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SCHREYER HONORS COLLEGE

DEPARTMENT OF CHEMICAL ENGINEERING

CONJUGATED BLOCK COPOLYMERS IN ORGANIC PHOTOVOLTAICS

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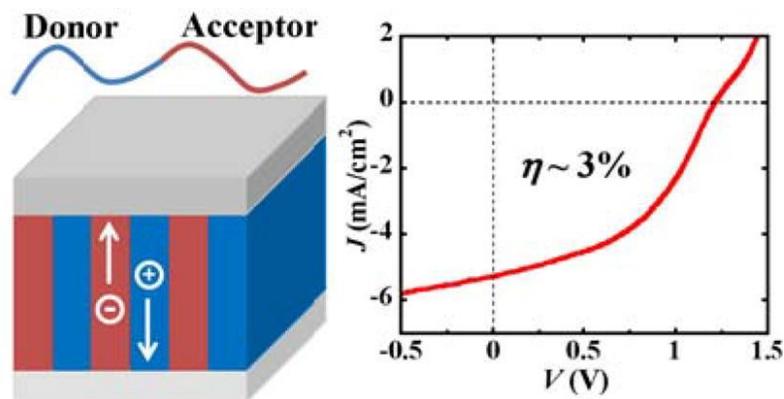
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ABSTRACT

Organic semiconductors for photovoltaic devices represent the next generation of solar cell technology. Yet limitations including weak intermolecular interactions, disorder at semiconductor interfaces, and lack of control over the active layer microstructure have resulted in devices that cannot compete with the power conversion efficiencies of traditional silicon technologies. Conjugated block copolymers address these restrictions as we demonstrate an ability to control donor-acceptor heterojunctions through microphase-separation by utilizing these polymers in the active layer of photovoltaic cells. Block copolymer-based devices present efficient power conversion well beyond devices composed of homopolymer blends. While traditional organic solar cells rely on fullerene electron acceptors, our block copolymer device functions without the use of such compounds and can achieve efficiencies upwards of 3%, rivaling P3HT:PCBM systems. Results of X-ray scattering characterization indicates that the block copolymer solar cells can self-assemble into mesoscale lamellar morphologies primarily containing face-on P3HT crystallite orientations. Through enhancing photoconversion efficiencies by controlling the microstructure at donor-acceptor interfaces, conjugated block copolymers serve as an exciting new technology in organic photovoltaics.



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Chapter 1

An Introduction to Organic Photovoltaics

Overview

Organic solar cells, the third generation of photovoltaic (PV) technology, represent a potentially inexpensive and scalable route to solar energy production in comparison to crystalline silicon and thin film predecessors. Due to their light weight, flexibility (as can be seen in Figure

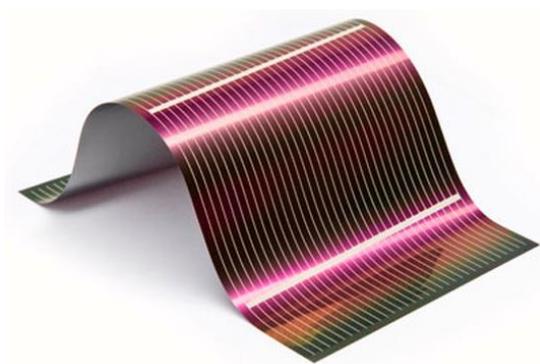


Figure 1-1 Image of an organic solar cell

1-1)¹, low temperature and pressure processing conditions, and potential to be manufactured through roll-to-roll printing, organic electronic materials hold many distinct advantages over current established solar technologies which are both expensive and energy intensive to produce.

The expense of these older silicon based technologies is currently a limiting factor in their ability to rival fossil fuels as a major source of energy for the global economy. Organic solar cells provide a potential circumvention of this limitation if their efficiencies can be improved.

Most organic solar cells follow a similar device structure consisting of a glass substrate, ITO anode, PEDOT:PSS hole conduction layer, polymer active layer, and aluminum cathode. Upon exposure to light, the photoexcitation of the semiconducting organic materials results in the formation of an exciton, or electron-hole pair. If the coupled positive and negative charges separate at the donor-acceptor interface, the charges can travel to the electrodes through the

bicontinuous donor-acceptor phases, resulting in direct current and the production of electricity from sunlight.

Evolution of Solar Technology

Daryl Chapin, Calvin Fuller, and Gerald Pearson are credited with the birth of PV technology in the United States when, in 1954, the three scientists of Bell Telephone Laboratories produced a silicon cell that could convert enough of the sun’s energy into electricity to run electrical equipment.² Significant efforts have been made in following years to improve the power conversion efficiency (PCE) and minimize manufacturing and materials costs of PV cells such that they can compete with fossil fuels as an economically viable source of electricity.

