CONJUGATED BLOCK COPOLYMERS: A BUILDING BLOCK
FOR HIGH-PERFORMANCE ORGANIC PHOTOVOLTAICS

A Dissertation in
Chemical Engineering

by

Changhe Guo

© 2014 Changhe Guo

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

December 2014
The dissertation of Changhe Guo was reviewed and approved* by the following:

Enrique D. Gomez  
Assistant Professor of Chemical Engineering  
Dissertation Advisor  
Chair of Committee

Scott T. Milner  
Joyce Chair and Professor of Chemical Engineering

Ralph H. Colby  
Professor of Materials Science and Engineering  
Professor of Chemical Engineering

Chris Noel Giebink  
Assistant Professor of Electrical Engineering

Michael Janik  
Associate Professor of Chemical Engineering  
Graduate Program Chair of the Department of Chemical Engineering

*Signatures are on file in the Graduate School.
ABSTRACT

State-of-the-art organic photovoltaics rely on kinetically trapped, partially phase-separated structures of donor/acceptor mixtures to create a high interfacial area for exciton dissociation and networks of bicontinuous phases for charge transport. Nevertheless, intrinsic structural disorder and weak intermolecular interactions in polymer blends limit the performance and stability of organic electronic devices. We demonstrate a potential strategy to control morphology and donor/acceptor heterojunctions through conjugated block copolymer 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 can self-assemble into well-ordered nanostructures ideal for photovoltaic applications. When utilized as the photovoltaic active layer, P3HT-b-PFTBT block copolymer devices demonstrate thermal stability and photoconversion efficiency of 3% well beyond devices composed of the constituent polymer blends.

Resonant soft X-ray scattering (RSOXS) is used to elucidate the structural origin for efficient block copolymer photovoltaics. Energy tuning in soft X-ray ranges gives RSOXS chemical sensitivity to characterize organic thin films with compositionally similar phases or complicated multiphase systems. RSOXS reveals that the remarkable performance of P3HT-b-PFTBT devices is due to self-assembly into nanoscale in-plane lamellar morphology, which not only establishes an equilibrium microstructure amenable for exciton dissociation but also provides pathways for efficient charge transport. Furthermore, we find evidence that covalent control of donor/acceptor interfaces in block
copolymers has the potential to promote charge separation and optimize the photoconversion process by limiting charge recombination.

To visualize the nanostructure in organic thin films, we introduce low energy-loss energy-filtered transmission electron microscopy (EFTEM) as an important alternative approach to generate contrast from differences in optoelectronic properties and enable chemical imaging of organic materials. The widely-studied polymer/fullerene system is used as a test sample to demonstrate the application of this technique for structure characterization in the active layer of organic solar cells.

In addition, well-ordered equilibrium nanostructures and covalent control of donor/acceptor interfaces make P3HT-\textit{b}-PFTBT an excellent model for studying the effect of crystalline texture in the active layer on charge transport and photovoltaic performance. Solvent additives are applied to induce a drastic texture change from mainly face-on to edge-on orientations in crystalline P3HT domains of block copolymer thin films. We find that P3HT-\textit{b}-PFTBT block copolymer devices demonstrate similar optimal performance, regardless of the dramatic changes in the predominant crystalline orientations adopted in P3HT domains. Our results provide further insights into the molecular organization required for efficient charge transport and device operation.
TABLE OF CONTENTS

List of Figures .................................................................................................................. viii
List of Tables .................................................................................................................... xviii
Preface ................................................................................................................................. xix
Acknowledgements .......................................................................................................... xx

Chapter 1. Introduction ........................................................................................................ 1
1.1 Motivation ....................................................................................................................... 1
1.2 Principles of Organic Photovoltaics ........................................................................... 5
1.3 Morphology Design for Efficient Organic Solar Cells ............................................. 10
1.4 Characterization of Photovoltaic Performance ....................................................... 12
1.5 References .................................................................................................................... 17

Chapter 2. Objectives and Approaches ............................................................................. 19
2.1 Structure Limitations in State-of-the-art Polymer Blend Solar Cells ..................... 19
2.2 Block Copolymer Strategy Towards Efficient Organic Photovoltaics ............... 25
2.3 Morphological Characterization of the Active Layer in Organic Solar Cells ........ 30
2.4 Dissertation Overview ............................................................................................... 37
2.5 References .................................................................................................................... 40

3.1 Introduction .................................................................................................................... 44
3.2 Results and Discussions ............................................................................................... 46
  3.2.1 Origin of Scattering Contrast in RSOXS ............................................................... 46
  3.2.2 RSOXS Characterization of Structure Evolution in P3HT/PCBM Mixtures ...... 48
  3.2.3 Energy Dependence of the Scattering Contrast in RSOXS Profiles ................. 49
  3.2.4 Composition Analysis of Elemental Maps from EFTEM Imaging .................. 51
  3.2.5 Signatures of Multiphase Formation in P3HT/PCBM Mixtures from RSOXS .... 56
3.3 Conclusions .................................................................................................................. 59
3.4 Materials and Methods ............................................................................................... 60
3.5 References .................................................................................................................... 62

Chapter 4. High-performance Conjugated Block Copolymer Photovoltaics through Microphase Separation ................................................................................................. 65
4.1 Introduction .................................................................................................................... 65
4.2 Results and Discussions ............................................................................................... 67
  4.2.1 Block Copolymer Photovoltaics Outperform Polymer Blend Solar Cells........ 67
  4.2.2 Structural Origin for Efficient Block Copolymer Photovoltaics from RSOXS .... 73
4.2.3 Control of Crystalline Orientations in Block Copolymer Thin Films ............77
4.2.4 Covalent Control of Donor-Acceptor Interfaces in Block Copolymer Photovoltaics.................................................................80
4.3 Conclusions..................................................................................81
4.4 Materials and Methods................................................................82
4.5 References....................................................................................86

Chapter 5. Orientation Control of Molecular Packing in Conjugated Block Copolymer Solar Cells and Implications for Photovoltaic Performance..........................91
5.1 Introduction..................................................................................92
5.2 Results and Discussions..............................................................96
  5.2.1 Orientation Control of Molecular Packing in Poly(3-hexylthiophene)-based Conjugated Block Copolymers..............................................96
  5.2.2 Effect of Solvent Additives on the Active Layer Morphology from Resonant Soft X-ray Scattering .................................................100
  5.2.3 Optimized Block Copolymer Photovoltaic Performance is Independent of the Crystalline Texture in the Active Layer.....................103
  5.2.4 Differences in Thickness Dependence of Block Copolymer Photovoltaic Performance at Various Processing Conditions.............105
5.3 Conclusions................................................................................111
5.4 Materials and Methods..............................................................111
5.5 References................................................................................114

6.1 Introduction................................................................................118
6.2 Results and Discussions.........................................................120
  6.2.1 Electronic Signatures of Organic Semiconductors at Low-loss Regions of Electron Energy-loss Spectrum.................................120
  6.2.2 Degradation of Electronic Structures in Organic Materials upon Electron Radiation.............................................................123
  6.2.3 Low Energy-loss Spectral Imaging of P3HT/PCBM Mixtures ..........127
6.3 Conclusions..............................................................................132
6.4 Materials and Methods............................................................133
6.5 References..............................................................................134

Chapter 7. Summary and Future Outlook .............................................137
7.1 Summary..................................................................................137
7.2 Further Optimization of Block Copolymer Solar Cells ........................................ 140
   7.2.1 Development of Long-range Order in Self-assembly Structures of Block 
         Copolymer Thin Films .................................................................................. 140
   7.2.2 Chemical Tuning of Optoelectronic Properties of Block Copolymer 
         Semiconductors ......................................................................................... 144
   7.2.3 Multicomponent Block Copolymer Photovoltaics Capable of Broad Light 
         Absorption .................................................................................................. 146
7.3 Study of Donor-Acceptor Interfacial Structure via Polarized RSOXS ............... 151
7.4 References ..................................................................................................... 155

Appendix A. Supporting Information for Chapter 4: High-performance Conjugated Block 
          Copolymer Photovoltaics through Microphase Separation ...................... 157 
  A.1 Morphological Characterization through RSOXS and GISAXS ............... 157 
  A.2 References ................................................................................................. 159 

Appendix B. Supporting Information for Chapter 6: Probing Nanoscale Morphology and 
          Local Electronic Transitions in Organic Semiconductors through Low-loss 
          Spectral Imaging in Transmission Electron Microscopy ....................... 160 
  B.1 Comparison of EELS and UV-Visible Absorption Data .......................... 160 
  B.2 Spectral Degradation of Organic Semiconductors upon Electron Radiation .. 162 
  B.3 Core-loss Elemental Maps of P3HT/PCBM Mixtures ............................. 165 
  B.4 References ................................................................................................. 166
List of Figures

Figure 1-1. Timeline of research cell efficiency records for various classes of photovoltaic devices certified by NREL, 2014. ................................................................. 2

Figure 1-2. Schematic illustration of standard printing processes for large-scale production of polymer-based photovoltaic cells. ................................................................. 2

Figure 1-3. Molecular structures and absorption spectra of naphtho[2,1-b:3,4-b’]dithiophene (NDT)-based copolymer semiconductors HMPNDT, PNDT-T and PNDT-BT. Tuning the chemical structure of the copolymer backbone allows alternation of the bandgap and optical absorption properties of polymer semiconductors. ................................................................. 3

Figure 1-4. Chemical structures of regioregular P3HT and PCBM semiconductors. Images are taken from Plextronics/Plexcore® PV website ................................................................. 5

Figure 1-5. Effect of conjugation length on HOMO/LUMO levels of conjugated molecules. With increasing conjugation length, the HOMO level increases while the LUMO level decreases, resulting in a lower bandgap, Eg. ................................................................. 6

Figure 1-6. Schematic of the standard device architecture for a polymer-based photovoltaic cell. The active layer composed of photovoltaic functional materials is sandwiched between the transparent anode and the metal cathode. ................................................................. 7

Figure 1-7. Energy level diagram at donor-acceptor interfaces illustrating the principle of organic photovoltaic operation including (a) light absorption, (b) exciton diffusion, (c) charge transfer and separation, and (d) charge transport and collection. Images are adapted from the 2010 review by Clarke and Durrant. ................................................................. 9

Figure 1-8. Schematic illustrations of photon absorption, exciton diffusion, charge separation, and charge transport in the active layer of organic solar cells. ................................................................. 9

Figure 1-9. Schematics of the active layer morphology for (a) planar heterojunction, (b) bulk heterojunction, and (c) an ideal ordered heterojunction polymer solar cells. lD is the exciton diffusion length in organic semiconductors ................................................................. 11

Figure 1-10. Current-Voltage (J-V) characteristics under simulated one sun illumination for P3HT/PCBM bulk heterojunction solar cells annealed at 165 °C for 10 min................................................................. 13

Figure 1-11. Molecular orbital energy levels of P3HT donor and PCBM acceptor. Various LUMO levels for PCBM haven been reported in the literature. The energy difference between the donor HOMO level and the acceptor LUMO level (HOMO_D–LUMO_A) determines the maximum voltage that can be generated in photovoltaic devices …15
**Figure 2-1.** Comparison of optical absorption spectrum for PCBM pristine films with AM 1.5 Global tilt solar spectrum. Data of solar spectrum come from Solar Spectral Irradiance: Air Mass 1.5 at website of National Renewable Energy Laboratory. ....19

**Figure 2-2.** (a) Chemical structures of PF8TBT and energy level diagram showing the HOMO and LUMO levels of P3HT, PF8TBT and PCBM. (b) Normalized absorption spectra of pristine films of P3HT, PF8TBT and PCBM.5 ................................................................. 21

**Figure 2-3.** Schematic illustrations of bulk heterojunction morphology in the active layer of organic solar cells. (a) As-cast polymer blend structure with a large area of donor-acceptor interfaces but poor transport pathways. (b) Mesoscopic phase separation developed in the active layer after thermal annealing with percolated domains for charge transport, although interfacial area is reduced. ................................................................. 22

**Figure 2-4.** Schematics of random molecular configurations near donor-acceptor interfaces in (a) polymer/fullerene and (b) polymer/polymer mixtures. ........................................... 23

**Figure 2-5.** Optical microscopy images of P3HT/PCBM mixtures (with weight ratio of 3:2) annealed at 120 °C for various times. Scale bar is 100 µm. Phase segregation becomes evident with increasing annealing time.18 ................................................................. 24

**Figure 2-6.** Molecular architectures for linear diblock and triblock copolymers. Each colored strand represents a polymer block comprised of a linear sequence of identical repeating units, labeled as A, B and C as shown in red, blue and green, respectively. The colored strands are joined by covalent bonding to form diblock (A-B) or triblock (A-B-C) copolymer macromolecules. ................................................................. 25

**Figure 2-7.** Theoretical equilibrium phase diagram for linear A-B diblock copolymers. Self-consistent mean-field theory predicts equilibrium morphologies including lamellar (L), gyroid (G), cylindrical (C), spherical (S), closely-packed spherical (CPS), and disordered structures, depending on the volume fraction of block A, \( f_A \), and a combination parameter \( \chi N \). \( \chi \) is the Flory-Huggins interaction parameter, which describes the interaction energy between dissimilar polymer segments. \( N \) is the degree of polymerization, that is the number of monomers of all types per macromolecule.21 ........................................ 26

**Figure 2-8.** Schematic representations of the equilibrium nanostructures commonly observed in coil-coil diblock copolymers A-B, as the volume fraction of block A, \( f_A \), increases. Ordered morphologies are labeled as S for spheres, C for cylinders, G for gyroid, and L for lamellae. Domains of polymer blocks A and B are indicated with blue and red regions, respectively.24 ........................................................................................................................................... 27

**Figure 2-9.** Schematic illustrations of block copolymer photovoltaic devices with an in-plane lamellar structure formed in the active layer. A molecular picture of the donor-
acceptor interfaces in the block copolymer architecture is shown on the right. Images are adapted from ref 25.

**Figure 2-10.** Design of block copolymers for photovoltaic applications via (a) non-conjugated linking with semiconducting small molecules as pendant groups\(^{27-28}\) or through (b) conjugated bonding to maintain full conjugation across the covalent donor-acceptor interfaces.\(^{31}\)

**Figure 2-11.** Schematics of equipment set-up for electron energy-loss spectroscopy (EELS) and energy-filtered transmission electron microscopy (EFTEM). The image is taken from the Electron Microscopy group homepage of the Department of Material Science and Metallurgy, University of Cambridge.

**Figure 2-12.** Bright field (BF), sulfur map (S), and carbon map (C) for a 1:1 P3HT/PCBM blend film annealed at 190 °C for 30 min. The same area of the sample is shown and images were taken at focus. The image intensities of sulfur map are proportional to the sulfur concentration and the light regions correspond to P3HT-rich domains. The carbon map shows inverted contrast to sulfur map with the dark regions corresponding to P3HT-rich fibers. Scale bar is 200 nm.

**Figure 2-13.** Energy-filtered TEM imaging of a 1:1 P3HT/PCBM blend film annealed at 110 °C for 10 min. (a) electron energy-loss spectra (EELS) from pure P3HT and PCBM films. Energy windows for imaging are drawn at 19 ± 4 eV and 30 ± 4 eV, where inelastic scattering is more intense from P3HT and PCBM, respectively. (b) Zero-loss image using only elastically scattered electrons. (c) 19 eV loss image, where P3HT domains are bright. (d) 30 eV image, where PCBM domains are bright. Scale bar is 50 nm as shown on the images.

