The miscibility and depth profile of PCBM in P3HT: thermodynamic information to improve organic photovoltaics

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Recent work has shown that poly(3-hexylthiophene) (P3HT) and the surface-functionalized fullerene 1-(3-methoxy-carbonyl)propyl(1-phenyl[6,6])C61 (PCBM) are much more miscible than originally thought, and the evidence of this miscibility requires a return to understanding the optimal morphology and structure of organic photovoltaic active layers. This manuscript describes the results of experiments that were designed to provide quantitative thermodynamic information on the miscibility, interdiffusion, and depth profile of P3HT:PCBM thin films that are formed by thermally annealing initial bilayers. It is found that the resultant thin films consist of a ‘bulk’ layer that is not influenced by the air or substrate surface. The composition of PCBM in this ‘bulk’ layer increases with increased PCBM loading in the original bilayer until the ‘bulk’ layer contains 22 vol% PCBM. The introduction of additional PCBM into the sample does not increase the amount of PCBM dispersed in this ‘bulk’ layer. This observation is interpreted to indicate that the miscibility limit of PCBM in P3HT is 22 vol%, which is the precise characterization of the depth profiles in these films shows that the PCBM selectively segregates to the silicon and near air surface. The selective segregation of the PCBM near the air surface is ascribed to an entropic driving force.

Introduction

Bulk heterojunction (BHJ) organic photovoltaics (OPV) have attracted significant interest as materials for sustainable solar energy conversion, due to their low cost, flexibility, ease of processing, and straightforward thin film formation.1–8 The BHJ design has led to power conversion efficiencies (PCE) of around 4–5% based on mixtures of poly(3-hexylthiophene) (P3HT) and the surface-functionalized fullerene 1-(3-methoxy-carbonyl)propyl(1-phenyl[6,6])C61 (PCBM).9 Power conversion efficiencies have further increased to over 7% using low band gap conjugated polymers, such as PBnDT-DTIIIBT.10 However, commercializing organic solar cells requires PCE up to ~10% and an improvement in device stability. Therefore, there is a tremendous need to be able to predictably create stable morphologies that can be tuned to provide optimum exciton dissociation and charge transport. Hence, understanding and controlling the donor/acceptor morphology in the OPV active layer is essential in optimizing BHJ solar cells.

The ideal morphology of P3HT/PCBM BHJ active layers has often been described as a bicontinuous system that comprises pure phase separated donor and acceptor domains. However, recent results clearly show that P3HT and PCBM are considerably miscible, which means that the BHJ active layer consists of three phases in the P3HT/PCBM mixture; a P3HT crystalline phase, a PCBM rich phase, and a miscible phase of amorphous P3HT and PCBM.11 The precise miscibility and interdiffusion of the conjugated polymer and fullerene in a BHJ active layer dramatically impact the morphology and structure in OPV devices, which intimately impact OPV function. This miscibility and 3-phase structure require a new model for the optimal morphology of OPV active layers, the development of which requires a more complete understanding of the thermodynamic trajectory that the conjugated polymer–fullerene mixture traverses during active layer fabrication. Understanding the thermodynamic driving force that guides the structure development during fabrication and annealing will prove to be a powerful tool to rationally develop thermodynamic pathways to form targeted structures. Equivalently, this thermodynamic information is needed to critically evaluate and provide constraints for further models of optimal OPV active layer structures.

The fact that PCBM readily mixes with P3HT has been shown by our group as well as others.11–14 Unfortunately, this previous work has been very qualitative in nature, primarily providing evidence of miscibility. In order to use the thermodynamics of the mixture to design model active layer structures and fabrication procedures, more quantitative thermodynamic information of P3HT and PCBM thin films, such as the precise concentration profile of the layers near the surfaces and the miscibility of PCBM in P3HT, is needed. The depth profile
near the air and substrate surface is important as it can impact the charge collection at the electrodes. For instance, a PCBM (acceptor) rich layer located at the air surface (near the cathode) and a P3HT (donor) rich layer located at the substrate (near the anode) should result in improved charge collection.