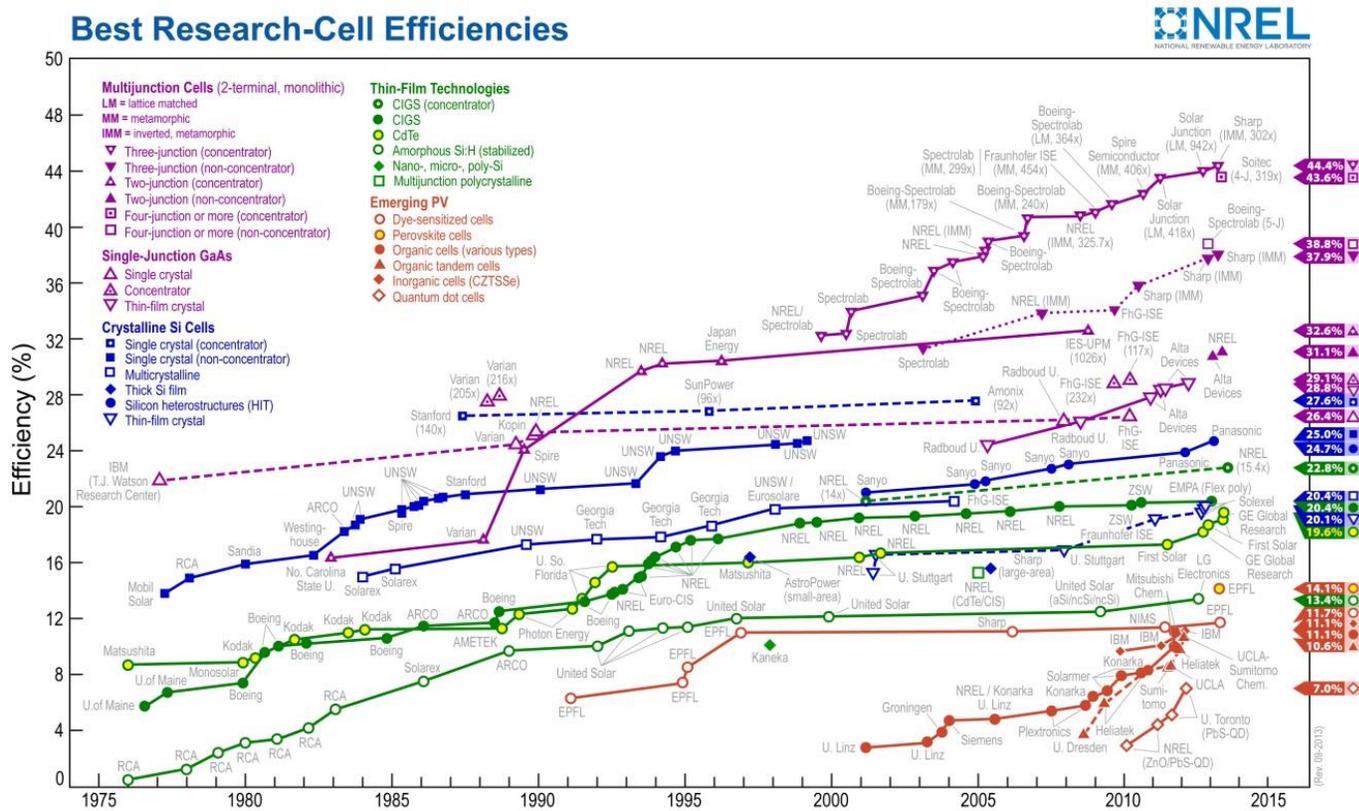


Figure 1-2 Evolution of PCE from 1976 – 2013 for various classes of PV technology

The National Renewable Energy Laboratories of the US Department of Energy has tracked the development of solar technology since the 1970s and annually publishes a report of world-record setting devices. Figure 1-2 represents the report published in 2013.³ Interest in organic cells has intensified since the early 2000s due to aforementioned benefits and has seen rapid and far greater improvements over the past few years than any other type of PV technology. Multiple world records are set every year making it difficult to quantify the exact increase in PCE from year to year, however we will take the example of Solarmer's world record setting 6.8% device in 2008 and compare it with Heliatek's 11.1% efficient device in 2013. The PCE has increased by 63% in 5 years, a remarkable feat unmatched by any other thin-film or silicon technologies.

Construction

The traditional organic solar cell architecture as fabricated for laboratory testing is visualized in Figure 1-3.⁴ It consists of 5 major components.

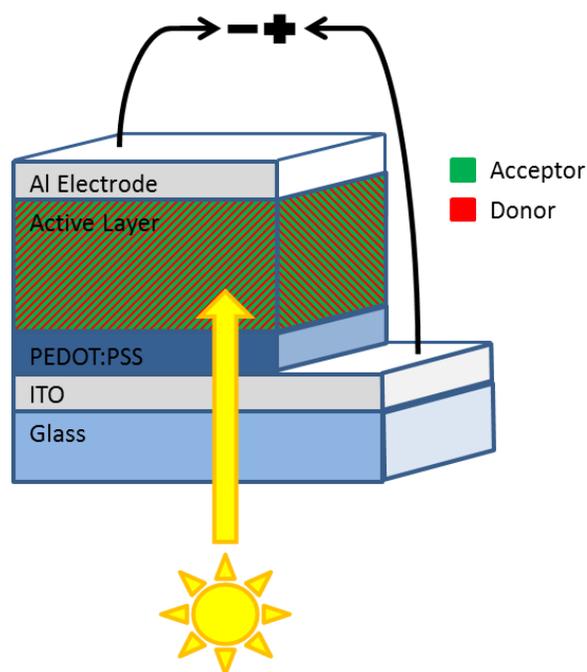


Figure 1-3 Typical device architecture

- 1.) Glass provides a stable and transparent substrate for PV fabrication upon which subsequent layers are spin coated. In industrial applications, this glass would be replaced by flexible plastic material for lighter weight and greater flexibility. The key substrate requirement is minimal light reflection since sunlight penetrates the device through the glass/plastic to generate excitons in the active layer.
- 2.) Indium Tin Oxide (ITO) is often etched onto glass as the anode since it is an electrically conductive and transparent material. Again, transparency is a critical anode characteristic since any light reflection will hinder device efficiency by reducing photon absorption in the active layer.
- 3.) Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), also known as PEDOT:PSS, serves as a hole conduction layer that connects the active layer to the anode. A critical feature in organic solar cells, PEDOT:PSS prevents electrons from travelling to the anode against the direct current in the cell and facilitates the extraction of holes to the anode. While other dopant layers have been researched due to the acidity and degradability of PEDOT:PSS, it remains a widely used component for the hole extraction layer.
- 4.) The active layer is responsible for charge generation via the photoelectric effect. It must consist of an electron donor and acceptor, yet these materials vary widely throughout the field of organic electronics. The 'traditional' and perhaps most widely studied devices consist of regioregular Poly(3-hexylthiophene-2,5-diyl) (or P3HT) as the electron donor and PCBM, a fullerene derivative, as the electron acceptor. For our system, this acceptor-donor happens to be one covalently contiguous molecule in which acceptor and donor molecules are connected to form a block copolymer.

- 5.) The cathode, typically composed of aluminum, forms the upper most layer of the device. Usually deposited by thermal vacuum evaporation to form a layer on the order of 10s of nanometers in thickness, the cathode extracts free electrons from the active layer.

Physics of the Organic Photoconversion Process

The process by which light is absorbed and converted into electricity in organic materials consists of four major steps: exciton formation through light absorption, exciton migration, charge separation, and charge migration.⁵

Step 1: Light Absorption and Exciton Formation

As an organic PV device is exposed to light, the active layer can absorb a photon of sufficient energy to create a photo-induced excited state, or exciton. Light can be absorbed on either the donor (D) or acceptor (A) phase to create such a state. This species of charged particle has a net neutral charge but consists of a tightly bound electron-hole pair that does not easily dissociate into a free electron-hole pair. In the example of light absorption by the donor, a π -electron can be promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) level, shown in Figure 1-4.⁶

