filters (1.0 μ m) prior to use and stored in a refrigerator otherwise. The d-PSS solution was prepared by dissolving 1.3% (by mass) in deuterium oxide (Sigma-Aldrich, >99.8%). d-PSS and D₂O were both stored in a desiccator when not in use. Isopropyl alcohol (anhydrous, >99.9%), acetone (HPLC grade), chloroform (>99.8%), and 1,2-dichlorobenzene (>99.8%) were used as received.

Device Characterization: P3HT-PCBM bulk heterojunction films were prepared for device measurements by spin-casting on to PEDOT-PSS coated indium tin oxide (ITO)-glass substrates in N2. The ITO-glass substrates (22 mm \times 22 mm) were cleaned via sonication in acetone and isopropyl alcohol (10 min each) and exposure to UV-ozone (10 min). The PEDOT-PSS layer was prepared by spin-casting (5000 imes $2 \cdot \pi/60$ rad s⁻¹ or 5000 rpm) in air and annealing (120 °C for 20 min) in N_2 . Bulk heterojunction films were spin-cast from a 30 or 15 mg mL⁻¹ 1,2-dichlorobenzene solution (≈0.4 mL solution deposited prior to spincasting) through a Teflon filter, which was heated for at least 12 h on the heating block (>>70 °C), but spun at room temperature (2000 rpm or 600 rpm for 60 s) in N_2 . The top surface of the BHJ film was deposited with Ca (20 nm) and Ag (100 nm, top layer) via a thermal evaporator (MBraun) and transferred to another glovebox via aluminized Mylar bags for device testing. The devices were measured under Ar atmosphere using an Agilent 4155C parameter analyzer. The photocurrent was measured under AM1.5G 100 mW cm⁻² illumination from a Thermo Oriel 96 000 150 W solar simulator that was filtered through a neutral density filter and an AM1.5G filter (Model AM0, Oriel Corp., Stratford, CT) and then transferred into the box via a liquid light guide (Model 77637, Newport Corp., Irvina, CA). The OPV device performance was referenced to a monosilicon photodiode fitted with a KG-5 visible color filter (Model S1133, Hamamatsu) calibrated by the National Renewable Energy Laboratory (NREL). All efficiency values reported in this work were corrected by the spectral mismatch factor. Four devices were measured for each film, and the efficiency reported is the average.

NMR Characterization: In applying the ¹H CRAMPS measurement to thin OPV films, it was necessary to develop a set of essential sample preparation protocols. These protocols were predominantly related to proton hygiene and included: 1) pre-cleaning the spin-coating apparatus and wafer backside; 2) using non-magnetic and pre-cleaned equipment for film removal; 3) performing film removal in an H₂O-free environment; 4) pre-cleaning the Si₃N₄ rotors, Kel-F caps, and all rotor packing equipment prior to transferring the films into the rotor; and 5) acquiring a ¹H CRAMPS spectrum of an empty rotor for proper background subtraction of residual protons in the probe. Omitting any of these elements was found to result in a pronounced background signal or other spectral artifact, particularly in the spin diffusion spectra. When correctly performed, these protocols permit the collection of thin-film ¹H CRAMPS spectra that are relatively free of background contributions.

BHJ films were prepared by spin-casting onto a d-PSS release layer utilizing the same BHJ casting and post-processing protocols as for device measurements. Films prepared with the normal PEDOT-PSS hole-injection layer exhibited residual PEDOT-PSS protons in the ¹H NMR



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spectrum. The d-PSS layer was cast onto clean Si (5000 $\times 2\pi/60$ rad s⁻¹ for 60 s) and annealed (120 °C for 20 min). Si was cleaned in a similar fashion to the ITO-glass substrates used for devices. Films were floated off of the Si wafers using D₂O in a fluoroware container in a N₂-purged glovebag and dried in a dessicator at room temperature for at least 12 h. Presence of water in the residual d-PSS layer resulted in a broad feature in the spin diffusion spectra.

Free-standing films were placed via Teflon tweezers into pre-cleaned Si₃N₄ rotors with Kel-F caps and spacers to minimize ¹H background signal. The Si₃N₄ rotor and Kel-F components were cleaned via sonicating in isopropanol for two 10-min periods followed by vacuum drying (<10⁻⁶ mbar) at slightly elevated temperature (50 °C) for at least 24 h. All rotor packing and film processing materials were cleaned in hot isopropyl alcohol for at least 10 min. Insufficient cleaning of any of the components resulted in a pronounced background signal, particularly in the spin diffusion spectra. Only clean D₂O (w/w% < 0.1% H₂O) was used for floating films since H₂O yields a pronounced peak in the ¹H CRAMPS spectrum. Furthermore, non-magnetic or Teflon tweezers were always used to avoid contaminating the film samples with magnetic particles which would cause pronounced spinning sidebands in the ¹H CRAMPS spectrum.

The P3HT-PCBM bilayer was formed by spin-coating a thin P3HT layer on to a Si wafer coated with 25 nm d-PSS. The 28 nm thick P3HT layer was then flattened via nanoimprint lithography, and was subsequently coated with 51 nm thick PCBM via evaporation.

Solid-state ¹H NMR experiments were performed at 300 MHz on a Bruker DMX300 spectrometer. CRAMPS experiments were performed using the MREV8 pulse sequence^[48] characterized by eight 1.5 µs $\pi/2$ pulses and a cycle time of 39.6 μ s. Each sample (\approx 0.1 mg) was placed into a 5-mm Si₃N₄ rotor and spun at 2525 \pm 5 Hz. Other typical parameters were: 300.13 MHz carrier frequency, 400 MREV-8 cycles (and FID points), 0.49 scaling factor. For spin diffusion experiments, a fixed, measureable polarization gradient was established between the protons of P3HT and PCBM such that the total spin diffusion integral was zero. This zero-integral preparation was established via selection of the proper number of MREV8 cycles (ten over exactly one rotor period) and frequency offset (4900 \pm 50 Hz). Longitudinal relaxation effects on $\Delta M(t_m)$ were eliminated by alternating between +z and -z initial polarizations (with corresponding addition and subtraction of alternating signals) and by subsequently multiplying by the appropriate correction factor.^[49] The initial average polarization of PCBM, M M^{PCBM}, was -(0.40 \pm 0.02); the initial polarization of P3HT, $\frac{M_{0}^{\text{BHT}}}{M_{2}^{\text{PHT}}}$, was +(0.08 \pm 0.02). The uncertainty of initial polarizations is due to subtle changes in the scaling factor and is accounted for in the error bars included in Figure 8.

Grazing-Incidence X-Ray Diffraction: GIXD measurements took place at the Stanford Synchrotron Radiation Lightsource (SSRL) at beam line 11-3 with an image plate detector and an incident energy of 12.735 keV and incidence angle $\approx 0.12^\circ$. All sample chambers were purged with helium flow during the scattering experiments to reduce beam damage and background scattering.

Photoluminescence Measurements: PL measurements were performed on an inverted fluorescence microscope connected to a grating spectrometer and a silicon-charged coupled device (CCD) camera. The samples were excited using an argon-ion laser ($\lambda_0 = 514.5$ nm, ≈ 5 mW) through a 20× microscope objective (numerical aperture, N.A., = 0.50). The PL was collected using the same objective and directed onto the grating spectrometer through a long-pass edge filter (cutoff ≈ 515 nm). PL spectra were collected using the spectrometer connected to the Si-CCD camera in the range 550 nm to 900 nm with five s acquisition time.

Supporting Information

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

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