**Figure 2-14.** Transmission geometry of resonant soft X-ray scattering (RSOXS) experiments. Films are placed normal to the incident beam (~ 200x300 µm) with scattered intensities \(I(\theta, \phi)\) recorded at all scattering angles, \(\theta\), using a CCD. RSOXS intensities \(I(\theta, \phi)\) probing the in-plane film morphology as shown on the right, can be integrated along the azimuth, \(\phi\), and thus converted into the canonical scattering profile as a function of scattering vector, \(q = 4\pi \sin(\theta/2)/\lambda\), \(\lambda\) is the X-ray wavelength.

**Figure 3-1.** Near edge X-ray fine structure (NEXAFS) spectra for pristine films of P3HT and PCBM near the carbon 1s to \(\pi^*\) transition regions. Open symbols represent experimental data and solid lines represent the individual peak fits. P3HT films show a spectral transition at 285.1 eV, while two resonant features are indentified at 284.5 and 285.8 eV for PCBM films. The spectra are displaced along the y-axis for clarity.

**Figure 3-2.** RSOXS intensity vs. scattering vector, \(q\), for 1:1 by mass P3HT/PCBM mixtures annealed at various temperatures for 30 min at the (a) carbon absorption edge.
(284.4 eV) and (b) oxygen absorption edge (525 eV). Data are published in ACS Macro Letters.  

**Figure 3-3.** Comparison of RSOXS intensities vs. scattering vector, $q$, at 284.4 and 525 eV for 1:1 by mass P3HT/PCBM mixtures annealed at (a) 190 °C (b) 165 °C, (c) 140 °C, and (d) 100 °C for 30 min. Data are published in ACS Macro Letters.  

**Figure 3-4.** Sulfur elemental maps generated through EFTEM with schematic illustrations for 1:1 by mass P3HT/PCBM mixtures annealed at (a) 190 °C and (b) 100 °C for 30 min. The image intensity is proportional to the sulfur concentration. Therefore, the light regions correspond to P3HT-rich regions. The domain purity can be computed from the image intensities. The scale bar is 100 nm. TEM images were taken at the Penn Regional Nanotechnology Facility, University of Pennsylvania. Data are published in ACS Macro Letters.  

**Figure 3-5.** Comparison of radially integrated Fast Fourier Transform (FFT) intensities vs $q$ ($q = 2\pi/d$, where $d$ is the length scale in real space) obtained from sulfur maps in Figure 3-4 with the RSOXS data at the carbon absorption edge (284.4 eV) for P3HT/PCBM films annealed at (a) 190 and (b) 100 °C, respectively. The peak intensities were normalized to 1. The FFT profiles were plotted at a different y-axis scale in order to compare with the RSOXS results. Data are published in ACS Macro Letters, Supporting Information.  

**Figure 4-1.** (a) Chemical structures of polymer P3HT and PFTBT, and block copolymer P3HT-$b$-PFTBT. Data are published in Nano Letters. (b) Energy level diagram of P3HT as a donor and PFTBT as an acceptor. The large energy difference between P3HT HOMO level and PFTBT LUMO level predicts a theoretical open-circuit voltage beyond 1 V.  

**Figure 4-2.** Current-voltage characteristics of polymer blend P3HT/PFTBT (1:2 by mass) and block copolymer P3HT-$b$-PFTBT photovoltaic devices annealed at 100 °C for 20 min and 165 °C for 10 min, respectively. P3HT/PFTBT solar cells are optimized at 100 °C for 20 min, while P3HT-$b$-PFTBT devices are optimized at 165 °C for 10 min. Devices were measured under simulated AM 1.5G irradiation with intensity of 97 mW/cm$^2$. Data are published in Nano Letters.  

**Figure 4-3.** (a) Absorption spectra of pristine P3HT, PFTBT and P3HT-$b$-PFTBT films. All films were cast from chloroform solutions. The absorption coefficients are calculated from the measured absorbance and film thicknesses. (b) External quantum efficiency (EQE) characteristics of a P3HT-$b$-PFTBT solar cell annealed at optimized conditions (165 °C for 10 min) compared with the UV-Visible absorption spectrum of P3HT-$b$-PFTBT films. Data are published in Nano Letters and the Supporting Information.
**Figure 4-4.** Near edge X-ray absorption fine structure (NEXAFS) studies of neat P3HT and PFTBT films. Films were annealed at optimized conditions (165 °C) for device performance. NEXAFS spectra were normalized to 1 at 320 eV to account for thickness variations. Significant contrast is observed at 285.4 eV, where the X-ray absorptions of P3HT and PFTBT differ. Data are published in Nano Letters, Supporting Information.

**Figure 4-5.** Comparison of the morphology in the active layers of optimized P3HT-b-PFTBT and P3HT/PFTBT photovoltaic devices using RSOXS. RSOXS data were acquired at the carbon absorption edge (285.4 eV) of a P3HT-b-PFTBT film annealed at 165 °C and a P3HT/PFTBT (1:2 by mass) blend annealed at 100 °C. RSOXS intensities are offset for clarity. Scattering data are presented as a Kratky plot of \( I(q)q^2 \) vs \( q \), where \( I(q) \) is the scattering intensity, and \( q \) is the scattering vector. RSOXS intensities \( I(q) \) as a function of \( q \) are shown in Appendix A. In optimized P3HT-b-PFTBT samples, a well-defined primary peak, \( q^* \) (~ 0.035 Å\(^{-1}\)), and second-order reflection, \( 2q^* \), are identified. Schematic illustration of the lamellar morphology is shown in the inset, with the average domain spacing indicated as \( d \). Data are published in Nano Letters.

**Figure 4-6.** RSOXS intensities of P3HT-b-PFTBT block copolymer and P3HT/PFTBT polymer blend thin films under various processing conditions. Profiles are offset for clarity. Scattering data were acquired at 285.4 eV, azimuthally integrated, and presented as a Kratky plot of \( I(q)q^2 \) vs \( q \), where \( I(q) \) is the scattering intensity, and \( q \) is the scattering vector. Data are published in Nano Letters, Supporting Information.

**Figure 4-7.** Molecular organization in P3HT-b-PFTBT thin films. (a) X-ray diffraction (XRD) patterns of neat P3HT, neat PFTBT, P3HT/PFTBT blend, and P3HT-b-PFTBT block copolymer films annealed at 165 °C. (b) Two-dimensional GIWAXS pattern for thin films of P3HT-b-PFTBT annealed at optimized conditions (165 °C) for device performance. The (100), (200), and (300) diffraction peaks of regioregular P3HT are strongly biased in the in-plane direction (\( q_y \)) and the (010) peak is apparent in the out-of-plane direction (\( q_z \)), suggesting face-on crystallites. Data are published in Nano Letters.

**Figure 4-8.** Size-Exclusion Chromatography (SEC) analysis of P3HT macroreagent and final block copolymer product. SEC analysis shows a clear shift of the molecular weight distribution for the final P3HT-b-PFTBT block copolymer compared with the starting P3HT macroreagent. The shoulder in the molecular weight distribution at long times indicates that some residual P3HT macroreagent is present (14 wt %). Data are published in Nano Letters, Supporting Information.

**Figure 5-1.** Schematic illustrations of crystal structure for regioregular P3HT. \( b \) axis denotes the direction of \( \pi-\pi \) interchain stacking between conjugated thiophene rings with a periodic spacing \( d_{010} \) of 0.38 nm. \( a \) axis indicates the alignment direction of alkyl side chains between polymer backbones characterized by an interchain distance \( d_{100} \) of around...
1.6 nm.\textsuperscript{12}  $c$ axis represents the conjugation direction along the chain backbone. The image is adapted from ref 13. .......................................................... 93

**Figure 5-2.** Two-dimensional wide-angle X-ray scattering images of spin-coated, 70-100 nm thick P3HT films with regioregularity of (a) 96\% and (b) 81\% on SiO$_2$/Si substrates, respectively. The vertical axes correspond to scattering normal to the film plane, while the horizontal axes correspond to scattering parallel with the plane of the film. The scattering data demonstrate two different orientations of ordered P3HT domains with respect to the field-effect transistor (FET) substrate, namely (a) edge-on and (b) face-on orientations, as shown in the insets.\textsuperscript{10} .......................................................... 94

**Figure 5-3.** Two-dimensional grazing-incidence wide-angle X-ray scattering (GIWAXS) patterns with schematic illustrations for dominant molecular orientations of P3HT crystals in P3HT-$b$-PFTBT block copolymer solar cells processed with 0\% (a, c) and 5\% (b, d) 1-chloronaphthalene (CN) solvent additives. All samples were annealed at 165 °C. Block copolymer films without solvent additive adopt predominant face-on orientations with π-stacking primarily out-of-plane in P3HT domains. When the solvent additive is present, however, P3HT crystals demonstrate a dramatic change in molecular packing from face-on to edge-on orientations. The two electrodes are Al (grey) and ITO (white), respectively.. .......................................................... 97

**Figure 5-4.** GIWAXS intensities as a function of azimuthal angle, \(\phi\), at P3HT (a) (100) and (b) (010) peaks for P3HT-$b$-PFTBT block copolymer thin films processed with 0\% and 5\% chloronaphthalene (CN) additives. Intensities were integrated over a \(q\) window of ± 0.06 Å\(^{-1}\) for the (100) peak and ± 0.10 Å\(^{-1}\) range for the (010) reflection. A linear background was subtracted from the integrated data, respectively, using intensities away from the Bragg peak of interest. .................................................................................. 99

**Figure 5-5.** Comparison of the morphology in the active layers of P3HT-$b$-PFTBT photovoltaic devices processed with 0\% and 5\% solvent additive using RSOXS. RSOXS data were integrated azimuthally and presented as (a) \(I\) vs \(q\) and (b) a Kratky plot of \(I(q)q^2\) vs \(q\), where \(I(q)\) is the scattering intensity and \(q\) is the scattering vector. Scattering data were acquired at the carbon absorption edge of 285.4 eV. Thin films of P3HT-$b$-PFTBT with 0\% and 5\% solvent additives were annealed at the optimal conditions (165 °C) for the device performance. Scattering profiles are offset for comparisons. A primary scattering peak, \(q^*\), and its higher-order reflections are identified for optimized P3HT-$b$-PFTBT samples with different concentrations of solvent additive. ................. 101

**Figure 5-6.** Average current-voltage characteristics of optimized P3HT-$b$-PFTBT photovoltaic devices processed with 0\% and 5\% solvent additive (a) under simulated one sun illumination and (b) in the dark environment. Data were averaged over six devices. P3HT-$b$-PFTBT solar cells with different concentrations of solvent additives are both
optimized at an annealing temperature of 165 °C. Devices were measured under simulated AM 1.5G irradiation with intensity of 95 mW/cm$^2$.

**Figure 5-7.** Comparison of UV-Visible absorptivity for P3HT-$b$-PFTBT thin films processed with 0% and 5% CN additives. Both films were annealed at 165 °C to match the optimum conditions for the device performance. Absorptivity data of block copolymer films are calculated from the absorbance data measured from UV-Visible spectroscopy.

**Figure 5-8.** The thickness dependence of photovoltaic performance for P3HT-$b$-PFTBT block copolymer solar cells processed with 0% and 5% solvent additives. (a) Fill factor, (b) open-circuit voltage, $V_{oc}$, (c) short-circuit current, $J_{sc}$, and (d) power conversion efficiency as a function of the active layer thicknesses. All devices were optimized at an annealing temperature of 165 °C. Device characteristics were measured under simulated AM 1.5G irradiation with intensity of 95 mW/cm$^2$.

**Figure 6-1.** (a) Raw electron energy-loss spectra (EELS) with zero-loss peaks (ZLPs) of rr-P3HT, PCBM, and PGeBTBT neat films at low energy-loss regions. rr-P3HT films were annealed at 150 °C for 12 hrs to highlight crystalline properties. The upturn at low energy losses (< 2.5 eV) is due to the energy spread of the incident beam. Distinct spectral features down to 1.5 eV can be identified from ZLPs. (b) ZLP-subtracted EELS spectra of rr-P3HT, PCBM and PGeBTBT neat films. EELS data are normalized by the incident intensity and the film thickness accordingly, and scaled with the maximum intensity of the PGeBTBT spectrum for comparison.

**Figure 6-2.** EELS data at various radiation exposures and integrated EELS intensities at low energy-loss regions as a function of electron dose for (a, d) rr-P3HT, (b, e) PCBM, and (c, f) PGeBTBT neat films. EELS Data of different materials were measured from the same sample area. ZLP-subtracted EELS intensities are integrated up to 4 eV for rr-P3HT, 8.5 eV for PCBM, and 2.6 eV for PGeBTBT. The solid lines represent data fits to an exponential decay. The peak positions of rr-P3HT are extracted from Gaussian fits to EELS spectra and plotted versus electron dose in (d).

**Figure 6-3.** Low energy-loss energy-filtered imaging of a P3HT/PCBM blend with a 1:1 weight ratio annealed at 190 °C for 30 min at (a-d) 3, 4, 5, and 6 eV with the slit width of 1.5 eV. Scale bar is 100 nm.

**Figure 6-4.** Component energy-loss spectra corresponding to P3HT- and PCBM-rich domains extracted from the spectral image series for P3HT/PCBM blend films annealed at 190 °C for 30 min. (a) Energy-filtered TEM image at 4 eV for P3HT/PCBM mixtures presenting bright fibers and a dark matrix. Scale bar is 100 nm. (b) Component spectra 1 and 2 that correspond to fibrous and matrix phases, respectively. Spectral data were
Figure 6-5. (a-b) Phase maps deconvoluted through principle component analysis for P3HT/PCBM blends annealed at 190 °C for 30 min. Phase maps (a) and (b) illustrate spatial distributions of the component spectra 1 and 2 in Figure 6-4b, respectively. Image (a) highlights P3HT fibers in bright regions, while image (b) shows inverted contrast with bright areas corresponding to PCBM-rich domains. (c) Composite image created by combining component images (a) and (b), demonstrating P3HT fibers (red) and a PCBM-rich matrix (green). Scale bar is 100 nm.

Figure 7-1. Schematics of short-range (left) and long-range (right) order formation in block copolymer thin films. Self-assembled block copolymers with short-range order implies a large amount of structural disorder with poorly-defined interfaces. Block copolymer thin films with long-range order present less disorder and sharper interfaces.

Figure 7-2. (a) TEM image of an polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) diblock copolymer samples after electric field alignment. The lamellar slice is parallel with the applied electric field, E₀, in the film plane. (b) Cross-sectional TEM image of 700 nm thick PS-b-PMMA films after annealing at 185 ± 5 °C under a ~40 V/µm electric field for 16 hrs. Scale bar is 100 nm. A vertically oriented cylindrical structure is aligned along the applied field direction.

Figure 7-3. (a) Structure of PEO-b-PMA/CB block copolymer membranes with lithium conducting poly (ethylene oxide) cylindrical domains aligned uniformly in the current flow direction. (c) The liquid-crystalline unit cell with mesogenic backbone residues anchored in the layers transverse to the long axes of PEO cylinders.