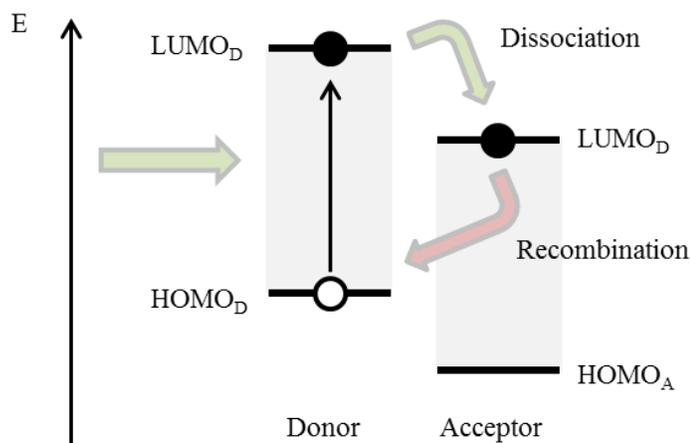


Figure 1-4 Schematic of charge transfer in excitonic solar cells

Step 2: Exciton Migration

In organic solar cells, exciton dissociation into separate positive and negatively charged particles requires an interface between an acceptor and donor component in the active layer. The particle (i.e. generated in the donor phase) can diffuse in an attempt to transfer to a lower energy level (the acceptor phase) or relax to ground state thereby releasing energy in radiative decay. Hence the exciton diffusion length and length scales of acceptor and donor domains are critical factors for efficiency. If the exciton diffusion length is much smaller than the domain size, photoexcitation will not produce separate charges for the generation of electricity because the exciton will relax to ground state before reaching a donor-acceptor interface. In summary, the exciton must reach the interface during its lifetime or else the solar cell will not work efficiently.

Step 3: Separation of Charges

Upon reaching the donor-acceptor interface, the exciton can dissociate into separate positive and negative charges no longer bound together in the donor or acceptor phase. If the electron in the LUMO of the donor is transferred to the LUMO of the acceptor, the Charge Transfer (CT) state is achieved. The CT state, however, must not be confused with the Charge Separated (CS) state as recombination can occur, shown in Figure 1-4, from the LUMO of the acceptor to the HOMO of the donor. CT refers to the point at which an exciton has separated into positive and negative charges on the donor and acceptor phases, respectively, yet still have interactions due to proximity across the interface. If the charges separate far enough apart they can enter the CS state and begin migration towards the electrodes. Recombination can likewise occur from the CT state, resulting in no free charges. This can also be visualized in Figure 1-5, where k_{CT} , k_{CS} , and k_{CR} represent the rate constants of charge transfer, charge separation and charge recombination, respectively.

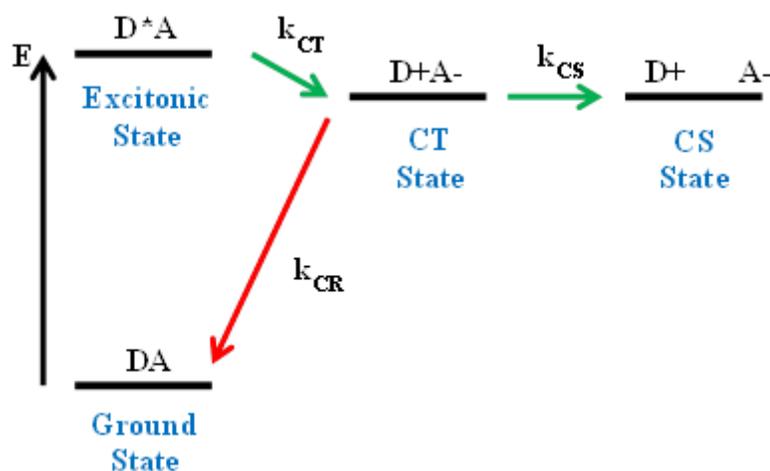


Figure 1-5 Diagram of charge transfer and charge separated states

Thus it becomes critical to maximize k_{CT} and k_{CS} while minimizing k_{CR} to achieve optimal efficiency within organic solar cells.

Step 4: Migration of Charge

Finally, the difference in electric potential between the ITO anode and Al cathode provides a driving force for charge movement after the free electrons and holes have been produced in the CS state. Holes travel through the continuous donor phase to the PEDOT:PSS layer, which selectively extracts holes to the anode. Similarly, electrons migrate to the cathode through the acceptor phase. A significant disadvantage of organic materials is the speed at which charges move through the active layer medium, known as charge mobility, in comparison to inorganic (specifically silicon) materials. Disorder of microstructures in organic materials is common and prevents the rapid movement of free charge, a problem not seen in the highly ordered structures of silicon solar cells.

Chapter 2

Block Copolymers in Organic Photovoltaics

Our study represents a significant step in organic PVs in which block copolymers are used as the sole active layer component to produce a device functioning at a high PCE (~3%) without the use of a fullerene derivative as an acceptor. Use of block copolymers for photovoltaics is not an entirely new concept, however, as other attempts have been made to utilize the unique properties of this class of material to enhance the efficacy of organic electronics.

Previous Advancements of PVs via Block Copolymers

Several attempts have been made to utilize block copolymers to control the microstructure of organic solar cells. Previous research, for example, has involved the use of P3HT-b-poly(4-vinylpyridine) (P3HT-b-P4VP) as a rod-coil block copolymer to improve upon the traditional P3HT:PCBM system.⁷ Some advantages of this strategy include increased face-on orientation of P3HT crystallites which facilitates hole extraction through the anode. Additionally, the P4VP coil blocks were utilized to inhibit PCBM crystallization and decrease the size of acceptor domains, leading to more interfaces for exciton diffusion. The advantages attributed by the block copolymer were significant enough to yield PCE for as cast films as standard P3HT:PCBM films with annealing.

Other creative uses of block copolymers include functionalizing blocks with perylene diimides (a class of small molecule with a large conjugation of π -orbitals) to create wire-like nanodomains with length scales similar to the exciton diffusion length of the absorbing species.⁸

In the same study, the use of the block copolymer also shifted the HOMO value of the donor to improve the driving force for exciton dissociation at the donor-acceptor interface. Utilizing a block copolymer rather than the dual blend for these perylene diimide derivate devices produces power efficiencies an order of magnitude greater.⁹

In many cases, block copolymers have been used as a ternary nanostructuring agent for systems with fullerene derivatives as acceptors and have not been used as a stand-alone active layer component to engineer the microstructure morphology of an organic solar cell active layer.¹⁰ Those that have did so by utilizing donor and acceptor blocks containing a non-conjugated backbone in at least one block, thereby preventing direct control of the interface.¹¹ However, recent successes have been realized in the synthesis and characterization of fully conjugated block co-polymers.