Due to the unique contrast between P3HT and PCBM in neutron scattering, the vertical depth profile of P3HT and PCBM mixtures can be determined using neutron reflectometry. In fact, neutron reflectometry has been used to monitor the depth profile of co-deposited approximately 1 : 1 mixtures of P3HT and PCBM. Excess PCBM was found at the silicon interface in one study and at both the silicon and air interfaces in others. In another study that uses neutron reflectometry to examine the P3HT/PCBM system, Lee and coauthors examined the depth profile of “bilayers” of P3HT and PCBM that are fabricated by spin-coating the bottom P3HT layer from one solvent, followed by spin-coating the second PCBM layer onto the P3HT layer using a second solvent, dichloromethane, that is presumably a non-solvent for P3HT. The change in the depth profile of these layers with thermal annealing is also studied by neutron reflectometry. However, dichloromethane is a marginal solvent for P3HT, which dissolves low molecular weight P3HT and swells the interface between the P3HT and PCBM. These results show that the two layers in this as-cast ‘bilayer’ are not well separated, where a significant amount of PCBM immediately mixes in the P3HT layer during the fabrication process. Therefore, the miscibility of PCBM in P3HT cannot be determined from these ‘bilayer’ samples, as their depth profiles are influenced by the fabrication procedure. Moreover, the impact of the PCBM content on the depth profile is not provided.

As a result, a set of experiments are designed to more precisely define the miscibility of PCBM in P3HT and to quantitatively monitor the depth profile of the PCBM in its equilibrated structure, including the surface composition of the thin films that are produced from initial bilayers at both the air and substrate interfaces. To realize this goal, a true bilayer of P3HT and PCBM is fabricated with well-separated P3HT and PCBM layers by float coating a P3HT layer onto a PCBM thin film. Thermal annealing allows the PCBM and P3HT to interdiffuse if there exists a thermodynamic driving force for the two components to do so. This geometry will thus result in a depth profile that will define the solubility limit of PCBM in P3HT, as only the PCBM that dissolves into the P3HT will diffuse into a P3HT layer during thermal annealing. Any PCBM that is above this solubility limit will remain in its original layer. Therefore, the depth profile of PCBM in the bilayer is monitored before and after thermal annealing by neutron reflectometry. To pursue the miscibility limit of PCBM in P3HT, bilayers with different PCBM/P3HT thickness ratios are examined. The detailed depth profile of PCBM in these thin films after annealing at 150 °C for 60 minutes provides unequivocal evidence of the equilibrium miscibility limits of P3HT in PCBM and precise characterization of the selective surface segregation of the PCBM in these thin films. This method is also broadly applicable to polymer : nanoparticle systems, and offers a unique method to understand the miscibility, interdiffusion, and surface segregation in polymer nanocomposites.

Experiments

Materials

[6,6]-Phenyl-C61-butryric acid methyl ester (PCBM, >99.5%) and regioregular poly-(3-hexylthiophene) (P3HT), M_n = 64 000 g mol^{-1}, were purchased from Sigma-Aldrich. Both were used as received. To fabricate thin films, P3HT and PCBM were dissolved in o-dichlorobenzene (ODCB) separately with selected concentrations and filtered through 0.44 μm PTFE syringe filters. P3HT–PCBM bilayers were fabricated by first spin casting PCBM onto clean silicon wafers at 1000 rpm for 60 seconds. Prior to spin-coating, the silicon wafers were cleaned by immersion in a 3 : 1 (v/v) mixture of concentrated sulfuric acid and 30% (v/v) hydrogen peroxide heated to ~70 °C for 15 min followed by rinsing with copious amounts of high purity water and drying under a stream of nitrogen. This was followed by spin-coating P3HT onto a silicon wafer at 1000 rpm for 80 seconds. To form the bilayer, the P3HT was then floated onto the surface of high purity water and captured by a PCBM coated silicon wafer. The sample was dried in air at an angle and then in an unheated vacuum oven for 24 hours to remove residual water. The relative thicknesses of the P3HT and PCBM layers were controlled to form bilayers with PCBM volume fractions of 11%, 25%, 30%, and 37%.

Neutron reflectometry

All reflectivity measurements were completed on the Liquids Reflectometer at the Spallation Neutron Source at Oak Ridge National Laboratory with a neutron wavelength varying from 2.75–5.75 Å and an effective q-range of 0.006–0.105 Å^{-1} (q = 4π/λ sin θ, where λ is the neutron wavelength and θ is the scattering angle). The reflectivity of model scattering length density profiles was fit to the measured scattering curves using Layers and Motofit Software to determine the structure of the thin films. The evolution of interfacial mixing between P3HT and PCBM in the bilayers was monitored before and after annealing at 150 °C for 60 min.