Figure 7-4. Chemical structures of selected (a) polymer donors such as PTB7, PCPDTBT, PSEHTT, and PTQ1, and (b) naphthalene diimide (NDI)-based polymer acceptors including P(NDI2OD-T2), PNDIS-HD, and P(NDI-TCPDTT).

Figure 7-5. Morphology schematics and simple representations of bulk and ordered heterojunction devices as many nanoscale devices connected in parallel for (a) binary and (b) multicomponent solar cells. Through proper material selections, multicomponent photovoltaics are capable of broad-band light absorption with different phases absorb light at different wavelength ranges.

Figure 7-6. Energy level diagrams and corresponding design of self-assembled triblock copolymers for multicomponent organic solar cells. (a) Material system containing one donor and two acceptors, where the HOMO/LUMO levels of acceptor 3 lie within the bandgap of acceptor 2. Significant charge recombination can occur unless phase 3 is
physically isolated from phase 2 in the active layer. (b) System composed of two donors and one acceptor with the energy levels of donor 3 inserted in the bandgap of donor 1. (c) A cascade-like energy level arrangement, with which charge transfer can occur at any donor-acceptor interfaces.

**Figure 7-7.** (a) Schematic of orientation of the C 1s to $\pi^*$ transition dipole moment of the pentacene molecule, normal to the aromatic plane. (b) Components of the optical constants (real, $\delta(\lambda)$, and imaginary, $\beta(\lambda)$, part) for pentacene, derived from domains whose average transition dipole moments, that is the aromatic plane normal directions, are preferentially aligned parallel or perpendicular to the incident electric field. $\beta(\lambda)$ is measured from transmission spectroscopy, whereas $\delta(\lambda)$ is calculated from $\beta(\lambda)$ using a Kramers-Kronig transformation.\textsuperscript{15}

**Figure 7-8.** (Left) Incident soft X-rays can be polarized in the plane normal to the propagation direction producing horizontally or vertically oscillated electric field $E$. The energy of a polarized X-ray beam is tuned to be resonant with the characteristic 1s to $\pi^*$ transition of carbon atoms in crystalline P3HT (right), making the scattering intensities sensitive to the molecular orientation. Absorption of P3HT can vary depending on the alignment of $\pi$-stacking direction with respect to the polarized electric field $E$.

**Figure 7-9.** (a) 2D RSOXS scattering image with symmetric azimuthal sectors from 0 to 90° for P3HT-$b$-PFTBT block copolymer thin films annealed at 165 °C. Data were obtained with horizontally (0°) polarized X-rays at 285.4 eV near the carbon absorption edge. Anisotropic scattering patterns revealed by (b) horizontally (0°) and (c) vertically (90°) polarized X-ray beam. The highest scattering intensity always occurs in the direction parallel to the polarized electric field.

**Figure A-1.** RSOXS intensities of P3HT-$b$-PFTBT and P3HT/PFTBT thin films under various processing conditions. (a) $I$ vs $q$ and (b) $Iq^2$ vs $q$, where $I$ is the scattering intensity, and $q$ is the scattering vector. Profiles are offset for clarity. Scattering data were acquired at 285.4 eV, azimuthally integrated in a, and presented as a Kratky plot of $I(q)q^2$ vs $q$ in b.

**Figure A-2.** GISAXS intensities vs in-plane scattering vector, $q_y$, for a P3HT-$b$-PFTBT film annealed at 165 °C.

**Figure B-1.** Comparison of electron energy loss spectra (EELS) and UV-Visible absorption data for (a) rr-P3HT, (b) rra-P3HT, (c) PGeBTBT and (d) PCBM neat films. Zero-loss peaks are subtracted using third order power law. EELS data are normalized by the incident intensities and the film thicknesses accordingly. UV-Visible absorption data are normalized by the film thicknesses.
Figure B-2. EELS data at various radiation exposures and integrated EELS intensities as a function of electron dose for (a-b) crystalline rr-P3HT, and (c-d) amorphous rra-P3HT. For rr-P3HT, EELS data at exposure dose beyond 4000 e/\text{nm}^2 are subtracted as an amorphous background from EELS spectra at lower dose. The subtracted EELS intensities are integrated to 4 eV and presented in (b). EELS intensities are integrated up to 4 eV for rra-P3HT. Solid lines are data fits to the exponential decay. Spectral peak positions of rr- and rra-P3HT are extracted from Gaussian fits to the EELS spectra and plotted in (b) and (d), respectively.

Figure B-3. Sulfur map of P3HT/PCBM mixtures with a weight ratio of 1:1 annealed at 190 \degree C for 30 min. Scale bar is 100 nm.
List of Tables

Table 3-1. Domain compositions by volume, $\phi$, obtained from EFTEM................................. 55

Table 4-1. Device characteristics$^a$ of P3HT/PFTBT blend and P3HT-\textit{b}-PFTBT block copolymer solar cells at different annealing conditions. ................................................................. 70

Table 4-2. Device characteristics$^b$ of P3HT/PFTBT polymer blend and P3HT-\textit{b}-PFTBT block copolymer solar cells with highest efficiencies. ................................................................. 71

Table 5-1. Device characteristics$^a$ of optimized P3HT-\textit{b}-PFTBT block copolymer solar cells processed with 0% and 5% volume fraction of 1-chloronaphthalene. ......................... 104

Table 6-1. Summary of decay rates and critical doses for EELS degradation of various organic semiconductors at the low-loss range. ................................................................. 126

Table B-1. Peak positions in EELS data compared to UV-Vis absorption spectra for various semiconductor polymers and a fullerene derivative.................................................. 162
PREFACE

This dissertation is devoted to developing next-generation high-performance organic photovoltaics through conjugated block copolymer strategy to control the active layer morphology and interfacial structures, and via advanced characterization techniques to establish a profound understanding of the processing-structure-performance relationships.

Yen-Hao Lin from Prof. Rafael Verduzco group at Rice University contributes to design and synthesis of conjugated block copolymers for photovoltaic applications in Chapter 4. Frances Allen supervised by Andrew Minor at National Center for Electron Microscopy of Lawrence Berkeley National Laboratory, contributes to principle component analysis of low energy-loss energy-filtered transmission electron microscopy (EFTEM) in Chapter 6.
ACKNOWLEDGEMENTS

The past four years have been a challenging and fulfilling time in my life. I would like to thank my advisor Prof. Enrique Gomez for his guidance and encouragements during my graduate career at Penn State. He has patiently guided me to build up interdisciplinary research skills and lead me on a pioneer project from ground-up. He always encourages and respects my ideas, and helps me become an independent scientist and engineer with strong problem-solving abilities. I would also like to thank my committee members as well as course instructors, Prof. Scott Milner, Prof. Ralph Colby, and Prof. Chris Noel Giebink for their advice and encouragements during my Ph.D. studies. The wealth of knowledge I have learned from them would continue to benefit my future career development.

I would not have been able to succeed without the support and helpful discussions from my labmates, collaborators, and scientists at National Laboratories and the Material Research Institute at Penn State. I would like to express my appreciation to our collaborator Prof. Rafael Verduzco, and his students Yen-Hao Lin and Kendall Smith for their contributions to material design and synthesis. My special appreciations go to scientists at Lawrence Berkeley National Laboratory, especially Cheng Wang and Anthony Young at Advanced Light Source for training me on RSOXS experiments, and Frances Allen, Chengyu Song and Jim Ciston at National Center for Electron Microscopy for their technical support on EFTEM technique. I also acknowledge the great help from Joseph Strzalka with GIWAXS and GISAXS measurements at Advanced Photon Source of Argonne National Laboratory.
Sincere thanks I give to all of my labmates and friends at the Gomez group, who have encouraged and helped me all the way through my Ph.D. studies. Thank you to Matthew Witman, a brilliant undergraduate student at Penn State for his work on device optimization. Thank you to Sameer Vajjala Kesava for his great help with EFTEM techniques, and Youngmin Lee for his helpful guidance in material synthesis. Also thank you to Thinh Le for his dedication in maintaining the lab equipment, without which I would have not been able to accomplish my research.

I would like to dedicate this work to my father Chunming Guo and my mother Li Wang for their unconditional support and love throughout my life. Thanks to all my relatives for their encouragements and concerns. Finally, a special thank you goes to Thinh Le for always being there for me to share my joys and sorrows, worries and success.
Chapter 1. Introduction

1.1 Motivation

The limited supply of fossil fuels and the detrimental air emissions underscore the urgent demands of renewable energy resources. Photovoltaic (PV) technology, directly harvesting sunlight for electrical power generation, has attracted increasing attention as a promising solution to the growing energy challenge. Since the 1950s, first-generation PV devices based on crystalline silicon and inorganic thin-film devices known as second-generation have been developed.\(^1\) As illustrated in Figure 1-1, great progress in device performance has been made in the field of inorganic photovoltaics, setting a world record efficiency of 44.4\%.\(^2\)\(^-\)\(^3\) However, fabrication of these inorganic solar cells is energy-intensive, as it requires high-quality purification and high-temperature processing.\(^1\)\(^,\)\(^4\)

Organic semiconductors can be an attractive alternative to conventional inorganic materials in solar cell applications. Organic photovoltaics (OPV) have the potential as a third generation to produce large-scale, low-cost and light-weight solar power.\(^1\)\(^,\)\(^5\)\(^,\)\(^6\) Semiconducting small molecules or conjugated polymers have large optical absorption coefficients, allowing the use of thin films with thicknesses of only several hundred nanometers. With solution-processable organic materials, organic solar cells can be fabricated on flexible substrates using high-output printing techniques in a roll-to-roll process for large-scale production (Figure 1-2).\(^5\)\(^,\)\(^6\) Such a solution-based low-temperature process can significantly reduce the fabrication cost compared to traditional silicon solar cells.
Figure 1-1. Timeline of research cell efficiency records for various classes of photovoltaic devices certified by NREL, 2014.  

Figure 1-2. Schematic illustration of standard printing processes for large-scale production of polymer-based photovoltaic cells.
Another unique advantage of organic semiconductors is their synthetic flexibility. Extensive possibilities in chemical structure design enable manipulation of the optoelectronic properties, such as molecular orbital energy levels and bandgaps.\textsuperscript{7,8} As shown in Figure 1-3, tuning the backbone structure in conjugated copolymers provides a valid approach to alter the bandgaps of polymer semiconductors, leading to distinct optical absorption properties. With appropriate combinations of the functional moieties, a variety of low-bandgap polymers capable of broad light absorption have been developed for efficient polymer solar cells.\textsuperscript{9-12}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1-3.png}
\caption{Molecular structures and absorption spectra of naphtho[2,1-b:3,4-b']dithiophene (NDT)-based copolymer semiconductors HMPNDT, PNDT-T and PNDT-BT. Tuning the chemical structure of the copolymer backbone allows alternation of the bandgap and optical absorption properties of polymer semiconductors.\textsuperscript{8}}
\end{figure}
Owing to new discoveries of high performing organic semiconductors, OPV devices have been improving rapidly in the past 10 years (Figure 1-1) with efficiencies currently beyond 10% (Mitsubishi Chemical). But this is still below the efficiency benchmark (~15-20%) required for economical large-scale power generation. To further enhance the performance of organic solar cells, however, encounters the challenge of optimizing the morphology in the photovoltaic active layer. Organic photovoltaic devices rely on blending of two materials, commonly a polymer as electron donor and a fullerene derivative as electron acceptor, to create a large interfacial area for efficient photogeneration of charges. On the other hand, the disordered nature in organic mixtures and weak intermolecular interactions between different materials give rise to the difficulties in structure control of polymer blends and limit the performance and stability of organic solar cells. Many efforts have focused on improving the active layer structure through a variety of processing approaches. Nevertheless, characterization of the complex morphology in organic semiconductor mixtures remains a major experimental challenge. The lack of techniques for a detailed analysis of the resulting structures limits our ability to establish an in-depth understanding of the processing-structure-property relationships. In this thesis, we explore the application of self-assembly of block copolymers for morphology and interfacial structure control in the active layer of organic photovoltaics. We will also discuss novel scattering techniques and high-contrast imaging methods for effective characterization of the hierarchical structure formation in organic thin films, providing complementary information to guide future efforts in OPV optimization.
1.2 Principles of Organic Photovoltaics

![Chemical structures of regioregular P3HT and PCBM semiconductors. Images are taken from Plextronics/Plexcore® PV website.](image)

**Figure 1-4.** Chemical structures of regioregular P3HT and PCBM semiconductors. Images are taken from Plextronics/Plexcore® PV website.

The chemical origin of semiconducting organic materials is the presence of conjugated backbones in either small molecules or polymer macromolecules. Figure 1-4 shows the chemical structures of commonly used organic semiconductors regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) for solar cell applications. A conjugated molecule is composed of alternating single and double carbon bonds and forms a series of overlapping π orbitals allowing delocalization of π electrons across the whole conjugated system. These delocalized π electrons give the semiconductor behaviors of organic materials. As shown in Figure 1-5, the molecular orbital energy levels become closely spaced as the conjugation length increases, resulting in band structures analogous to the valence and conduction bands defined in solid-state inorganic semiconductors. The energy difference between highest occupied molecular orbital (HOMO) level and lowest unoccupied molecular orbital (LUMO) level at the band
edges governs the bandgap of an organic semiconductor with a strong influence on their optical and electronic properties.

**Figure 1-5.** Effect of conjugation length on HOMO/LUMO levels of conjugated molecules. With increasing conjugation length, the HOMO level increases while the LUMO level decreases, resulting in a lower bandgap, \( E_g \).

A standard photovoltaic device is fabricated in a sandwich geometry as shown in Figure 1-6, with the active layer between a transparent anode and a metal cathode. The active layer is composed of photovoltaic functional semiconductors. Sunlight that comes through the top transparent anode, such as indium tin oxide (ITO), will be absorbed and converted into free charge carriers inside the active layer. Then free charges need to be transported to the corresponding electrodes and directed into the external circuit to do electrical work.
Figure 1-6. Schematic of the standard device architecture for a polymer-based photovoltaic cell. The active layer composed of photovoltaic functional materials is sandwiched between the transparent anode and the metal cathode.²¹

Photogeneration of charges in organic solar cells comprises a series of sequential processes as summarized in Figure 1-7 using the energy level diagram. Organic photovoltaic operation requires two components: an electron donor and an electron acceptor with certain differences in their HOMO and LUMO energy levels. As shown in panel a, the absorption of a photon with energy $h\nu$ in donor materials can promote an electron from HOMO level into LUMO level and leave a positive hole behind. Different from inorganic solar cells where optical excitations directly generate free charge carriers, the photoexcited electron and hole in organic semiconductors are tightly bound by electrostatic Coulomb force and form an electron/hole pair called exciton. This is largely due to the low dielectric constant and short-range electron delocalization in organic materials.²¹ Driven by a concentration gradient, excitons can diffuse to donor-acceptor interfaces within their diffusion length as indicated in panel b of Figure 1-7. Beyond the diffusion length, excitons will recombine to the ground state with no contributions to
current. At interfaces in panel c, given that electrons tend to fill lower energy levels, excitons can undergo dissociation through electron transfer from donor to acceptor materials driven by their energy difference at LUMO levels, and form spatially separated charges across the interface known as charge-transfer (CT) states. Similarly, photogenerated excitons in the acceptor material can also be quenched at the interface by hole transfer from acceptor to donor materials due to the energy offset at HOMO levels. Therefore, sufficient energy level difference at the donor-acceptor interface is a prerequisite to overcoming the strong binding energy of excitons in order for charge generation. Further separation of the interfacial charge-transfer states yields free electrons and holes (Panel c), which can then be transported within donor and acceptor phases to the corresponding electrodes and produce current (Panel d).