Motivation for Our Study

Donor-acceptor interfaces are critical in the photoconversion process and for efficient device performance in excitonic solar cells.⁵ Inorganic semiconductors hold a distinct advantage over organic semiconducting materials: optical excitation results in free charge carriers. To create current in organic photovoltaic devices, tightly bound charge transfer states must dissociate near the donor-acceptor interfaces. Thus engineering organic heterojunctions through design of chemical structure and optimization of processing conditions is a requirement for organic solar cells to reach their maximum potential. Herein lies one of the greatest challenges of this technology: organic solar cells currently rely on kinetically trapped, partially phase-separated structures to create large donor-acceptor interfacial areas for exciton dissociation and randomly generated bicontinuous networks for charge extraction.^{12,13} Consequently, demonstrating control of the donor-acceptor interface in advanced organic photovoltaic technologies has been nearly impossible.

In this study, we demonstrate that micro-phase separated block copolymers, comprised of one electron donor and one electron acceptor block, can address several challenges of microstructure and interfacial control. Block copolymers self-assemble into mesoscale morphologies at equilibrium in the range of 5-500 nm and well-structured morphologies arise due to the junctions between blocks. These characteristics result in an active layer that is ideal for performance in organic solar cells.

We report that poly(3-hexylthiophene) – *block* – poly((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (P3HT-*b*-PFTBT) block copolymers, shown in Figure 2-1 with P3HT and PFTBT homopolymers, can be used as the sole active layer component in an organic solar cell and result in efficient device performance. Most significantly, the active layer morphology adopts an in-plane lamellar structure consisting of repeating donor-acceptor domains based on the block in each copolymer. Additionally, in the P3HT donor domains, the crystallites form predominantly face-on orientation to facilitate hole extraction. Block copolymer devices obtain remarkable performances of near 3% efficiencies, open-circuit voltages around 1.2 V, and short-circuit currents around 5 mA/cm² without the use of a fullerene acceptor. Hence conjugated block copolymers provide a promising route to high efficiency organic solar cells through interfacial control.

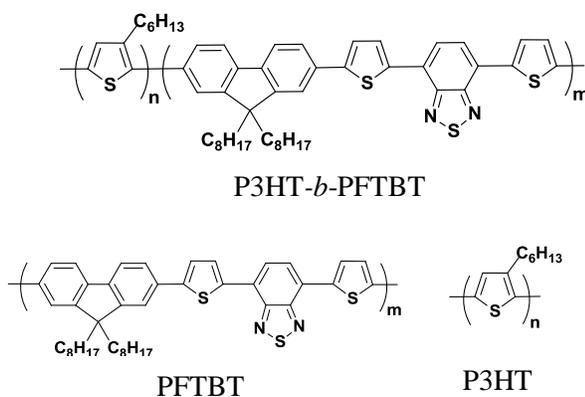


Figure 2-1 Chemical structures of P3HT-*b*-PFTBT, PFTBT, and P3HT

Chapter 3

Experimental Materials and Methods

The following section describes the experimental method for preparing and testing organic solar cells. The entire process takes approximately 24 hours from initial solution preparation to testing, with an approximate 10 hours of manual activity throughout this time range. While the steps in this process varied greatly throughout the study in an attempt to experimentally optimize device efficiency, the examples given in this experimental represent the processing conditions for the best block copolymer device.

Materials

Regioregular P3HT was purchased from Merck (96% H-T regioregular, $M_n = 26$ kg/mol, polydispersity = 2.0). All other reagents and solvents were purchased from Sigma Aldrich and used as received. P3HT-*b*-PFTBT block copolymers were synthesized by the Verduzco group at Rice University. ITO-coated glass substrates of 20 ohm/sq were purchased from Xin Yan Technology, Hong Kong. Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (or PEDOT:PSS) was purchased from Heraeus Clevios. Anhydrous chloroform for solution making was purchased from Sigma Aldrich (> 99%).

Solar Device Fabrication and Testing

Polymer solutions for device active layers were made with anhydrous chloroform. 1:2 P3HT:PFTBT mixtures by mass were made at a concentration of 10 mg/ml, while P3HT-*b*-PFTBT solutions were made at a total concentration of 5 mg/ml. Solutions were stirred for ~ 20-

22 hours at 95 °C before spin coating in a tightly sealed sample container and wrapped in multiple layers of parafilm to ensure no evaporation of solvent.

Solar devices, following the conventional architecture depicted in Figure 1-3, consisted of glass/ITO/PEDOT:PSS(65 nm)/active layer (60-70 nm)/Al(75 nm). Glass/ITO substrates were cleaned thoroughly with soap and water, followed by 20 min sonication in acetone and 20 min sonication in isopropyl alcohol. ITO was subjected to UV ozonation for 15 min to destroy any final impurities. PEDOT:PSS was spin coated on the ITO substrate for 2 min at 4000 rpm (equating to an approximate thickness of 65 nm). ITO/PEDOT:PSS substrates were annealed at 165 °C in air for 10 min to remove water from the dopant layer and immediately transferred into a nitrogen atmosphere glove box.

P3HT:PFTBT and P3HT-b-PFTBT were spin coated on ITO/PEDOT:PSS substrates at hot solution temperatures of 95 °C for 1 min at various spin speeds to maintain thin film thickness around 60-70 nm, measured by a TENCOR P-10 surface profiler. Devices were annealed at 165 °C or 100 °C for 5 minutes to remove residual solvent from the film. Next, vacuum thermal evaporation (performed at 10^{-6} torr) was used to deposit aluminum at a thickness of 75 nm. Devices were subsequently annealed at 165 °C or 100 °C for various times in between photovoltaic testing.

Device performance was quantified by photovoltaic measurements taken in a nitrogen atmosphere. The light source was a xenon lamp solar simulator (Newport Model SP92250A-1000), which provided simulated AM 1.5G illumination of 97 mW/ cm². Current-voltage measurements for solar cells were obtained with a Keithley 2636A Sourcemeter.

Chapter 4

Experimental Results and Discussion

We have experimentally demonstrated that poly(3-hexylthiophene) – block – poly((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (P3HT-b-PFTBT) block copolymers provide an effective active layer composition for energy conversion in photovoltaic devices. The devices function without the use of a fullerene acceptor, a traditional component in organic photovoltaics. X-ray scattering data indicates the block copolymers self-assemble into lamellar morphologies with alternating electron donor and acceptor domains and have a crystalline P3HT block with mainly face-on orientation. Efficiencies near 3% were obtained with open-circuit voltages around 1.2 V, and short-circuit currents above 5 mA. Hence block copolymers provide a strategy for controlling the microstructure and developing high performance organic solar cells.

Homopolymer Blend Optimization

Previous results show an optimized P3HT:PFTBT blend with efficiencies around 1.5%. Before exploring the effects of introducing the block copolymer into the system, these results had to be reproduced with available materials as a control device. Optimization of the processing conditions for the polymer blend were carried out by sequentially testing how solution heating, film thickness, and varying weight fractions affected device efficiency.