Assuming Fickian diffusion, the time needed for a PCBM molecule to diffuse the thickness of the film can be readily estimated. Using literature values for the diffusion coefficient of PCBM (2.5 × 10^{-14} m^2 s^{-1} at 140 °C), the PCBM molecule will traverse a 1700 Å film (the thickest film studied) in less than a second. Thus, the samples measured at 60 minutes have had adequate time to readily reach equilibrium.

Unfortunately, it is not possible to directly extract structural information of the scattering sample from the measured reflectivity. To circumvent this limitation, the reflectivity of a model scattering length density (SLD) depth profile is calculated and compared to the experimentally measured reflectivity. The reflectivity of the model depth profile is iteratively refined until the calculated and experimental reflectivity profiles match. With foreknowledge of the sample scattering characteristics and suitable constraints imposed to maintain a physically realistic system, the fitting provides a result that accurately reflects the scattering structure of the sample. One constraint used in the fitting of these data includes a mass balance of the P3HT and PCBM in the sample.

The depth profile of the spin-cast bilayers and subsequently annealed bilayers was modeled using 2–5 layers.
The SLD, thickness, and roughness of each layer were freely varied. A model is assumed to accurately reflect the structure of the sample when the model reflectivity profile converges with the experimental profile, where the quality of fit is gauged using $\chi^2$ statistics described by eqn (1), and the mass balance of the model system is within 5% of the mass balance of the sample.

$$\chi^2 = \sum (R_{\text{q,calc}} - R_{\text{q,exp}})^2 / R_{\text{q,exp}}^2$$  \hspace{1cm} (1)

In eqn (1), $R_{\text{q,calc}}$ and $R_{\text{q,exp}}$ are the calculated and experimental reflectivities. The SLD profile is then analyzed to obtain the concentration depth profile of each component in the system. For instance, the PCBM concentration depth profile is determined using eqn (2),

$$\phi(z)_{\text{PCBM}} = (\rho(z) - \rho_{\text{P3HT}}) / (\rho_{\text{PCBM}} - \rho_{\text{P3HT}})$$  \hspace{1cm} (2)

where $\phi(z)_{\text{PCBM}}$ is the volume fraction of PCBM at depth $z$, $\rho(z)$ is the experimental scattering length density at depth $z$, and $\rho_{\text{P3HT}}$ and $\rho_{\text{PCBM}}$ are the SLD of P3HT and PCBM, respectively. In order to quantitatively analyze the reflectivity curves, the accurate scattering length density (SLD) of each component is needed. The density of crystalline P3HT is taken as 1.12 g cm$^{-3}$, based on X-ray diffraction data and the density of amorphous P3HT is estimated to be $\sim 10\%$ less than that of crystalline P3HT, 1.01 g cm$^{-3}$. Using these values, the scattering length densities of crystalline P3HT and amorphous P3HT are calculated to be $0.69 \times 10^{-6}$ Å$^{-2}$ ($\rho_{\text{P3HT,c}}$) and $0.62 \times 10^{-6}$ Å$^{-2}$ ($\rho_{\text{P3HT,a}}$) respectively. Unfortunately, the exact percent crystallinity of P3HT in these thin films is not known precisely. However, a recent work in our lab suggests that 20% crystallinity is a reasonable value, and thus a SLD of $0.64 \times 10^{-6}$ Å$^{-2}$ is used for the P3HT phase in these bilayer samples. Given the proximity of $\rho_{\text{P3HT,c}}$ and $\rho_{\text{P3HT,a}}$, any error in this assumption will not significantly impact the results presented below. The density of crystalline PCBM is reported to be 1.67 g cm$^{-3}$ for crystals formed from ODCB. Following the assumption that amorphous PCBM is 10% less dense than crystalline PCBM, the SLD of amorphous PCBM is calculated from its density and composition to be $4.4 \times 10^{-6}$ Å$^{-2}$, which agrees with previous work and our fitting of the neutron reflectivity profile of a spin-cast PCBM monolayer.

**Results**

The experimentally determined specular neutron reflectivity, as well as that of the fitted model, are presented in Fig. 1 for the spin-cast and thermally annealed bilayer samples with 11% PCBM. The data are plotted as $R_q^2$ as a function of $q$ to more clearly observe deviations between the experimental and fitted reflectivities. Inspection of Fig. 1 shows that the reflectivity of the spin-cast bilayer contains a broad shoulder in the $q$ range between $\sim 0.02$ - $0.06$ Å$^{-1}$. This broad shoulder is the result of the pure PCBM layer in the as-cast sample. This shoulder is eliminated from the reflectivity curve of the thermally annealed sample, indicating the loss of this PCBM upon thermal annealing. The scattering length density profiles of the fitted model are then analyzed to extract the depth profile of PCBM in the thin film, which further verifies this interpretation.