In summary, current generation in organic photovoltaics involves a series of subsequent steps including light absorption, exciton diffusion, charge separation, and charge transport as illustrated in the schematic of the active layer structure (Figure 1-8).
Figure 1-7. Energy level diagram at donor-acceptor interfaces illustrating the principle of organic photovoltaic operation including (a) light absorption, (b) exciton diffusion, (c) charge transfer and separation, and (d) charge transport and collection. Images are adapted from the 2010 review by Clarke and Durrant.\textsuperscript{21}

Figure 1-8. Schematic illustrations of photon absorption, exciton diffusion, charge separation, and charge transport in the active layer of organic solar cells.\textsuperscript{22}
1.3 Morphology Design for Efficient Organic Solar Cells

Efficient power conversion demands a simultaneous optimization of the fundamental photophysical processes regarding photon absorption, charge generation and charge transport, all of which are sensitive to the morphology developed in the active layer. In most semiconducting polymers, excitons can only diffuse a short distance approximately 5-10 nm during their lifetime.\textsuperscript{23, 24} Thus, it is critical to control the domain size comparable to the exciton diffusion length, so that photoexcited electron-hole pairs can reach the donor-acceptor interface for charge separation before recombination occurs. On the other hand, the active layer thickness in an OPV device is desired to be around 100-200 nm, far beyond the exciton diffusion length, in order to maximize the number of excitons generated upon photon absorption. In addition, separated free charges near interfaces require continuous pathways for charge transport throughout the active layer to the corresponding electrodes. The intricate balance between optimizing light absorption, charge separation, and charge transport gives rise to the challenge in morphology design for high-performance organic solar cells.

The first relatively efficient organic photovoltaic device was reported by Tang in 1986 with a power conversion efficiency (PCE) of 1%,\textsuperscript{25} employing a donor/acceptor bilayer structure as illustrated in Figure 1-9a. However, the short exciton diffusion length $l_D$ only allows the photoexcited states within the 10 nm range near the planar interface to undergo dissociation. Excitons generated outside this effective region will rapidly relax to the ground state, resulting in significant exciton losses. Consequently, the mismatch between the exciton diffusion length ($\sim$10 nm) and the typical optical absorption depth ($\sim$100 nm) in organic semiconductors limit the performance of bilayer photovoltaic devices.
Figure 1-9. Schematics of the active layer morphology for (a) planar heterojunction, (b) bulk heterojunction, and (c) an ideal ordered heterojunction polymer solar cells. $l_D$ is the exciton diffusion length in organic semiconductors.

A major breakthrough in morphology design to overcome the primary issue in bilayer solar cells is the introduction of a so-called bulk heterojunction (BHJ) structure.\textsuperscript{26} As shown in Figure 1-9b, the BHJ morphology involves an interpenetrating network of bicontinuous donor and acceptor phases with domain sizes on the order of exciton diffusion lengths. Such a kinetically trapped,\textsuperscript{16-18,27} partially phase-separated structure of donor and acceptor mixtures creates a high interfacial area throughout the thick active layer ($\sim 100$ nm) for exciton dissociation and thus reduces the distance that excitons need to travel before reaching the interface. As a result, photogeneration of charges is significantly increased, leading to great progress in device performance of organic photovoltaics based on polymer/fullerene mixtures.\textsuperscript{12,14,28} Nevertheless, the complex blend structures in BHJ solar cells engender another challenge in developing interconnected pathways for charge transport while maintaining a large surface area in the bulk film at the same time. In consideration of the balance between maximizing the interfacial area and retaining bicontinuous transport pathways, an ideal active layer morphology evolved from the BHJ structure was proposed for OPV applications.\textsuperscript{14,15}
Figure 1-9c pictures the schematic of an ordered BHJ structure, where donor and acceptor phases are interspaced on a length scale close to the exciton diffusion length (~10-20 nm), providing easy access to the interface for charge separation. Meanwhile the interdigitated and percolated donor and acceptor domains that are perpendicular to both electrodes form direct pathways for charge transport. Such a well-organized nanostructure is not easy to obtain given the disordered nature of polymer mixtures. Novel strategies and approaches are warranted to enable full control over the active layer morphology for developing high-performance organic solar cells.

1.4 Characterization of Photovoltaic Performance

Current-voltage (J-V) characteristics can be measured to determine the photovoltaic device performance. Figure 1-10 shows the current density (J) responses as a function of voltage bias (V) from a polymer/fullerene solar cell under simulated one sun illumination (red solid curve). In the dark, organic photovoltaic devices with donor-acceptor heterojunctions exhibit diode behavior. Upon light illumination, the solar cell device acts as a photocurrent generator supplying power when it is operated in the fourth quadrant of the J-V coordinate (Figure 1-10).

Device parameters that are commonly used to characterize the photovoltaic performance of organic solar cells include the open-circuit voltage (V_{oc}), the short-circuit current (J_{sc}), and fill factor (FF). As shown in the light J-V curve (Figure 1-10), V_{oc} is defined as the voltage produced when the device current equals zero. J_{sc} is the current density at zero bias when there is no potential drop across the cell. V_{oc} and J_{sc} represent
the maximum voltage and current that can be reached in the power generation regime at the fourth quadrant.

**Figure 1-10.** Current-Voltage (J-V) characteristics under simulated one sun illumination for P3HT/PCBM bulk heterojunction solar cells annealed at 165 °C for 10 min.

From the J-V data, the power output (product of J and V) as a function of bias is calculated as the black dash curve in Figure 1-10. A maximum power density $|P_{\text{max}}|$ is found and dictates the optimum operation condition for efficient power conversion in organic solar cells. Division of $|P_{\text{max}}|$ by the product of $J_{\text{sc}}$ and $V_{\text{oc}}$ yields another important parameter fill factor (FF) defined in equation (1-1), describing the shape, specifically “squareness” of J-V characteristics:

$$\text{FF} = \frac{|P_{\text{max}}|}{V_{\text{oc}} \cdot J_{\text{sc}}}$$

(1-1)
Finally, the efficiency of an OPV device, $\eta$, is determined by the ratio between the maximum output power density ($|P_{max}|$) and the incident light intensity ($P_{in}$), which can then be expressed in terms of the intrinsic parameters: $V_{oc}$, $J_{sc}$ and FF as shown in the equation (1-2) below:

$$\eta = \frac{|P_{max}|}{P_{in}} = \frac{V_{oc} \cdot J_{sc} \cdot FF}{P_{in}}$$

(1-2)

The separation of electrons and holes at donor-acceptor heterojunctions (as mentioned in section 1.2) leads to a potential difference across the interface. The voltage generation in organic solar cells strongly depends on the molecular orbital energy levels of the donor and acceptor materials. Figure 1-11 demonstrates the energy level diagram of P3HT donor and PCBM acceptor.$^{7,13,29}$ The energy difference between the donor HOMO level and the acceptor LUMO level sets an upper limit for the open-circuit voltage $V_{oc}$ of a particular material combination.$^{30}$ The physical meaning of fill factors in organic solar cells is currently not clear. But there is evidence that charge transport properties in the active layer of photovoltaic devices play an important role.$^{31}$
Various LUMO levels for PCBM have been reported in the literature.\(^7,^{13,29}\) The energy difference between the donor HOMO level and the acceptor LUMO level (HOMO\(_D\)-LUMO\(_A\)) determines the maximum voltage that can be generated in photovoltaic devices.

The maximum current generation, \(J_{sc}\), as we have discussed in section 1.2, is an integrated result of light absorption, exciton diffusion and dissociation, charge separation, and charge transport and collection. In order for a better understanding of the photoconversion process in organic solar cells, spectrally resolved measurements of the external quantum efficiency (EQE) can be carried out. External quantum efficiency is defined as the ratio of output electrons to the incident photons as a function of wavelength, \(\lambda\). Integrating the EQE spectrum with the incident light intensity predicts the \(J_{sc}\) that can be obtained from a photovoltaic device under a given illumination condition. EQE is equal to the multiplication of the performance of all the steps in the solar energy conversion process\(^{14}\) as indicated in equation (1-3):

\[
EQE(\lambda) = \eta_{abs}(\lambda) \eta_{diff}(\lambda) \eta_{cs}(\lambda) \eta_{tr}(\lambda)
\]

(1-3)
where $\eta_{abs}$, $\eta_{diff}$, $\eta_{cs}$, and $\eta_{tr}$ represent the efficiencies of photon absorption, exciton diffusion, the electron-hole pair separation, and free carrier transport (including charge collection at electrodes), respectively.

The photon absorption efficiency, $\eta_{abs}$, is mainly governed by the material optical properties and the solar cell architecture that may affect the light transmission and reflection. While the other efficiency parameters, $\eta_{diff}$, $\eta_{cs}$, and $\eta_{tr}$, define the internal quantum efficiency (IQE) of organic solar cells,\textsuperscript{14} which is more sensitive to the internal active layer morphology and the electronic structures at donor-acceptor interfaces. IQE is the ratio between the number of electrons generated by the photovoltaic operation to the number of photons already absorbed in the active layer. IQE data can be calculated from the EQE spectrum if the light absorption efficiency of the solar cell device is properly accounted for, as shown in equation (1-4):

$$IQE(\lambda) = \frac{EQE(\lambda)}{\eta_{abs}(\lambda)}$$

(1-4)
1.5 References


Chapter 2. Objectives and Approaches

2.1 Structure Limitations in State-of-the-art Polymer Blend Solar Cells

Currently, organic photovoltaic devices with the highest performance utilize a bulk heterojunction (BHJ) structure,\(^1\) in which a bicontinuous interpenetrating network is produced by the spontaneous phase separation of donor and acceptor mixtures. Recent work on polymer/fullerene BHJ solar cells has pushed the efficiency record towards 8% for single junction organic photovoltaics.\(^2,3\) Further improvement in device performance, however, is hampered by the weak absorption of fullerene derivatives (e.g. PCBM) in the range of solar spectrum as shown in Figure 2-1. In addition, the deep lowest unoccupied molecular orbital (LUMO) level of PCBM (~ 3.7-4.2 eV) limits the open-circuit voltage \((V_{oc})\) typically below 0.7 eV (See Chapter 1, Figure 1-11).

**Figure 2-1.** Comparison of optical absorption spectrum for PCBM pristine films with AM 1.5 Global tilt solar spectrum. Data of solar spectrum come from Solar Spectral Irradiance: Air Mass 1.5 at website of National Renewable Energy Laboratory.
As an alternative to fullerene-based OPVs, all-polymer solar cells, where the active layer is composed of a polymer donor and a polymer acceptor, offer great flexibility in the design of materials with optimum energy levels and complementary absorption properties. For example, polyfluorene-based copolymers have been proved to be a promising electron acceptor material to replace PCBM in conjunction with established polymer donors like poly(3-hexylthiophene) (P3HT). Polyfluorenes (PFs) were originally developed for light-emitting diodes with a large band gap producing blue light. Copolymerization of fluorene with other groups such as dithienyl-benzothiadiazole (TBT) produces materials with lower band gap, improved electron transport, and tunable LUMO levels suitable for photovoltaic applications. An example of alternating polyfluorene copolymers is poly((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(3-hexylthien-5-yl)-2,1,3-benzothiadiazole]-2’,2”-diyl) (F8TBT). Figure 2-2 compares the energy levels and UV-Visible absorption spectra of P3HT, PCBM, and PF8TBT neat films. PF8TBT exhibits red-absorbing properties with respect to PCBM and provides efficient photon capturing from solar radiation. More importantly, the higher (relative to the vacuum level) LUMO level of PF8TBT (~ 3.15 eV) dictates a larger energy gap between the donor HOMO and the acceptor LUMO levels and contributes to a high $V_{oc}$ beyond 1 V in P3HT/PF8TBT blend photovoltaics. With increasing synthetic efforts on the design of semiconducting polymers, all-polymer solar cells have improved steadily in recent years achieving efficiencies beyond 6%, comparable to polymer/fullerene devices.
Despite the great progress in photovoltaic devices based on polymer/fullerene or polymer/polymer mixtures, the commonly exploited blend structure has several intrinsic drawbacks that limit our ability to explore the full potentials of these high-performing organic semiconductors. One challenge lies in the delicate balance between maximizing the interfacial area for charge separation and maintaining domain connectivity for charge transport. For well-mixed polymer blends as shown in Figure 2-3a, microscopic phase separation with small domains is favorable for exciton diffusion and dissociation, thus maximizing charge photogeneration. However, the formed small domains in such a well-blended system are not percolated, but rather isolated and dispersed in the matrix phase. In the absence of interconnected pathways for charge transport, these isolated domains serve as defects to trap the generated charges locally and facilitate charge recombination, resulting in significant carrier losses. To address this problem, processing methods such as thermal annealing have been applied to promote phase separation in the active layer.
Figure 2-3. Schematic illustrations of bulk heterojunction morphology in the active layer of organic solar cells. (a) As-cast polymer blend structure with a large area of donor-acceptor interfaces but poor transport pathways. (b) Mesoscopic phase separation developed in the active layer after thermal annealing with percolated domains for charge transport, although interfacial area is reduced.

As shown in Figure 2-3b, polymer crystallization and domain coarsening upon thermal processing can produce better phase continuity in the bulk for efficient charge extraction, although charge generation is relatively reduced due to the larger domain size. With the proper control of mesoscale phase separation, the overall device performance is improved.\textsuperscript{10} On the other hand, this fact also implies an inherent limitation of the bulk heterojunction morphology. That is, our ability to simultaneously optimize the interfacial area and bicontinuous pathways for efficient photovoltaic operation is limited in polymer blend solar cells.

Another limitation is the disorder at donor-acceptor interfaces. The electronic structure near donor-acceptor heterojunctions is critical to the charge separation process in excitonic organic photovoltaics.\textsuperscript{11,12} Recent work by Giebink et al. suggests that tuning the electronic coupling across the interface is a key to minimizing the charge recombination rate and improving yields of charge generation.\textsuperscript{13} It follows that proper control of the molecular orientations between donor and acceptor at organic
heterojunctions\textsuperscript{14} is a requirement to fully optimize the photovoltaic conversion process. In partially miscible polymer/fullerene (Figure 2-4a) or polymer/polymer blends (Figure 2-4b), nevertheless, weak intermolecular interactions (van der Waals force) between different organic materials make it almost impossible to control the interfacial structure.

\textbf{Figure 2-4.} Schematics of random molecular configurations near donor-acceptor interfaces in (a) polymer/fullerene and (b) polymer/polymer mixtures.