Figure 4-1 indicates how high temperatures are required to fully dissolve PFTBT in solution. Without heating during the solution making process, device efficiency suffers significantly since PFTBT's insolubility prevents its deposition onto the substrate during spin

coating. Due to the volatility of chloroform, heating beyond 90 °C was not explored since evaporative losses during the spin coating process became too significant.

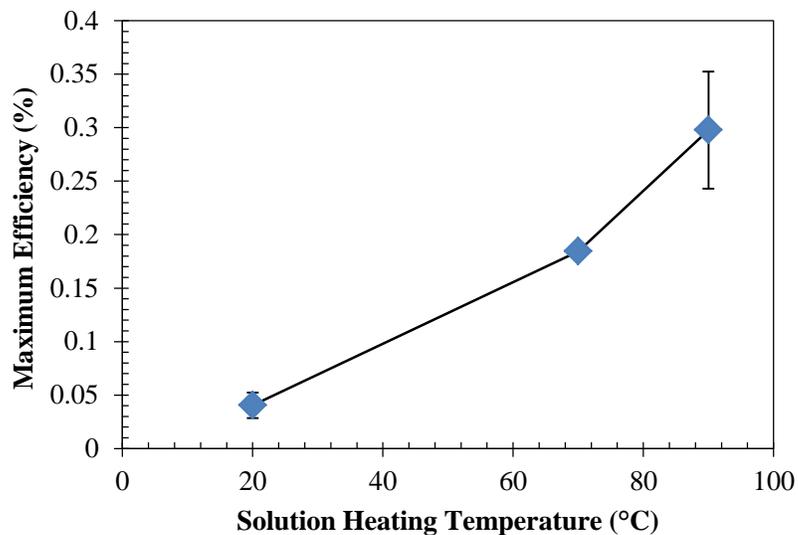


Figure 4-1 Blend efficiency versus solution heating

Efficiencies of devices made from 1:1 P3HT:PFTBT solutions in chloroform at various heating temperatures. Devices were annealed at 165°C for 10 minutes.

Following steps were taken to optimize total concentration of polymer in solution, shown in Figure 4-2. Film thickness is highly dependent on solution concentration and spin coat speed and has important consequences on the absorbance and charge transport within the film. For the 1:1 P3HT:PFTBT system, it was determined that a total concentration of 10 mg/mL and a spin coat speed of 3000 rpm yielded the best device efficiency.

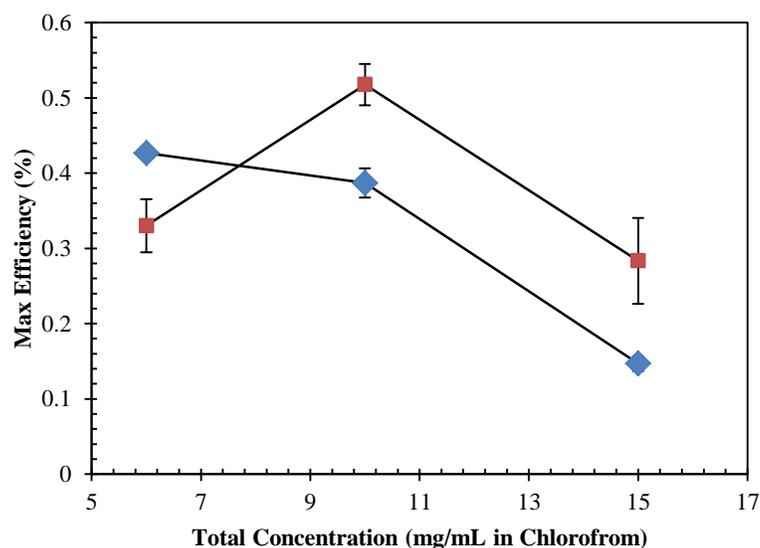


Figure 4-2 Blend efficiency versus total concentration

Blend efficiencies are plotted as a function of total polymer concentration for 1000 rpm spin coating (◆) and 3000 rpm spin coating (■).

The ratio of P3HT to PFTBT in the active layer was varied in the final step of blend optimization. It was found that higher mass fractions of PFTBT relative to P3HT yielded the best efficiencies, a likely result of the insolubility of PFTBT in chloroform even at low concentrations. An optimal ratio of 1:2 P3HT:PFTBT was determined and provided an approximate 4 times increase in efficiency over a 2:1 P3HT:PFTBT system. These findings, displayed in Figure 4-3, gave an optimal power conversion efficiency of 0.84 ± 0.06 %. After this final optimization of the composition of the blend system, the processing parameters were established for the control P3HT:PFTBT devices.

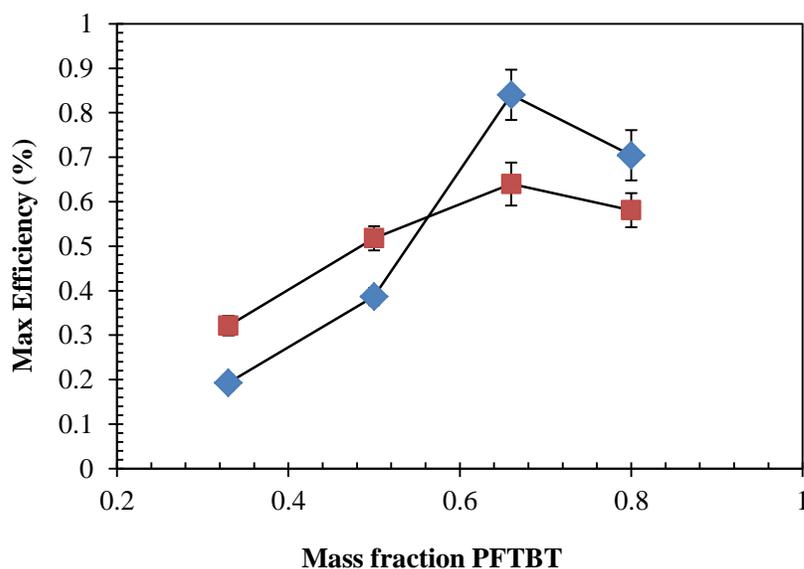


Figure 4-3 Blend efficiency versus PFTBT weight ratio

Blend efficiencies are plotted as a function of PFTBT weight fraction for 1000 rpm spin coating (◆) and 3000 rpm spin coating (■).

Finalized processing parameters for P3HT:PFTBT devices are summarized in Table 4-1.

The most important results of these findings dictates that significant heating throughout the solution mixing process and mass ratio of 1:2 P3HT:PFTBT is critical for devices functioning near 1% PCE.