The PCBM depth profile of the sample with 11% PCBM is therefore presented in Fig. 2. This analysis shows that the thickness of PCBM in the initial bilayer is about 150 Å with a rough surface. The surface roughness of the PCBM layer is due to the limited thickness of this film. The resultant PCBM depth profile quickly changes after thermal annealing. The density profile of the top layer, which was initially pure P3HT, is now a homogeneous mixture of P3HT and PCBM, with a loading of PCBM of 6.6%, which is shown in the plateau region at $z \sim 300$ – 600 Å. This clearly indicates that PCBM readily forms a miscible mixture with P3HT upon thermal annealing, where the P3HT and PCBM mix when the loading of PCBM is 6.6%. Additionally, there remains a PCBM rich layer at the silicon interface and a P3HT rich at the air interface.

The interdiffusion of PCBM into the P3HT layer can be more clearly observed by monitoring the change in structure of the bilayer with 25% PCBM upon thermal annealing. The reflectivity of the as-cast 25% PCBM bilayer is presented in Fig. 3, exhibiting the Kiessig fringes that indicate the bilayer nature of the structure before annealing. Significant changes in the reflectivity are observed after the sample is annealed at 150 °C. The disappearance of these Kiessig fringes as shown in
Fig. 3 indicates the broadening of the P3HT–PCBM interface and loss of the bilayer nature of the depth profile. For instance the decrease in the amplitude of the fringes, which is associated with the SLD contrast between these layers, is a direct result of the interdiffusion of PCBM into the P3HT. The resultant PCBM depth profiles are shown in Fig. 4. This figure shows how the initially well-separated P3HT and PCBM layers intermix as the PCBM infuses into the P3HT layer. The thermally annealed sample exhibits a plateau region at z \approx 800–1100 Å, which indicates the presence of a homogeneous mixture of P3HT and PCBM. The loading of PCBM in the portion of the thin film that is not impacted by the air or silicon surface is 19%. Inspection of this depth profile shows that the PCBM selectively segregates to the air and silicon surfaces in this thin film, which is consistent with previously reported results. This previous work reports that the depth profile of an as-cast co-deposited P3HT : PCBM mixture consists of a surface layer that is depleted in PCBM and a PCBM rich layer next to the substrate. Upon thermal annealing, the PCBM surface depletion is suppressed, indicating that the annealing process facilitates the movement of PCBM to the film air surface, which is consistent with our results.

Similar structural development is found upon thermal annealing the bilayer with 30% PCBM, as shown in Fig. 5. The Kiessig fringes of the as-cast bilayer disappear upon thermal annealing, commensurate with a shift in the critical edge brought about by intermixing of the layers. These changes, again, indicate the diffusion of PCBM into the P3HT layer. The density profiles of PCBM before and after annealing at 150 °C are shown in Fig. 6, where a plateau region is found at z = 600 Å–1000 Å. Inspection of this plateau shows that the miscibility of PCBM in P3HT in this regime is 22%. Therefore, as more PCBM is added to the sample the amount of P3HT that is miscible with P3HT increases from 7% to 22%. Moreover, the selective segregation of the fullerene to the film air surface also occurs in this sample, with an apparent increase in the surface excess of fullerene.

To more precisely define the miscibility limit of PCBM in P3HT, the concentration of PCBM in the film is increased to 37%, which is very similar to the PCBM concentration in the 1 : 0.8 P3HT : PCBM mixture, the ratio often used in OPV active layers. Similar observations are found in the structural development of the bilayer with thermal annealing as observed in the 30% PCBM sample, as shown in Fig. 7. The Kiessig fringes of the as-cast film disappear with thermal annealing, accompanied by a shift in the position of the critical edge, indicative of a loss of the bilayer structure caused by the inter-diffusion.
of the PCBM into the P3HT layer. The resultant depth profiles of PCBM in the as-cast and annealed samples are shown in Fig. 8. In this sample, the plateau region is found at $z \approx 600 \text{ Å}–1000 \text{ Å}$. Interestingly, analysis of this plateau indicates that the miscibility of PCBM in P3HT is also 22%, identical to that of the sample with 30% PCBM. Therefore, the loading of the PCBM in the miscible region of the sample does not increase as more PCBM is added to the system, indicating that the miscibility limit of PCBM in P3HT is 22% in these samples. This is commensurate with previous studies that have estimated the miscibility limit to be $\sim 20\%$.\textsuperscript{11,14,16} Moreover, the precise depth profile of PCBM in these thin films also indicates that the selective segregation of the fullerene to the air surface further increases as the concentration of PCBM in the bilayer increases from 30% to 37%.