Furthermore, a kinetically-trapped blend structure is usually formed during film deposition and processing.\textsuperscript{15} This non-equilibrium mesoscopic morphology in the active layer is not stable when exposed to heat, and thus limits the stability and lifetime of organic solar cells.\textsuperscript{16, 17} From a thermodynamic point of view, phase separation in polymer blends is a result of the interplay between enthalpy penalty and entropy of mixing. Due to the large size of polymer molecules, the entropy contribution from polymer mixing is very small. The high interaction energy between different molecules is unfavorable to mixing and drives phase separation in polymer blends at equilibrium. In solution, the solvent molecules screen the polymer/fullerene or polymer/polymer
interactions and the system can form a homogeneously mixed phase. During solution spin-coating, as the solvent evaporates, the increasing interaction energy between different organic semiconductors drives spontaneous phase separation. As the solvent concentration decreases, however, the polymer chains become less mobile. Until a point when the glass transition occurs, the as-cast film morphology is frozen or kinetically trapped with mesoscale phase separation. But thermal annealing above the glass transition temperature can increase the mobility of polymer chains and further drives phase separation towards equilibrium. During this structure evolution process, macroscopic phase segregation with domain coarsening will take place.

![Figure 2-5](image)

**Figure 2-5.** Optical microscopy images of P3HT/PCBM mixtures (with weight ratio of 3:2) annealed at 120 °C for various times. Scale bar is 100 µm. Phase segregation becomes evident with increasing annealing time.

Moreover, many semiconducting polymers and small molecules are semi-crystalline materials. Crystallization of organic semiconductors serves as another driving force for phase separation in the active layer. Figure 2-5 presents a series of optical microscopy images for blend films of P3HT and PCBM mixtures annealed at 120 °C for various
times. We can see clearly that clusters are formed after four hours at 120 °C and they continue growing with long-time annealing. During this thermal annealing process, P3HT crystallizes to form crystalline phases. Meanwhile the excluded PCBM molecules from the crystalline domains diffuse to form large aggregates as we see in Figure 2-5. Clearly, novel strategies and approaches are in need to create nanostructures at equilibrium for developing more efficient and stable polymer solar cells.

2.2 Block Copolymer Strategy Towards Efficient Organic Photovoltaics

Figure 2-6. Molecular architectures for linear diblock and triblock copolymers. Each colored strand represents a polymer block comprised of a linear sequence of identical repeating units, labeled as A, B and C as shown in red, blue and green, respectively. The colored strands are joined by covalent bonding to form diblock (A-B) or triblock (A-B-C) copolymer macromolecules.

Block copolymers with self-assembly properties are of great promise to circumvent many of the challenges related to the complicated blend morphology in polymer/fullerene and polymer/polymer OPVs. As shown in Figure 2-6, block copolymers are a class of macromolecules, in which two or more chemically different polymer blocks are joined together through covalent bonding. The incompatibility between dissimilar polymer
segments drives the material to phase segregate into distinct domains of the polymer constituents. On the other hand, the covalent linkage binds the polymer blocks together and thus prevents macroscopic phase separation. As a result of the delicate balance between the repulsive interactions and chain connectivity, block copolymers undergo a thermodynamic self-assembling process referred as microphase separation to form well-ordered nanoscale structures.\textsuperscript{21}

\textbf{Figure 2-7.} Theoretical equilibrium phase diagram for linear A-B diblock copolymers. Self-consistent mean-field theory predicts equilibrium morphologies including lamellar (L), gyroid (G), cylindrical (C), spherical (S), closely-packed spherical (CPS), and disordered structures, depending on the volume fraction of block A, $f_A$, and a combination parameter $\chi N$. $\chi$ is the Flory-Huggins interaction parameter, which describes the interaction energy between dissimilar polymer segments. N is the degree of polymerization, that is the number of monomers of all types per macromolecule.\textsuperscript{21}

A great deal of theoretical and experimental work has been done to understand the self-assembly properties of flexible coil-coil diblock copolymers.\textsuperscript{21-23} Figure 2-7 presents the equilibrium phase diagram for a linear A-$b$-B diblock copolymer predicted by the self-
consistent mean-field theory.\textsuperscript{21, 23} The equilibrium morphology is mainly determined by the block copolymer composition, $f$, and a product parameter, $\chi N$. $N$ is the degree of polymerization. $\chi$ is the Flory-Huggins interaction parameter, which describes the miscibility of two polymer segments.\textsuperscript{21, 24} A negative value of $\chi$ drives single-phase mixing. Whereas positive $\chi$ values indicate net repulsive interactions favoring phase separation, which is typically the case for systems containing chemically distinct molecules with no strong favorable interactions. The product, $\chi N$, reflects the segregation strength of the dissimilar polymer constituents.\textsuperscript{24} When $\chi N$ exceeds a critical value ($\geq 10$), the block copolymer segregates into a periodically ordered structure on the nanometer length scale.\textsuperscript{15, 24} Below the critical value, entropic mixing dominates over enthalpic interactions, and a disordered structure is thermodynamically formed. In the strong segregation regime, a variety of ordered nanostructures with different symmetries including spherical, cylindrical, gyroid and lamellar morphologies as shown in Figure 2-8 can be produced depending on the volume fraction $f$ of the constituent block.

![Figure 2-8](image)

**Figure 2-8.** Schematic representations of the equilibrium nanostructures commonly observed in coil-coil diblock copolymers A-B, as the volume fraction of block A, $f_A$, increases. Ordered morphologies are labeled as S for spheres, C for cylinders, G for gyroid, and L for lamellae. Domains of polymer blocks A and B are indicated with blue and red regions, respectively.\textsuperscript{24}
Among them, the lamellar structure is an ideal morphology candidate for solar cell applications. Figure 2-9 illustrates the schematic of an organic photovoltaic device with standing-up lamellae formed in the active layer. In the horizontal direction, the lamellar domain size can be controlled on the order of 10 nm, which matches the exciton diffusion length and provides a large amount of interfacial area for charge separation. In the vertical direction between the electrodes, percolated alternating donor and acceptor phases form direct pathways for unhindered charge transport. Advantageous over polymer blend solar cells, block copolymer photovoltaics offer an opportunity to optimize charge separation and charge transport simultaneously.

**Figure 2-9.** Schematic illustrations of block copolymer photovoltaic devices with an in-plane lamellar structure formed in the active layer. A molecular picture of the donor-acceptor interfaces in the block copolymer architecture is shown on the right. Images are adapted from ref 25.

In addition to serving as a nanostructure template, the covalent bonding of block copolymers at the joint interface also provide a route to control the interfacial structure for efficient charge separation. Design of block copolymers for organic photovoltaics must consider incorporation of electron donating and accepting functionalities into
distinct polymer blocks. Several examples of donor-acceptor block copolymers as shown in Figure 2-10a have been developed by attaching a donor polymer chain to a non-conjugated backbone with semiconducting small molecules as acceptor pendant groups. However, the non-conjugated linking between donor and acceptor blocks does not directly control the electronic structure near donor/acceptor interfaces. Indeed, the insulating nature at organic heterojunctions and in at least one polymer segment could hamper the charge transfer process and the subsequent carrier transport, resulting in poor photovoltaic performance. The non-conjugated donor-acceptor block copolymers might be more suitable as compatibilizers to stabilize the blending of donor and acceptor materials in the active layer and thus improve the thermal stability of the resulting ternary blend organic solar cells.

Figure 2-10. Design of block copolymers for photovoltaic applications via (a) non-conjugated linking with semiconducting small molecules as pendant groups or through (b) conjugated bonding to maintain full conjugation across the covalent donor-acceptor interfaces.
Alternatively, the semiconducting properties of block copolymers can be derived by directly linking a polymer donor with a polymer acceptor as shown in Figure 2-10b to maintain conjugation across the copolymer chain.\textsuperscript{31} Such a fully conjugated donor-acceptor block copolymer incorporates the electronic functionalities with self-assembly properties and has great potentials to serve as the active layer itself instead of using a polymer blend. The conjugated interface can effectively constrain the relative orientations between donor and acceptor blocks. Moreover, the block copolymer architecture where donor/acceptor interfaces are governed by moieties near the junction opens a variety of possibilities for the interfacial structure control through tuning the chemical structure at the covalent linkage.\textsuperscript{32}

As such, we hypothesize that neat conjugated donor-acceptor block copolymers are a viable strategy to control the active layer morphology and interfacial structures for high-performance organic photovoltaics.

### 2.3 Morphological Characterization of the Active Layer in Organic Solar Cells

Efforts in morphology control for efficient organic photovoltaics must confront the challenge in characterizing the structure formation in the active layer of OPVs. Characterization of phase separation in thin films of organic semiconductors has been a strong focus of recent work.\textsuperscript{15,33-35} In the most studied devices comprised of P3HT and PCBM mixtures, high-resolution imaging has been attempted mainly by atomic force microscopy (AFM),\textsuperscript{33, 35, 36} and transmission electron microscopy (TEM).\textsuperscript{36-38} AFM explores surface contrast to provide topographic images, but yields little information
regarding the nanostructure in the bulk film. \cite{15, 35} TEM is suitable to probe the volume-averaged structural information about the in-plane thin-film morphology. But mass contrast is weak between organic materials. It is thus difficult to distinguish organic phases from typical bright-field TEM imaging, especially for poorly ordered systems. \cite{16, 35}

Alternative to conventionally TEM, material contrast between P3HT and PCBM can be enhanced by imaging with inelastically scattered electrons using energy-filtered transmission electron microscopy (EFTEM). Figure 2-11 demonstrates the schematic of the EFTEM set-up. The incident electron beam is monoenergetic with a narrow range of high kinetic energies on the order of 100 keV. After interacting with the specimen, some of the electrons will lose energy due to inelastic scattering events in the materials. The transmitted electron beam is thus polyenergetic and can be dispersed according to their energy losses by the magnetic prism in the microscope. Detecting the energy distribution of electrons passing through the sample generates an electron energy-loss spectrum (EELS). Inelastic losses that correspond to the chemical compositions and characteristic electronic transitions in the materials appear as absorption edges and fine structures in EELS data. Alternatively, by inserting an energy-selecting slit in front of the detector, transmitted electrons of a certain energy-loss with a defined energy bandwidth can be systematically selected for energy-filtered imaging in the EFTEM mode.
Inelastic interactions of particular interest in organic materials include inter-band transitions, plasmon excitations, and inner shell ionizations. Kozub et al. have illustrated the application of EFTEM imaging at ionization edges (100-300 eV) characteristic of the constituent atoms in organic semiconductors to map the elemental distributions in different phases\textsuperscript{16}. Sulfur and carbon maps of P3HT/PCBM mixtures annealed at 190 °C are compared in Figure 2-12 with a bright-field image taken from the same sample area. Material contrast is significantly improved in elemental mapping due to the large differences in sulfur and carbon densities between P3HT and PCBM (See chemical
structures in Chapter 1, Figure 1-4). In addition, the intensity of the elemental image is directly proportional to the local elemental concentration and can be translated into the material composition within domains. For example, given that only P3HT contains sulfur atoms, the sulfur map reveals the presence of P3HT-rich fibers as the bright regions and a PCBM-rich matrix in the low-intensity areas. While the carbon map of P3HT/PCBM blend shows inverted contrast due to the higher carbon density in PCBM relative to that in P3HT.

Recent work also reports on energy-filtered imaging at plasmon loss energies (~ 20-30 eV) to characterize the structure formation in thin films of P3HT/PCBM mixtures.\textsuperscript{39, 40} As shown in Figure 2-13a, a significant shift in plasmon excitation energies of P3HT (~ 21.5 eV) and PCBM (~ 25 eV) is present, arising from differences in the electronic
structures of organic materials. These discriminating plasmon features provide complementary contrast that distinguishes between P3HT and PCBM phases in the blend structure as shown in Figure 2-13 panel c and d.\(^{39}\)

**Figure 2-13.** Energy-filtered TEM imaging of a 1:1 P3HT/PCBM blend film annealed at 110 °C for 10 min. (a) electron energy-loss spectra (EELS) from pure P3HT and PCBM films. Energy windows for imaging are drawn at 19 ± 4 eV and 30 ± 4 eV, where inelastic scattering is more intense from P3HT and PCBM, respectively. (b) Zero-loss image using only elastically scattered electrons. (c) 19 eV loss image, where P3HT domains are bright. (d) 30 eV image, where PCBM domains are bright. Scale bar is 50 nm as shown on the images.\(^{39}\)
However, plasmon resonances are broad, and often overlap or vary little between different organic materials. Also, elemental mapping is only effective when there are significant differences in elemental compositions between the materials. As a result, EFTEM imaging based on inner shell ionization or plasmon loss excitations is still limited for compositionally similar phases or complex multicomponent systems. A novel contrast mechanism with high chemical sensitivity to organic materials is in demand for structure characterization of organic solar cells involving various combinations of materials.

Supplementary to real-space imaging, reciprocal space methods such as X-ray scattering techniques have been developed for quantitative characterization of the nanostructure in polymer films. These scattering experiments rely on the interference of scattered X-rays to produce patterns in the reciprocal space, which carry the information about periodic structures present in the materials. Small-angle X-ray scattering (SAXS) is often used to probe the order formation in block copolymer samples. The weak interactions of hard X-rays (~ 10 keV) with organic materials require an optimal sample thickness on the order of 1 mm for SAXS measurements in transmission geometry. For organic photovoltaics, however, the interest lies in the study of thin films with thickness typically around 100 nm. Consequently, traditional transmission X-ray scattering techniques are not applicable for characterizing the active layer of organic solar cells. Grazing-incidence small-angle X-ray scattering (GISAXS) overcomes the limitation of conventional SAXS on studies of polymer thin films. GISAXS experiment is performed in the reflection geometry with a small incident angle (below 1°) close to the critical angle of the materials enabling film penetration, and below
the critical angle of the substrate to minimize the scattering intensities from the substrate.\textsuperscript{46} In addition, the grazing-incidence geometry allows X-ray beam to access a large sample volume even in thin films and thus improves the scattering intensities. Previous work by Kozub et al. has focused on the use of GISAXS to quantitatively characterize the morphological evolution in thin films of P3HT/PCBM blends upon annealing, and structural parameters such as the domain spacing of the formed morphology are probed.\textsuperscript{16}

However, the chemical selectivity of GISAXS is limited, which limits its application for organic materials with little electron density contrast\textsuperscript{47} or complicated multiphase systems. A recent advance in structure characterization of polymer thin films is the development of resonant soft X-ray scattering (RSOXs).\textsuperscript{44,47-49} In the soft X-ray regime, absorption is significant for organic materials due to the lower photon energies (~165-2000 eV) that match the core electron transitions of the constituent atoms such as carbon, oxygen and nitrogen. Fine structures in the X-ray absorption spectrum carry information about the chemical bonding environment and the adjacent functional moieties. Thus, excellent chemical sensitivity can be achieved even for polymers with identical elemental compositions by tuning the X-ray energies to different molecular resonances that are characteristic of each material. Subtle differences in material resonant absorption can be exploited to obtain greatly enhanced scattering intensity over hard X-ray techniques.\textsuperscript{44} Consequently, RSOXS enables transmission scattering experiments on polymer thin films as illustrated in Figure 2-14 and provide direct information about the in-plane morphology of the active layer of organic solar cells.\textsuperscript{49, 50}
Figure 2-14. Transmission geometry of resonant soft X-ray scattering (RSOXS) experiments. Films are placed normal to the incident beam (~ 200×300 µm) with scattered intensities $I(\theta, \phi)$ recorded at all scattering angles, $\theta$, using a CCD. RSOXS intensities $I(\theta, \phi)$ probing the in-plane film morphology as shown on the right, can be integrated along the azimuth, $\phi$, and thus converted into the canonical scattering profile as a function of scattering vector, $q (q = 4\pi\sin(\theta/2)/\lambda$, $\lambda$ is the X-ray wavelength).50

2.4 Dissertation Overview

In this thesis, we demonstrate a paradigm shift in structure design for efficient organic photovoltaics (OPV) using self-assembled block copolymers, and present advanced techniques for morphological characterization of polymer thin films, which provide important information to guide future efforts in OPV optimization.