Table 4-1 Important Parameters for Homopolymer Blend Optimization

| <i>Processing Condition</i> | <i>Parameter</i> |
|-----------------------------|------------------------|
| Solution heating | 90°C for 20 – 22 hours |
| Mass ratio P3HT:PFTBT | 1:2 |
| Solution concentration | 10 mg/mL |
| Spin coating speed | 1000 rpm |

Block Copolymer Improvements

After optimization of the homopolymer system, solar cell devices with P3HT-b-PFTBT for the active layer were fabricated and compared with the original P3HT:PFTBT devices. A study was conducted in which the mass fraction of block copolymer was varied from 0 to 100%. For devices with some fraction of the homopolymer blend, the weight ratio of the individual P3HT:PFTBT was 1:2 as determined by experimental optimization. Initial results indicated a promising trend: when added to a homopolymer blend, block copolymers can be used to improve the efficiency of devices, shown in Figure 4-4.

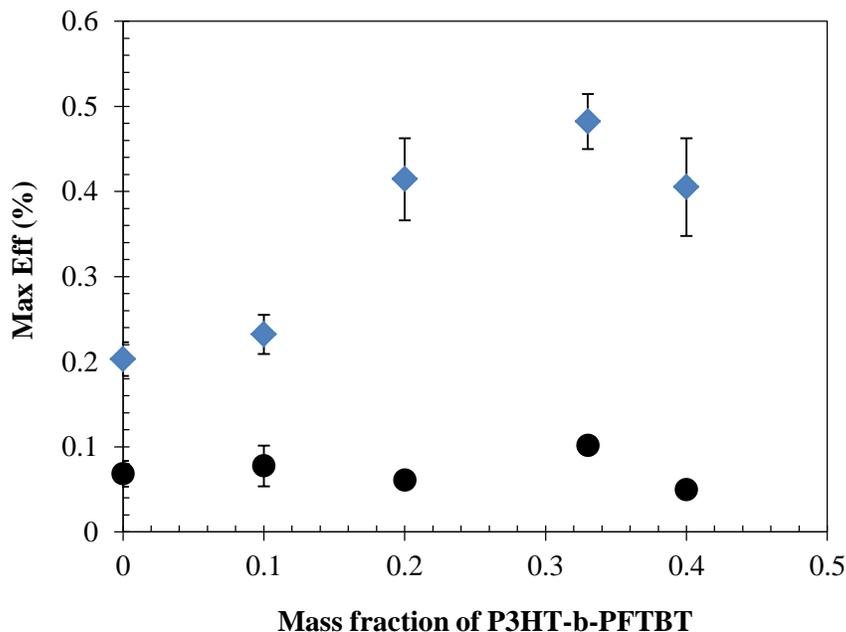


Figure 4-4 PCE at varying overall mass fraction of P3HT-b-PFTBT devices annealed at 165 °C for 10 min (◆) and unannealed (●).

Figure 4-4 indicates an approximate 2.5 times increase in efficiency by incorporating a block copolymer mass fraction of 0.33 into the active layer.

Later synthesized batches of P3HT-b-PFTBT and further device optimization reproduced this trend yet with significantly higher efficiencies and active layers solely consisting of block copolymer were fabricated with remarkable results. Figure 4-5 delineates the massive

improvements achievable when using P3HT-b-PFTBT composition rather than the homopolymer blend in the active layer.

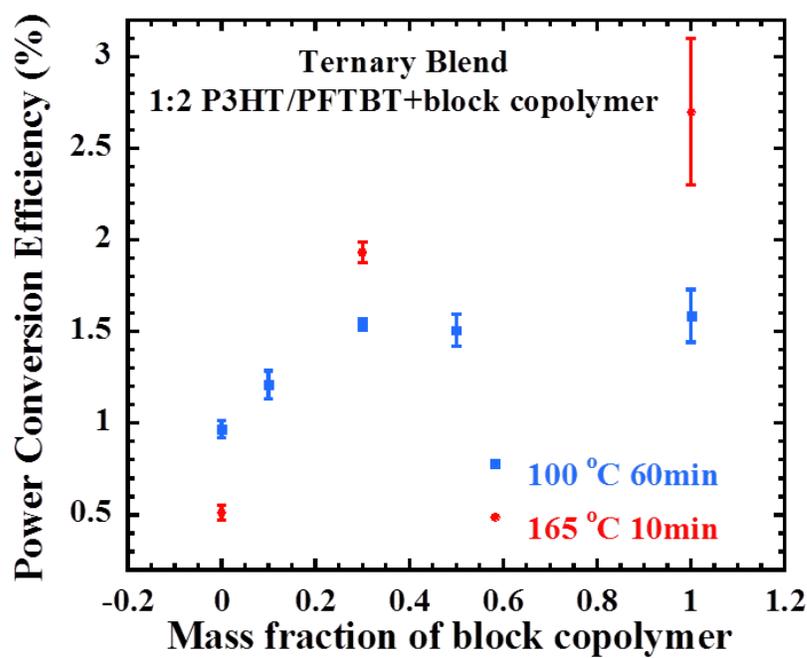


Figure 4-5 Repetition of PCE at varying overall mass fraction of P3HT-b-PFTBT. Reprinted (adapted) with permission from Guo, C.; Lin, Y.; Witman, M.; Smith, K.; Wang, C.; Hexamer, A.; Stralka, J.; Gomez, E.; Verduzco, R. Conjugated block copolymer photovoltaics with near 3% efficiency through microphase separation. *Nano Lett.* 13, 2957–63 (2013). Copyright (2013) American Chemical Society.

Clearly the block copolymer system represents a viable and significant improvement to the homopolymer blend since, at the optimized annealing temperature of 165 °C, the PCE increases by a factor of more than 5. While the greatest blend efficiency was achieved at 100 °C, the device efficiency was still reduced by a factor of 2.5 from the optimized block system at 165 °C.

Characteristic current-voltage curves for blend and block copolymers are presented in Figure 4-6. Blend devices were optimized for thermal annealing at 100 °C for 20 min while P3HT-b-PFTBT solar cells were optimized for thermal annealing at 165 °C for 10 min.