**Discussion**

The traditional picture of the optimal bulk heterojunction morphology in OPV active layers has customarily envisioned an interconnected bicontinuous, 2 phase structure, where each phase is $\sim 20 \text{ nm}$. Recent results,\textsuperscript{11–14,16} however, have indisputably shown that conjugated polymers and fullerenes are much more miscible than originally thought, which is inconsistent with this optimal morphology. This unexpected miscibility presents new opportunities as well as uncertainties that must be addressed in order to develop stable organic photovoltaic devices with power conversion efficiencies greater than 10%. The miscibility, thin film depth profile and interdiffusion of the conjugated polymer and fullerene must be understood more thoroughly to rationally control the morphology and structure of OPV active layers.

The results presented here clearly document the miscibility and interdiffusion of PCBM in P3HT. The diffusion of PCBM into P3HT upon thermal annealing was monitored by neutron reflectometry, where the depth profile after annealing clearly shows a plateau region in the central portion of the thin film. This plateau region is the portion of the film that is not influenced by the air or silicon surface, and therefore tracks the miscibility of PCBM in P3HT. A plot of the concentration of PCBM in the plateau region as a function of the percent PCBM in the bilayer (Fig. 9) shows that at low PCBM loading, the amount of PCBM dissolved in the P3HT increases linearly with PCBM in the original bilayer. This continues until the amount of dissolved PCBM reaches 22%, after which additional PCBM loading does not increase the amount in the miscible layer. This is consistent with the PCBM/P3HT mixture crossing a binodal line on the phase diagram, where additional PCBM “phase separates” into a PCBM rich phase.

Careful inspection of Fig. 9 shows that the amount of PCBM dissolved in P3HT is less than the original loading of PCBM that is in the fabricated bilayer. This discrepancy is the result of the selective segregation of PCBM to the silicon and air interface, depleting the concentration of PCBM in the plateau region of the depth profile. Thermal annealing of P3HT–PCBM bilayers clearly allows the diffusion of PCBM into P3HT, resulting in an equilibrium distribution of the PCBM in the thin film.

The active layer in most OPV devices is fairly thin ($\sim 100–250 \text{ nm}$), and therefore the depth profile of the film near the top and bottom interfaces will substantially impact the structure and function of the thin film. In the equilibrated systems presented here, the selective segregation of PCBM near the air surface is observed in the samples with a PCBM...
selective surface segregation of components in a thin polymer
film mixture, where entropy dominates the selective surface
segregation of PCBM in these thin films.

The competition between enthalpy and entropy in defining the
miscibility of PCBM in a conjugated polymer in thin films is
accurate when they account for the precise depth profiles of both
components. This is an important differentiation when comparing
these to previously reported results.

Conclusion
In summary, a set of experiments have been designed and
completed to quantitatively define the miscibility limit of
PCBM in P3HT. The depth profiles of PCBM in P3HT in
equilibrium thin films that are formed by thermal annealing an
initial bilayer are determined by neutron reflectometry. The
miscibility of PCBM in P3HT as a function of PCBM loading
shows that PCBM diffuses into the P3HT layer to form a
miscible layer that is 22% PCBM or less. If the amount of
PCBM available in the sample for this miscible region is
greater than 22%, a miscible region of 22% PCBM is formed,
with excess fullerenes excluded from this miscible region, indicating
that the miscibility limit of PCBM in P3HT is 22 vol%.

Moreover, the reported results show that PCBM selectively
segregates to the air interface due to entropic reasons upon
thermal annealing to an equilibrium structure and show that
the interfacial excess of PCBM at the air surface, \( z^* \), increases
as the amount of PCBM in the original bilayer increases.
Furthermore, this method is also broadly applicable to
polymer : nanoparticle systems and offers a straightforward
method to understand the miscibility, interdiffusion, and surface
segregation in polymer nanocomposites.

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