Chapter 3 illustrates the extensive applicability of resonant soft X-ray scattering (RSOXS) to characterize the phase separation in the active layer of organic solar cells. The energy dependence of RSOXS data measured from P3HT/PCBM mixtures as a model system indicates the formation of a multiphase system, which is consistent with the composition analysis of elemental maps obtained through energy-filtered transmission electron microscopy (EFTEM).
In Chapter 4, we demonstrate control of morphology and donor/acceptor heterojunctions in organic solar cells through microphase-separated conjugated block copolymer 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-\textit{b}-PFTBT). When utilized as the active layer of photovoltaic cells, P3HT-\textit{b}-PFTBT block copolymer devices show efficient photoconversion with near 3% efficiencies, well beyond devices comprised of P3HT/PFTBT polymer blends. Morphological characterization from RSOXS reveals that the remarkable performance of block copolymer solar cells is due to self-assembly into nanoscale lamellar structures. The combination of photovoltaic device results and structural characterization implies that covalent control of donor-acceptor interfaces in the block copolymer architecture is a potential route for controlling the interfacial molecular order and charge separation process to enhance organic photovoltaic performance.

Chapter 5 examines the effect of crystalline texture in the active layer on charge transport and device performance of organic solar cells using P3HT-\textit{b}-PFTBT photovoltaics as a model system. Solvent additive processing is employed to induce a texture change from mostly face-on to edge-on orientations in the crystalline P3HT domains, while the PFTBT block remains amorphous. We find that the optimum photovoltaic performance of block copolymer solar cells is independent of the predominant crystalline orientations adopted in P3HT crystals. This observation provides further insights into the optimal molecular packing within the nanoscale domains for efficient charge transport and photovoltaic performance. We propose that a proper
control of the orientation distribution enabling inter-crystallite connections may be important for optimizing charge transport and photovoltaic device operation.

In Chapter 6, we introduce an alternative EFTEM imaging method at low electron energy-loss regions that correspond to inter-band transitions of organic semiconductors, to characterize the structure formation in polymer thin films. Based on differences in chemical bonding of organic materials, high-contrast micrographs are obtained to reveal the phase separation of P3HT/PCBM mixtures. Through statistical analysis of the serial spectral images acquired from EFTEM, further details about domain compositions and local electronic transitions in the active layer of organic solar cells are probed.

Finally, main conclusions from this work are summarized in Chapter 7, followed by some suggestions for improving block copolymer photovoltaics in the future. To be specific, developing novel approaches to promote long-range order in the self-assembly structures could be important to access the full potential of block copolymer solar cells. In addition, chemical tuning of block copolymer semiconductors is a powerful tool to further optimize photovoltaic device performance through improving optical absorption and tuning donor-acceptor interfaces. Eventually, development of multicomponent block copolymer photovoltaics may serve as the platform to achieve unprecedented combinations of efficient light absorption, high photovoltages, and control of donor-acceptor heterojunctions in single-component organic solar cells. At last, we briefly discuss an extended technique from RSOXS using polarized soft X-rays, with the potential to probe the molecular orientations near donor-acceptor interfaces in organic thin films.
2.5 References


Resonant soft X-ray scattering (RSOXS) is a complementary tool to existing reciprocal space methods, such as grazing incidence small-angle X-ray scattering, for studying order formation in polymer thin films. In particular, RSOXS can exploit differences in absorption between multiple phases by tuning the X-ray energy to one or more resonance peaks of organic materials containing carbon, oxygen, nitrogen or other atoms. Here, we have examined the structural evolution in poly(3-hexylthiophene-2,5-diyl)/phenyl-C$_{61}$-butyric acid methyl ester mixtures by tuning the X-rays to resonant absorption energies of carbon and oxygen. Our studies reveal that the energy dependence of RSOXS scattering profiles indicates the formation of multiple phases in the active layer of organic solar cells, which is consistent with elemental maps obtained through energy-filtered transmission electron microscopy.

3.1 Introduction

Solution-processed organic photovoltaics (OPVs) have the potential to produce large-scale, low-cost and renewable power in the form of flexible thin films.$^{1-4}$ State-of-the-art OPV devices rely on the bulk heterojunction architecture,$^{5-6}$ where spontaneous phase separation of electron donor and acceptor materials forms the morphology necessary for high-performance organic solar cells.$^{7-9}$ Many reports have explored control of the nanostructure through a variety of processing approaches, including varying the blend ratio,$^{10}$ choice of solvent,$^{11}$ thermal and solvent annealing,$^{12}$ and the inclusion of
additives. Nevertheless, our ability to correlate these factors with OPV performance is limited due to the lack of techniques for detailed characterization of the morphology.

Many recent efforts have focused on the characterization of phase separation in the active layer of organic solar cells. In the most studied devices comprised of poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), structure formation has been studied via scanning probe microscopy (SPM), transmission electron microscopy (TEM), and X-ray techniques. But mass contrast is weak in TEM images for films with fine structures, and SPM techniques like atomic force microscopy require surface contrast to provide topographic images yielding limited information. We have previously utilized energy-filtered transmission electron microscopy (EFTEM) and grazing-incidence small-angle X-ray scattering (GISAXS) to examine the morphological evolution in P3HT/PCBM mixtures. EFTEM couples spectroscopy and microscopy to significantly improve the contrast and map the local elemental composition by imaging with inelastically scattered electrons. GISAXS can quantitatively characterize the structure in thin films of organic semiconductor mixtures. The chemical sensitivity of GISAXS is limited, however, which limits the application of this technique for blends with little mass contrast or in complicated multiphase systems.

In this chapter, we demonstrate that resonant soft X-ray scattering (RSOXS) is an important complementary tool to existing reciprocal space methods for characterizing the morphology in organic thin films. The use of RSOXS for block copolymers and polymer/polymer mixtures has shown greatly enhanced scattering intensity and contrast over conventional hard X-ray scattering. Utilizing X-ray energies that match the core
electron transitions of the constituent atoms in organic materials enables RSOXS to provide elemental selectivity and chemical sensitivity to exploit differences in absorption between multiple phases. Here, we report the application of RSOXS coupled with EFTEM to characterize the phase separation in P3HT/PCBM mixtures, which are commonly utilized as the active layer of organic solar cells, by tuning the X-ray energy to the absorption edges of carbon and oxygen. We demonstrate the ability of RSOXS to characterize multiphase formation in organic semiconductor mixtures, which is beyond the capabilities of GISAXS, using P3HT/PCBM films as a model system.

3.2 Results and Discussions

3.2.1 Origin of Scattering Contrast in RSOXS

In the soft X-ray spectrum (~ 165-2000 eV) where absorption is significant for organic materials, the amplitude of the scattered field from each phase scales strongly with its complex refractive index $n(\lambda)$, which is composed of a dispersive component $\delta(\lambda)$ and an absorptive component $\beta(\lambda)$. The scattering contrast arises from the difference in $n(\lambda)$, or $\delta(\lambda)$ and $\beta(\lambda)$, between different phases as described in equation (3-1).

$$I \propto \frac{\Delta n \Delta n^*}{\lambda^4} = \frac{(\Delta \beta)^2 + (\Delta \delta)^2}{\lambda^4}$$

(3-1)
where $\Delta n$ is the difference in $n(\lambda)$ between two phases and $\Delta n^*$ is the complex conjugate of $\Delta n$. Because the energies of the core levels (1s) of carbon, nitrogen and oxygen are located in the soft X-ray range, energy resolutions near 0.2 eV give rise to direct sensitivity to chemical bonding of organic materials.

![Near edge X-ray fine structure (NEXAFS) spectra for pristine films of P3HT and PCBM near the carbon 1s to $\pi^*$ transition regions.](image)

**Figure 3-1.** Near edge X-ray fine structure (NEXAFS) spectra for pristine films of P3HT and PCBM near the carbon 1s to $\pi^*$ transition regions. Open symbols represent experimental data and solid lines represent the individual peak fits. P3HT films show a spectral transition at 285.1 eV, while two resonant features are identified at 284.5 and 285.8 eV for PCBM films. The spectra are displaced along the y-axis for clarity.\(^{29}\)

For example, near-edge X-ray absorption fine structure (NEXAFS) studies of neat P3HT and PCBM films in Figure 3-1 have shown that the absorption is sensitive to small changes of the X-ray energy near the carbon absorption edge (~ 280-320 eV).\(^{29}\) P3HT exhibits resonant absorption at 285.1 eV, whereas two resonances are found at 284.5 and 285.8 eV for PCBM. The carbon 1s to $\pi^*$ transitions in P3HT and PCBM differ by 0.6 eV, such that scattering is enhanced at these energies where the absorption differs.
significantly. In addition, the presence and absence of resonant scattering at the oxygen absorption edge (525 eV) can be another source of scattering contrast given that only PCBM contains oxygen atoms. Thus, the subtle differences in the absorption between P3HT and PCBM near the C edge and differences in elemental composition can be used to generate scattering contrast between domains which vary in P3HT/PCBM composition using RSOXS.

3.2.2 RSOXS Characterization of Structure Evolution in P3HT/PCBM Mixtures

![Graph](image)

**Figure 3-2.** RSOXS intensity vs. scattering vector, $q$, for 1:1 by mass P3HT/PCBM mixtures annealed at various temperatures for 30 min at the (a) carbon absorption edge (284.4 eV) and (b) oxygen absorption edge (525 eV). Data are published in ACS Macro Letters.\(^{40}\)

Figure 3-2 presents the RSOXS intensity as a function of the in-plane scattering vector, $q$, performed at the carbon absorption (284.4 eV) and oxygen absorption (525 eV) edges for P3HT/PCBM mixtures annealed at variable temperatures. The intensities were
normalized in order to compare the scattering profiles qualitatively. The broad peak or shoulder near 0.01-0.02 1/Å indicates the presence of structure within the film. We note that the shape of scattering intensities at 284.4 eV shown in Figure 3-2a are analogous to that observed in previously reported GISAXS results for P3HT/PCBM mixtures in the hard X-ray regime (10 keV), suggesting that scattering is dominated by the structure factor of the morphology.\textsuperscript{18, 30} Unfortunately, the use of a central stop for the CCD detector prevented the acquisition of accurate information at low scattering vectors (below 0.008 Å\textsuperscript{-1}), which is required to develop a reliable quantitative understanding of RSOXS data and to compare with GISAXS. Nevertheless, the RSOXS profiles at the carbon absorption energy (284.4 eV) display a gradual shift of peak positions towards low $q$ range with increasing annealing temperatures, suggesting that the structure of P3HT-rich domains coarsens upon annealing and the domain spacing grows. At the oxygen absorption edge (525 eV), however, the RSOXS profiles differ significantly with the annealing temperature, indicating an energy dependence of the shape of the scattering profiles.

**3.2.3 Energy Dependence of the Scattering Contrast in RSOXS Profiles**

The comparisons of RSOXS scattering profiles at 284.4 eV and 525 eV for films annealed at 190, 165, 140 and 100 °C are displayed in Figure 3-3. After annealing at 190 or 165 °C, we find that the scattering profiles at the carbon (284.4 eV) and oxygen (525 eV) edges match, but after annealing at 140 or 100 °C the scattering profiles differ. The dependence of RSOXS data on the absorption edges at different X-ray energies results
from the change in scattering contrast between domains. Thus, the scattering profiles at carbon and oxygen absorption energies are constant for P3HT/PCBM mixtures annealed at high temperatures regardless of the scattering contrast between domains, but the profiles are distinct for samples annealed at low temperatures.

![Comparison of RSOXS intensities vs. scattering vector, q, at 284.4 and 525 eV for 1:1 by mass P3HT/PCBM mixtures annealed at (a) 190 °C (b) 165 °C, (c) 140 °C, and (d) 100 °C for 30 min. Data are published in ACS Macro Letters.](image)

**Figure 3-3.** Comparison of RSOXS intensities vs. scattering vector, $q$, at 284.4 and 525 eV for 1:1 by mass P3HT/PCBM mixtures annealed at (a) 190 °C (b) 165 °C, (c) 140 °C, and (d) 100 °C for 30 min. Data are published in ACS Macro Letters.⁴⁰
The contrast variations observed in RSOXS studies must be related to differences in phase separation of P3HT/PCBM films under different processing conditions. That is, when two distinct domains are present modulating the scattering contrast does not change the shape of the scattering profiles (although the scattering intensities vary significantly). In contrast, when three or more distinct domains are present and the scattering contrast varies with the X-ray energy then the scattering profiles can vary to reflect different periodicities associated with the different phases or domains. For example, RSOXS data at different X-ray energies reflect multiple periodicities when three distinct domains are present in triblock copolymers.\textsuperscript{31} We will return to the origins of the variation in scattering contrast with X-ray energy below, after discussion of morphological characterization using energy-filtered TEM experiments.

### 3.2.4 Composition Analysis of Elemental Maps from EFTEM Imaging

Images of the active layer morphology of P3HT/PCBM mixtures annealed at 190 and 100 \textdegree C obtained from EFTEM are shown in Figure 3-4 as sulfur elemental maps. The difference in sulfur composition of P3HT and PCBM generates high-contrast micrographs through inelastic scattering events. Because none of the major edges of the constituent elements (C, S, O, H) overlap, the intensity of the image is directly proportional to the total amount of sulfur,\textsuperscript{32} and can be translated to the concentration of P3HT within domains if the thickness of the film is known. Thus, the light regions in the image correspond to P3HT-rich domains while the dark regions correspond to PCBM-rich domains. Figures 3-4a and 3-4b show the presence of P3HT fibers in a PCBM-rich
matrix. The film structure after annealing at 100 °C is significantly less defined than the structure after annealing at 190 °C, due to the limited polymer chain mobility at lower temperatures near the glass transition point.