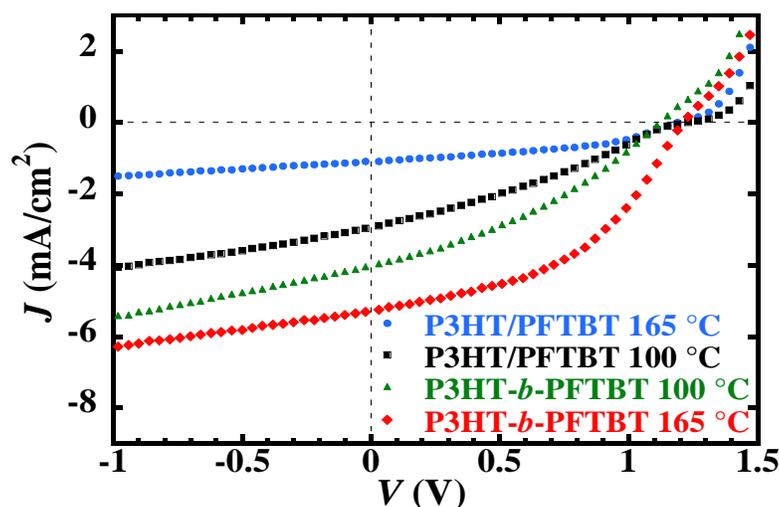


Figure 4-6 Photovoltaic performance of block copolymer and blend solar cells Characteristic current-voltage curves for 1:2 by mass P3HT:PFTBT and P3HT-b-PFTBT solar cells annealed at 165°C for 10 min and at 100°C for 20 min. Reprinted (adapted) with permission from Guo, C.; Lin, Y.; Witman, M.; Smith, K.; Wang, C.; Hexamer, A.; Stralka, J.; Gomez, E.; Verduzco, R. Conjugated block copolymer photovoltaics with near 3% efficiency through microphase separation. *Nano Lett.* 13, 2957–63 (2013). Copyright (2013) American Chemical Society.

For these characteristic curves, the parameters contributing to the PCE are summarized in

Table 4-2.

Table 4-2 Device Performance for P3HT-b-PFTBT blocks and P3HT:PFTBT blends at various annealing conditions

| | <i>efficiency</i> (%) | <i>short-circuit current</i> (mA/cm ²) | <i>open-circuit voltage</i> (V) | <i>fill factor</i> |
|-------------------------------|--------------------------|---|------------------------------------|--------------------|
| 100 °C 20 min polymer blend | 1.0 ± 0.1 | 2.6 ± 0.3 | 1.22 ± 0.02 | 0.33 ± 0.02 |
| 165 °C 10 min polymer blend | 0.5 ± 0.1 | 1.0 ± 0.1 | 1.16 ± 0.03 | 0.42 ± 0.02 |
| 100 °C 20 min block copolymer | 1.5 ± 0.1 | 3.7 ± 0.2 | 1.13 ± 0.04 | 0.35 ± 0.01 |
| 165 °C 10 min block copolymer | 2.7 ± 0.4 | 5.0 ± 0.3 | 1.14 ± 0.08 | 0.45 ± 0.02 |

*Testing performed under simulated AM 1.5G irradiation with intensity of 97 mW/cm².

For the optimized block copolymer system at 165 °C for 10 min, the average PCE was found to be 2.7 ± 0.4% with a V_{OC} of 1.14 ± 0.08 V, a J_{SC} of 5.0 ± 0.3 mA/cm², and a fill factor of 0.45 ±

0.02. For the optimized blend system at 100 °C for 20 min, the average efficiency was $1.0 \pm 0.1\%$ and mainly driven by a large reduction in the J_{SC} and fill factor. Regardless of which comparable annealing conditions are examined, the block copolymer consistently outperformed the blend. The highest efficiencies achieved for any single device are additionally shown in Table 4-3.

Table 4-3 Best devices for block copolymer and blend

| | <i>efficiency</i> (%) | <i>short-circuit</i> <i>current</i> (mA/cm ²) | <i>open-circuit</i> <i>voltage</i> (V) | <i>fill factor</i> |
|------------------------------|--------------------------|---|--|--------------------|
| Best device, block copolymer | 3.1 | 5.2 | 1.23 | 0.47 |
| Best device, blend | 1.1 | 2.9 | 1.22 | 0.30 |

*Testing performed under simulated AM 1.5G irradiation with intensity of 97 mW/cm².

RSOXS Characterization

For optimized P3HT-b-PFTBT and P3HT:PFTBT annealing conditions of 165 °C for 10 min and 100 °C for 20 min, respectively, resonant soft X-ray scattering (RSOXS) data provided insights into the a fundamental film characteristics that allowed block copolymer devices to outperform the blend. RSOXS intensities as a function of the scattering vector, which is a function of the X-ray wavelength and the scattering angle, are presented in Figure 4-7.

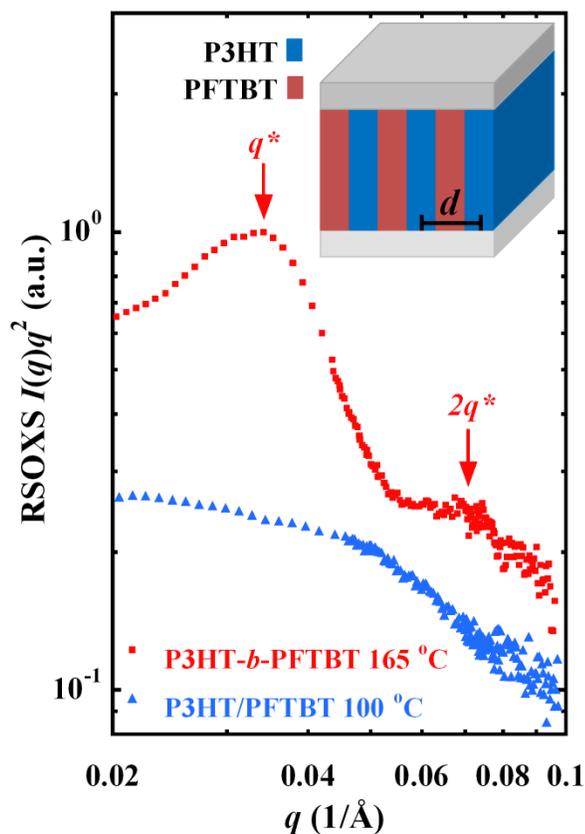


Figure 4-7 Comparison of active layer morphologies of P3HT-b-PFTBT and P3HT:PFTBT by RSOXS. Data was acquired at an X-ray energy of 285.4 eV and at optimized annealing conditions for both classes of devices. The figure represents a Kratky plot where $I(q)$ is the scattering intensity and q is the scattering vector. P3HT:PFTBT devices show no energy peaks, while P3HT-b-PFTBT shows a significant primary peak q^* and weak second-order reflection peak $2q^*$. The lamellar structure implied by this data is visually represented by the inset image. Reprinted (adapted) with permission from Guo, C.; Lin, Y.; Witman, M.; Smith, K.; Wang, C.; Hexamer, A.; Stralka, J.; Gomez, E.; Verduzco, R. Conjugated block copolymer photovoltaics with near 3% efficiency through microphase separation. *Nano Lett.* 13, 2957–63 (2013). Copyright (2013) American Chemical Society.