**Figure 3-4.** Sulfur elemental maps generated through EFTEM with schematic illustrations for 1:1 by mass P3HT/PCBM mixtures annealed at (a) 190 °C and (b) 100 °C for 30 min. The image intensity is proportional to the sulfur concentration. Therefore, the light regions correspond to P3HT-rich regions. The domain purity can be computed from the image intensities. The scale bar is 100 nm. TEM images were taken at the Penn Regional Nanotechnology Facility, University of Pennsylvania. Data are published in ACS Macro Letters.
For a two component system A and B, the local domain purity in an elemental map can be computed from equation (3-2) based on the elemental density of the two components, \( \rho_{i,A} \) and \( \rho_{i,B} \) for element \( i \),

\[
\phi_A(x, y) = \frac{(\bar{\phi}_A - k)}{\bar{I}_i} \frac{\bar{t}}{t(x, y)} I_i(x, y) + k
\]

(3-2)

where \( \phi_A(x, y) \) is the local volume fraction of component A integrated over the sample thickness, \( \bar{\phi}_A \) is the average concentration of A in the sample, \( k = \rho_{i,B}/(\rho_{i,B} - \rho_{i,A}) \), \( \bar{I}_i \) is the intensity averaged over the entire elemental map, \( t(x, y) \) is the local relative thickness probed directly from the thickness map, \( \bar{t} \) is the relative thickness averaged over the entire thickness map, and \( I_i(x, y) \) is the local intensity of the elemental map. The thickness maps must be obtained from the same sample areas as the elemental maps. Equation 3-2 is only valid when the absorption edges do not overlap, and as such, is most useful for elemental maps generated from energy-filtered TEM images taken at core-loss energies. Given that sulfur is only present in P3HT \( (k = 0) \), a reduced equation can be used to map the local P3HT composition, \( \phi_{P3HT}(x, y) \), from sulfur maps:

\[
\phi_{P3HT}(x, y) = \frac{\bar{\phi}_{P3HT}}{\bar{I}_S} \frac{\bar{t}}{t(x, y)} I_S(x, y)
\]

(3-3)
\( \bar{\phi}_{P3HT} \) is the average P3HT volume fraction in the film. Measurements of the fluorescence yield in NEXAFS experiments have demonstrated that the compositions of P3HT/PCBM films are equal to the compositions in solutions.\textsuperscript{29} We assume that the composition of the imaged area is equal to the composition of the entire film; thus, \( \bar{\phi}_{P3HT} \) is given by the P3HT/PCBM ratio in solution (0.58 volume fraction) prior to spin-coating. We note that this assumption is supported by the consistency of results obtained over many different images.\textsuperscript{18, 33} After averaging results over 10 regions in the sulfur map of films annealed at 190 °C, we find that the volume fraction of P3HT is 0.43 ± 0.03 for PCBM-rich domains, and 0.98 ± 0.05 for P3HT fibers perpendicular to the film surface (brightest circular regions in Figure 3-4a). A domain composition of 0.99 ± 0.06 P3HT by volume is further confirmed for the center of horizontal fibers by assuming one cylindrical fiber with diameter of around 20 nm in a PCBM-rich matrix. The domain concentrations were estimated in a similar way for films annealed at 100 °C as illustrated in Figure 3-4b. In this case, the images suggest that pure PCBM domains (1 ± 0.04) exist if we assume spherical PCBM aggregates in a P3HT/PCBM mixed matrix. Similar results are obtained through analysis of the contrast using equation (3-2) in carbon maps (images not shown) instead of sulfur maps as summarized in Table 3-1.
Table 3-1. Domain compositions by volume, $\phi_i$, obtained from EFTEM

<table>
<thead>
<tr>
<th>Annealing condition</th>
<th>Element map</th>
<th>$\phi_{P3HT}$ (P3HT-rich domain)</th>
<th>$\phi_{P3HT}$ (mixed domain)</th>
<th>$\phi_{PCBM}$ (PCBM-rich domain)</th>
</tr>
</thead>
<tbody>
<tr>
<td>190 °C, 30 min</td>
<td>Sulfur</td>
<td>0.99 ± 0.06</td>
<td>-</td>
<td>0.57 ± 0.03</td>
</tr>
<tr>
<td>190 °C, 30 min</td>
<td>Carbon</td>
<td>0.97 ± 0.04</td>
<td>-</td>
<td>0.55 ± 0.04</td>
</tr>
<tr>
<td>100 °C, 30 min *</td>
<td>Sulfur</td>
<td>0.93 ± 0.05</td>
<td>0.52 ± 0.03</td>
<td>1 ± 0.04</td>
</tr>
<tr>
<td>100 °C, 30 min *</td>
<td>Carbon</td>
<td>0.91 ± 0.04</td>
<td>0.52 ± 0.03</td>
<td>0.98 ± 0.06</td>
</tr>
</tbody>
</table>

*Data for samples annealed at 100 °C may be inaccurate due to the possibility of overlapping domains.

Our previous work demonstrates that three distinct phases are possible in P3HT/PCBM mixtures.\(^{18,33}\) P3HT will never fully crystallize, leaving an amorphous mixture of P3HT and PCBM as long as PCBM itself does not crystallize as a result of thermodynamic effects or processing. Nevertheless, amorphous P3HT and PCBM can phase separate if the interaction energy is high enough, leading to the formation of a nearly pure PCBM phase and a mixed P3HT/PCBM phase due to the asymmetric Flory-Huggins phase diagram (See Figure 3b of ref 18).\(^{18}\) Hence, we conclude that at lower annealing temperatures (i.e. 100 °C or 140 °C) the sulfur map displays three phases including essentially pure P3HT ($0.93 \pm 0.05$), pure PCBM ($1 \pm 0.04$) and a mixture of amorphous P3HT and PCBM ($\phi_{P3HT} = 0.52 \pm 0.03$), obtained from the light, dark and grey regions respectively. We assume that the mixed phases are amorphous because no crystallization of PCBM or co-crystallization of P3HT and PCBM has been observed in our samples or
in X-ray diffraction experiments for the processing conditions studied here.\textsuperscript{24, 34, 35} In particular, the bottom substrate can have a strong effect on the crystallization of PCBM,\textsuperscript{36} and our samples are annealed as free-standing films (TEM) or on Si\textsubscript{3}N\textsubscript{4} (RSOXS). As the annealing temperature increases to 190 °C, the increased miscibility of PCBM in P3HT\textsuperscript{35, 37} could drive the mixture to form a two-phase system composed of essentially pure P3HT fibers (0.99 ± 0.06) and a PCBM-rich matrix phase ($\phi_{P3HT} = 0.43 ± 0.03$).

\textbf{3.2.5 Signatures of Multiphase Formation in P3HT/PCBM Mixtures from RSOXS}

The combination of the energy-dependence of the RSOXS scattering profiles (Figure 3-3) and the elemental maps from EFTEM (Figure 3-4) suggests that more than two phases exist at 100 °C and 140 °C, and only two phases exist at 165 °C and 190 °C. Length scales extracted from Fourier transforms of micrographs as shown in Figure 3-5 are in reasonable quantitative agreement with scattering results, although a full quantitative comparison which includes domain compositions requires further analysis and absolute scattering intensities. Furthermore, because 2D images are projections of 3D structures, interpretation of TEM micrographs can be convoluted when the density of features is high.\textsuperscript{38} As a consequence, our analysis of domain compositions for images obtained after annealing at 100 °C, such as in Figure 3-4b, is speculative because we cannot rule out overlapping domains. RSOXS remains the most reliable method to characterize multiphase formation in thin-film mixtures of organic materials and we note that our elemental maps are consistent with the RSOXS results.
Figure 3-5. Comparison of radially integrated Fast Fourier Transform (FFT) intensities vs \( q \) (where \( q = \frac{2\pi}{d} \), and \( d \) is the length scale in real space) obtained from sulfur maps in Figure 3-4 with the RSOXS data at the carbon absorption edge (284.4 eV) for P3HT/PCBM films annealed at (a) 190 and (b) 100 °C, respectively. The peak intensities were normalized to 1. The FFT profiles were plotted at a different y-axis scale in order to compare with the RSOXS results. Data are published in ACS Macro Letters, Supporting Information.\(^{40}\)

We propose a hypothesis to explain how the scattering contrast is altered by the energy change based on the discovery of multiphase formation in P3HT/PCBM mixtures. Given the composition dependence of optical constants at soft X-ray energies, the mixed phase can be characterized with an average index of refraction weighted by its volume fraction. Thus, RSOXS can exploit differences in absorption between phases of distinct domain purities. For the two-phase system (190 °C) in Figure 3-4a, contrast is between pure P3HT and mixtures of amorphous P3HT and PCBM, which is independent of the absorption energy as evident in Figure 3-3a. Thus, the primary scattering peaks of RSOXS profiles probe information about the average domain spacing of P3HT regions.\(^{30}\) For the three-phase system (100 °C), scattering data is composed of a superposition of scattering originating from periodicities corresponding to P3HT and PCBM-rich domains.
that can correspond to different length scales. Because the mixed phase \( \phi_{P3HT} = 0.52 \pm 0.03 \) has a volume-averaged refractive index of the two components, contrast with either of the pure phases is similar, making extracting information about each individual phase challenging. At the oxygen absorption energy (525 eV, Figure 3-3d), for example, a weak feature around \( q = 0.015 \text{ Å}^{-1} (\sim 40 \text{ nm}) \) is barely identifiable. This length scale could correspond to the average domain spacing of P3HT-rich phases, which would be consistent with the structures observed through FFT analysis of the elemental maps in Figure 3-5 and previously reported GISAXS characterization.\(^{18}\) The upturn in intensities at low-\( q \) of the scattering data can be attributed to larger scale structures and potentially macrophase separation. At the carbon absorption edge (284.4 eV) scattering corresponding to the shorter length scale (\( \sim 40 \text{ nm} \)) dominates. Thus, we speculate that contrast at 284.4 eV is mainly between pure P3HT against the integration of the other two phases (pure PCBM and mixtures of amorphous P3HT and PCBM).

We postulate that the strong enhancement of scattering from P3HT domains is due to the contrast in molecular orientation of crystalline P3HT fibers and amorphous P3HT in mixed phases. Recent work by Collins et al. has demonstrated that the orientational dependence of the index of refraction at the C 1s to \( \pi^* \) transitions can lead to scattering profiles which are dominated by the difference in orientation between domains.\(^{39}\) The X-ray absorption at the \( \pi^* \) transition when the \( \pi \) orbitals are aligned with the X-ray polarization is three times the absorption of isotropically oriented \( \pi \) orbitals. In P3HT/PCBM mixtures, scattering from the crystalline domains (pure P3HT phases) would be enhanced at energies corresponding to the \( \pi^* \) transitions. As a result, the scattering contrast would differ at 284.4 eV from 525 eV, since no orientational
dependence is expected at the oxygen edge. Hence, tuning the X-ray energy can modulate the contrast and provide evidence for the formation of multiple phases. In addition, RSOXS experiments with polarized X-rays may also elucidate orientational correlations, although a detailed analysis of the scattering contrast is impeded by the lack of a quantitative model describing the relationship between X-ray energy, X-ray polarization and scattering contrast.

3.3 Conclusions

In summary, we have demonstrated the ability of RSOXS to characterize the multiphase formation in the active layer of organic solar cells. The strong resonant absorption of organic materials in the soft X-ray regime enables RSOXS to obtain high scattering contrast with chemical sensitivity and elemental selectivity. The energy dependence of the scattering profiles measured from P3HT/PCBM mixtures as a model system is consistent with the sulfur maps obtained through EFTEM. That is, the energy tuning afforded by RSOXS is able to modulate the scattering contrast generated between multiple phases, thus accessing structure information about different domains in P3HT/PCBM mixtures. Further, RSOXS characterization of the morphology in organic photovoltaics is potentially extendable to other combinations of organic materials, or even much more complicated multiphase (>2) systems. For instance, multicomponent mixtures are difficult to fully investigate using hard X-ray techniques alone, while RSOXS may be a powerful tool to exploit contrast between each of the multiple
components by tuning the X-ray energy to one or more resonance peaks corresponding to the chemistry of constituent organic materials.

3.4 Materials and Methods

Solutions of regioregular P3HT (96 \% H-T regioregular, \(M_n = 26\) kg/mol, polydispersity = 2.0, Merck) and PCBM (>99.5\%, Nano-C) were made with anhydrous chlorobenzene (Sigma-Aldrich) in a nitrogen-filled glovebox. Solutions were stirred for a minimum of 10 hrs and heated to 90 °C for 10 seconds prior to use to ensure dissolution.

For Resonant Soft X-ray Scattering (RSOXS) experiments, thin films (100 ± 10 nm thickness) of P3HT/PCBM with 1:1 weight ratio were cast from 24 mg/mL solutions onto about 65 nm poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), PEDOT:PSS, (Clevios P, H.C. Starck) films deposited on silicon wafers. Silicon wafers were cleaned through sonication for 20 min in acetone and then in isopropanol for 20 min followed by 10 min of ultraviolet light ozonation. As-cast films were floated-off in deionized water and picked up with 5 mm × 5 mm silicon frames supporting a 1 mm × 1 mm, 100 nm thick Si₃N₄ window. Samples were then dried for 24 hrs at room temperature under vacuum and subsequently annealed on a calibrated digital hot plate in a N₂ glovebox.

RSOXS measurements were conducted at beamline 11.0.1.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory. Scattering was performed in the transmission geometry in vacuum at various X-ray energies around 284.4 and 525.0 eV with linear polarization. Data were radially integrated and presented as a function of the
scattering vector, $q = 4\pi\sin(\theta/2)/\lambda$, $\lambda$ is the X-ray wavelength and $\theta$ is the scattering angle). RSOXS data were corrected for dark currents and scattering from the silicon nitride window.

In a similar manner as for RSOXS samples, P3HT/PCBM thin films (70 ± 10 nm thickness) for transmission electron microscopy (TEM) were spun cast on PEDOT:PSS deposited on silicon substrates from 15 mg/mL solutions in a N$_2$ glovebox. Films were floated-off in deionized water and picked up with copper TEM grids followed by drying under vacuum for 24 hrs and thermal annealing in the N$_2$ glovebox.

TEM experiments were performed at the Penn Regional Nanotechnology Facility, University of Pennsylvania on a JEOL 2010F FEG HRTEM/STEM or at the National Center for Electron Microscopy, Lawrence Berkeley National Laboratory on a Zeiss LIBRA 200MC. Bright field images, zero-loss energy filtered and unfiltered images (to generate thickness maps), and energy filtered images near core-loss absorption edges (to generate elemental maps) were captured from the same sample areas.

Elemental maps were computed from energy-filtered TEM images using the standard three-window method.$^{32}$ In this technique, the background can be extrapolated from two images taken at pre-edge energies assuming an inverse power law dependence on energy. The extrapolated background is then subtracted from the post-edge image, generating an elemental map. The intensity of sulfur maps is proportional to the amount of sulfur, thus directly related to the concentration of P3HT within domains. The domain composition was calculated by averaging the intensities in ten regions in carbon and sulfur maps as described in Section 3.2.4.
3.5 References


34. Gomez, E. D.; Barteau, K. P.; Wang, H.; Toney, M. F.; Loo, Y. L. *Chemical Communications* **2011**, *47*(1), 436-438;


Chapter 4. High-performance Conjugated Block Copolymer Photovoltaics through Microphase Separation

Organic electronic materials have the potential to impact almost every aspect of modern life including how we access information, light our homes, and power personal electronics. Nevertheless, weak intermolecular interactions and disorder at junctions of different organic materials limit the performance and stability of organic interfaces and hence the applicability of organic semiconductors to electronic devices. Here, we demonstrate control of donor-acceptor heterojunctions through microphase-separated conjugated block copolymers. The 3% block copolymer device efficiencies are achieved without the use of a fullerene acceptor. X-ray scattering results reveal that the remarkable performance of block copolymer solar cells is mainly due to self-assembly into mesoscale lamellar morphologies with covalently confined interfaces. Conjugated block copolymers thus provide a pathway to enhance performance in excitonic solar cells through control of donor-acceptor interfaces.