The position of the primary and secondary peaks at $q^* = 0.035 \text{ \AA}^{-1}$ and $2q^* = 0.070 \text{ \AA}^{-1}$ are indicative of self-assembly of a lamellar microstructure with a domain size of 18 nm. Hence individual domains are approximately 9 nm long and separate on a smaller length scale than the requirements for exciton diffusion length in organic materials of less than 10 nm.¹⁴ With no distinguishable repeating domain in the blend thin-film, the block copolymer exhibits an ability to control the donor-acceptor interface through lamellar blocks and gives justification for the vast improvements seen in the PCE. The lamellar morphology provides a structure suitable for

exciton dissociation and for self-assembled pathways that facilitate hole and electron transport to the electrodes. It must be noted that this lamellar morphology is evident only at 165 °C annealing (not at 100 °C) and that the device efficiency doubles for 165 °C annealing, shown in Table 4-2. Hence the remarkable photovoltaic performance of the block copolymer device is attributed to the self-assembled mesostructure of the active layer.

GIWAXS Characterization

While RSOXS data explored the in-plane orientation of the lamellar donor-acceptor domains, X-ray diffraction (XRD) and grazing incidence small-angle X-ray scattering (GISAXS) in 2-D (out-of-plane scattering in the q_z direction and in-plane scattering in the q_y direction) were used to determine the face-on orientation of P3HT crystallite stacking. Figure 4-8 displays the results of the 2D GIWAXS experiments.

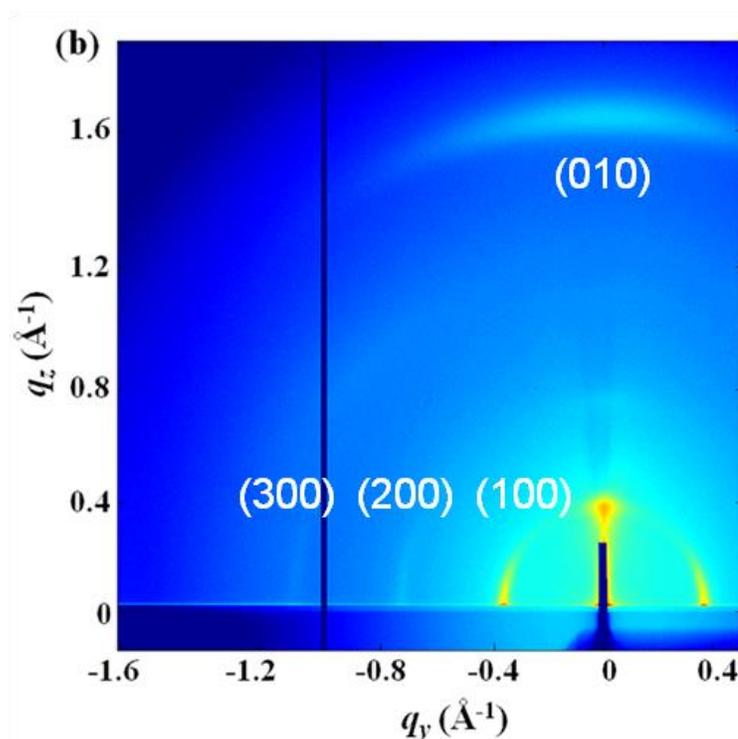


Figure 4-8. 2D GIWAXS scattering data for P3HT-b-PFTBT films annealed for optimal device PCE. The (100), (200), and (300) peaks of P3HT are biased in the in-plane orientation (q_y) while the (010) peak occurs in the out-of-plane orientation indicating face-on P3HT crystallite stacking. Reprinted (adapted) with permission from Guo, C.; Lin, Y.; Witman, M.; Smith, K.; Wang, C.; Hexamer, A.; Stralka, J.; Gomez, E.; Verduzco, R. Conjugated block copolymer photovoltaics with near 3% efficiency through microphase separation. *Nano Lett.* 13, 2957–63 (2013). Copyright (2013) American Chemical Society.

Here diffraction peaks (100), (200), and (300) of P3HT (corresponding to scattering vectors, q , of 0.4, 0.8 and 1.2 \AA^{-1} , respectively), indicate the spacing of the alkyl side chains along the regioregular P3HT backbone. They are strongly in-plane in the q_y direction, suggesting the polymer backbone runs parallel to the substrate upon which the thin film is cast. Furthermore, the (010) peak, corresponding to intermolecular π - π stacking between adjacent P3HT blocks, exhibits scattering only in the out-of plane direction, q_z . This indicates the P3HT forms face-on stacking (or stacking of π - π orbitals perpendicular to the substrate), which likely increases the hole extraction efficiency as charge transfer occurs quickly in the π - π direction towards the electrodes.¹²

Chapter 5

Conclusions and Future Work

The results of this study represent a large advancement in the field of organic photovoltaics as it has demonstrated control over the mesoscale structure of the active layer. Block copolymer devices exhibit unique structural self-assembly characteristics in polymer solar cells, such as in-plane lamellar domain sizes less than the exciton diffusion length in organic semiconductors and face-on orientation of P3HT crystallite domains. These allow more efficient charge separation and faster hole transport to the electrodes, providing evidence for the block copolymer's significant outperformance of the homopolymer blend in regards to power conversion efficiencies.

Further studies could result in improved understanding of block copolymer photovoltaics and strategies for further advancement of their efficiency. Computational studies of the donor-acceptor interface between P3HT and PFTBT must be performed to understand the kinetics of charge transfer and recombination in the block copolymer system. Thus far it is hypothesized that the microstructure morphology of the block copolymer active layer results in significantly reduced charge recombination in comparison to the polymer blend. Pi orbital overlap in the face-on orientation stacking of the blocks is a potential indicator of reduced exciton recombination and could be quantified through future computational modeling.

The block copolymer active layer also introduces the physics of intramolecular recombination not seen in the polymer blend films. When an exciton forms on the donor block, recombination of the exciton on the adjoining acceptor block is possible, while in the polymer blend this type of decay can only occur on an intermolecular level. Understanding how excitonic

intramolecular decay occurs may be a key piece of information for optimizing block copolymer photovoltaics in the future. For example, adding molecular structures other than simple carbon-carbon bonds to connect the donor and acceptor blocks could yield higher charge transfer rates.

Outside of the studied P3HT-b-PFTBT system, blocks could be varied to have complementary absorbance to maximize light harvesting. P3HT and PFTBT have overlapping absorbance bands which limits the overall efficiency of the system.

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