4.1 Introduction

Excitonic photovoltaics are a class of devices where donor-acceptor interfaces are critical for photogeneration of charges and efficient device performance.\textsuperscript{1-4} In contrast to many inorganic semiconductors where optical excitations generate delocalized free charge carriers, current generation in organic photovoltaics depends on dissociation of tightly bound charge transfer states near donor-acceptor interfaces. For instance, a recent model by Giebink et al. suggests that tuning the electronic coupling at donor/acceptor
interfaces is crucial to minimizing the recombination rate of charge transfer states while maintaining yields of exciton dissociation near unity.\textsuperscript{5} It follows that tuning the chemical structure and local order at organic heterojunctions is a requirement to access the full potential of organic solar cell materials. Unfortunately, organic solar cells rely on kinetically-trapped, partially phase-separated structures of donor/acceptor mixtures to create a high surface area for exciton dissociation and networks of bicontinuous phases for charge extraction.\textsuperscript{6-12} As a consequence, molecular control of the interface in state-of-the-art organic photovoltaics is nearly impossible.

Microphase-separated block copolymers comprised of electron donor and electron acceptor polymers can address many of the current challenges in morphology and interfacial structure control for photovoltaics. The equilibrium self-assembly of block copolymers into mesoscale (5-500 nm) well-ordered morphologies where interfaces are governed by moieties near the junction between blocks\textsuperscript{13,14} is ideal for the active layer of organic solar cells. While several examples of block copolymers with donor and acceptor blocks have been reported, the majority contain a non-conjugated insulating backbone in at least one polymer block and consequently do not directly control donor/acceptor interfaces.\textsuperscript{15-20} Recent work has demonstrated significant progress in the design, synthesis, and characterization of fully conjugated block copolymers,\textsuperscript{21-23} but it remains a challenge to achieve efficient charge photogeneration in photovoltaic device architectures.

We demonstrate 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 can be utilized as the active layer for efficient photovoltaic device
These block copolymers self-assemble to form in-plane lamellar morphologies with alternating electron donor and acceptor domains and a dominant face-on orientation in the crystalline P3HT block. Even without the use of fullerene, we obtain efficiencies near 3%, remarkable open-circuit voltages of 1.2 V, and short-circuit currents above 5 mA/cm² from block copolymer devices. These results demonstrate that conjugated block copolymers are a viable strategy for morphology and interfacial control for high performance organic solar cells.

4.2 Results and Discussions

4.2.1 Block Copolymer Photovoltaics Outperform Polymer Blend Solar Cells

The chemical structures of P3HT, PFTBT and block copolymer P3HT-\textit{b}-PFTBT are shown in Figure 4-1a. In block copolymers, P3HT and PFTBT blocks are joined directly via covalent bonding to form a fully conjugated macromolecule. Details about material synthesis are included in section 4.4. The synthesized P3HT-\textit{b}-PFTBT is roughly symmetric in composition, with 56 wt% P3HT and a total weight-averaged molecular weight of 29 kg/mol (See results from size-exclusion chromatography in Section 4.4 Materials and Methods). The energy levels of PFTBT as an electron acceptor are well aligned with those of P3HT as an electron donor (Figure 4-1b), such that the difference between the lowest unoccupied molecular orbital (LUMO) of PFTBT (~ 3.5 eV) and the highest occupied molecular orbital (HOMO) of P3HT (~ 4.9 eV) can yield open-circuit voltages above 1 V. High open-circuit voltages have indeed been demonstrated for solar cells where the active layer is comprised of blends of P3HT and other
dioctylfluorene bisthieny1-benzothiadiazole alternating copolymers, or ternary blends composed of similar conjugated block copolymers as P3HT-\(b\)-PFTBT with donor and acceptor homopolymers, or polymer blends with fluorene benzothiadiazole alternating copolymers as acceptor molecules.

Figure 4-1. (a) Chemical structures of polymer P3HT and PFTBT, and block copolymer P3HT-\(b\)-PFTBT. Data are published in Nano Letters. (b) Energy level diagram of P3HT as a donor and PFTBT as an acceptor. The large energy difference between P3HT HOMO level and PFTBT LUMO level predicts a theoretical open-circuit voltage beyond 1 V.
Solar cell devices with P3HT/PFTBT blends as active layers are compared with devices comprised of P3HT-\textit{b}-PFTBT block copolymers in Figure 4-2. All devices have an active layer thickness of 60-70 nm and were thermally annealed after deposition of the cathode (Al). As shown in Table 4-1, devices made from P3HT/PFTBT blends exhibited a maximum power conversion efficiency of 1.0%, which is comparable to the performance reported previously for devices which utilize blends of P3HT and other PFTBT-based polymers as the active layer.\textsuperscript{25} Solar cells made from P3HT/PFTBT blends were optimized at 1:2 weight ratios of P3HT:PFTBT after annealing at 100 °C for 20 min. Longer annealing times or higher annealing temperatures lead to a drop in performance, potentially due to macroscopic phase separation.

\textbf{Figure 4-2.} Current-voltage characteristics of polymer blend P3HT/PFTBT (1:2 by mass) and block copolymer P3HT-\textit{b}-PFTBT photovoltaic devices annealed at 100 °C for 20 min and 165 °C for 10 min, respectively. P3HT/PFTBT solar cells are optimized at 100 °C for 20 min, while P3HT-\textit{b}-PFTBT devices are optimized at 165 °C for 10 min. Devices were measured under simulated AM 1.5G irradiation with intensity of 97 mW/cm\textsuperscript{2}. Data are published in Nano Letters.\textsuperscript{67}
Table 4-1. Device characteristics\textsuperscript{a} of P3HT/PFTBT blend and P3HT-\textit{b}-PFTBT block copolymer solar cells at different annealing conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>Efficiency (%)</th>
<th>Short-circuit Current (mA/cm\textsuperscript{2})</th>
<th>Open-circuit Voltage (V)</th>
<th>Fill Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 °C 20 min polymer blend</td>
<td>1.0 ± 0.1</td>
<td>2.6 ± 0.3</td>
<td>1.22 ± 0.02</td>
<td>0.33 ± 0.02</td>
</tr>
<tr>
<td>165 °C 10 min polymer blend</td>
<td>0.5 ± 0.1</td>
<td>1.0 ± 0.1</td>
<td>1.16 ± 0.03</td>
<td>0.42 ± 0.02</td>
</tr>
<tr>
<td>100 °C 20 min block copolymer</td>
<td>1.5 ± 0.1</td>
<td>3.7 ± 0.2</td>
<td>1.13 ± 0.04</td>
<td>0.35 ± 0.01</td>
</tr>
<tr>
<td>100 °C 90 min block copolymer</td>
<td>1.7 ± 0.1</td>
<td>4.1 ± 0.1</td>
<td>1.14 ± 0.02</td>
<td>0.35 ± 0.01</td>
</tr>
<tr>
<td>165 °C 10 min block copolymer</td>
<td>2.7 ± 0.4</td>
<td>5.0 ± 0.3</td>
<td>1.14 ± 0.08</td>
<td>0.45 ± 0.02</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Under simulated AM 1.5G irradiation with intensity of 97 mW/cm\textsuperscript{2}.

If the active layer is comprised of P3HT-\textit{b}-PFTBT block copolymers, devices yield average efficiencies of 1.5% under annealing conditions optimal for polymer blend devices (100 °C for 20 min) and higher efficiencies of around 1.7% with an extended annealing time of 90 min at 100 °C (Table 4-1). Optimal performance, however, is achieved at higher annealing temperatures. After annealing for 10 minutes at 165 °C, average power conversion efficiencies of 2.7 ± 0.4% with short-circuit currents ($J_{sc}$) of 5.0 ± 0.3 mA/cm\textsuperscript{2}, open-circuit voltages ($V_{oc}$) of 1.14 ± 0.08 V and fill factors of 0.45 ± 0.02 were measured for devices under simulated solar conditions made from block copolymers. The nearly three-fold increase in device performance with respect to optimized devices comprised of polymer blends is due to enhancements of the short-circuit currents and fill factors. Nevertheless, fill factors in all of our devices do not
exceed 0.5, a result of the inflection point near open-circuit conditions visible in the current-voltage characteristics shown in Figure 4-2. We attribute the presence of an inflection point to problems in charge extraction due to either an imbalance in charge transport or accumulation of charge at an interface.\textsuperscript{30,31} As shown in Table 4-2, the best overall efficiency among our devices was recorded at 3.1\% with an open-circuit voltage of 1.23 V. This device performance is remarkable for solar cells based on donor-acceptor block copolymers\textsuperscript{15-17, 32, 33}, and for non-fullerene solution-processed organic photovoltaics\textsuperscript{34-37}.

**Table 4-2.** Device characteristics\textsuperscript{b} of P3HT/PFTBT polymer blend and P3HT-\textit{b}-PFTBT block copolymer solar cells with highest efficiencies

<table>
<thead>
<tr>
<th></th>
<th>efficiency (%)</th>
<th>short-circuit current (mA/cm\textsuperscript{2})</th>
<th>open-circuit voltage (V)</th>
<th>fill factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best device, block copolymer</td>
<td>3.1</td>
<td>5.2</td>
<td>1.23</td>
<td>0.47</td>
</tr>
<tr>
<td>Best device, blend</td>
<td>1.1</td>
<td>2.9</td>
<td>1.22</td>
<td>0.30</td>
</tr>
</tbody>
</table>

\textsuperscript{b}Under simulated AM 1.5G irradiation with intensity of 97 mW/cm\textsuperscript{2}.

The optical absorption spectra of P3HT, PFTBT, and P3HT-\textit{b}-PFTBT pristine films are compared in Figure 4-3a. The absorption of P3HT peaks around 520 nm. While PFTBT demonstrates two absorption bands around 390 and 540 nm. The absorption profile of P3HT-\textit{b}-PFTBT films preserves the features of the constituent homopolymers and a similar optical bandgap (~ 2 eV) as P3HT is deduced from the absorption edge. As a result, the absorption coefficient of P3HT-\textit{b}-PFTBT block copolymers is enhanced at
longer wavelengths (450-600 nm) due to the overlapping absorption ranges of P3HT and PFTBT, while absorption at short wavelengths (300-420 nm) is mainly attributed to the PFTBT block.

![Absorption spectra of pristine P3HT, PFTBT and P3HT-b-PFTBT films. All films were cast from chloroform solutions. The absorption coefficients are calculated from the measured absorbance and film thicknesses. (b) External quantum efficiency (EQE) characteristics of a P3HT-b-PFTBT solar cell annealed at optimized conditions (165 °C for 10 min) compared with the UV-Visible absorption spectrum of P3HT-b-PFTBT films. Data are published in Nano Letters and the Supporting Information.]

Figure 4-3. (a) Absorption spectra of pristine P3HT, PFTBT and P3HT-b-PFTBT films. All films were cast from chloroform solutions. The absorption coefficients are calculated from the measured absorbance and film thicknesses. (b) External quantum efficiency (EQE) characteristics of a P3HT-b-PFTBT solar cell annealed at optimized conditions (165 °C for 10 min) compared with the UV-Visible absorption spectrum of P3HT-b-PFTBT films. Data are published in Nano Letters and the Supporting Information.  

67
Figure 4-3b shows external quantum efficiency (EQE) of P3HT-b-PFTBT devices annealed at 165 °C and the absorption spectrum of pristine P3HT-b-PFTBT films. Optimized block copolymer devices display relatively high photoconversion efficiencies over a broad range of wavelengths (namely 350-610 nm) with EQE values of 20-35%, which are significant for thin-film photovoltaics based on only polymeric materials. Interestingly, an EQE value of 31% was recorded at 400 nm where the exciton generation is mostly attributed to the optical absorption of PFTBT, suggesting efficient exciton dissociation from photoexcitations in the acceptor domains. Integrating the EQE results predicts a \( J_{sc} \) of 4.7 mA/cm\(^2\) with an AM 1.5G reference spectrum. This is consistent with a measured \( J_{sc} \) of 5.0 mA/cm\(^2\) under AM 1.5G simulated solar conditions for the same device (~ 5% error). We attribute the small discrepancy to degradation in air, as EQE measurements took place in ambient. Indeed, devices which have undergone EQE measurements exhibit reduced \( J_{sc} \) (< 4 mA/cm\(^2\)) when tested under 1 sun conditions in a N\(_2\) atmosphere.

4.2.2 Structural Origin for Efficient Block Copolymer Photovoltaics from RSOXS

Resonant soft X-ray scattering (RSOXS) and grazing-incidence X-ray scattering measurements were carried out to elucidate the basis for the enhanced performance of block copolymer devices compared to devices made from polymer blends. RSOXS is a powerful tool for characterizing the phase separation in polymer thin films with limited phase contrast or in complicated multiphase systems.\(^{38-41}\) Differences in the core electronic transitions of organic materials in the soft X-ray regime greatly enhance
scattered intensities over hard X-ray scattering, enabling transmission X-ray scattering experiments of thin polymer films. Figure 4-4 compares the near edge X-ray absorption fine structure (NEXAFS) spectra of neat P3HT and PFTBT films. Significant contrast exists at 285.4 eV for RSOXS experiments, where the C 1s to π* transition differs between P3HT and PFTBT.

![NEXAFS spectra comparison](image)

**Figure 4-4.** Near edge X-ray absorption fine structure (NEXAFS) studies of neat P3HT and PFTBT films. Films were annealed at optimized conditions (165 °C) for device performance. NEXAFS spectra were normalized to 1 at 320 eV to account for thickness variations. Significant contrast is observed at 285.4 eV, where the X-ray absorptions of P3HT and PFTBT differ. Data are published in Nano Letters, Supporting Information.67

Figure 4-5 presents RSOXS intensities as a function of scattering vector, \( q \) (\( q = 4\pi \sin(\theta/2)/\lambda \), \( \lambda \) is the X-ray wavelength and \( \theta \) is the scattering angle), taken at 285.4 eV X-ray energy for P3HT/PFTBT polymer blend and P3HT-b-PFTBT block copolymer thin films annealed at 100 and 165 °C, respectively. The film annealing conditions match the optimum for the active layer of devices. Scattering data from polymer blends show little
structure. Scattering profiles from P3HT-b-PFTBT block copolymer films are distinct from scattering data of polymer blends (Figure 4-5 and original I(q) profiles in Figure A-1 of the Supporting information in Appendix A) or polymer/fullerene mixtures.\textsuperscript{10, 42} A primary scattering peak at \( q^* = 0.035 \ \text{Å}^{-1} \) and a weak second-order peak at \( 2q^* = 0.070 \ \text{Å}^{-1} \) are evident in data from thin films of block copolymers annealed at 165 °C. The positions of the scattering peaks at \( q^* \) and \( 2q^* \) are a signature of self-assembly into block copolymer lamellar microdomains\textsuperscript{43, 44} with a domain spacing of approximately 18 nm. The individual domain sizes are therefore roughly 9 nm, comparable to the exciton diffusion length in organic semiconductors (~ 10 nm).\textsuperscript{45}

RSOXS experiments in the transmission geometry exclusively explore the in-plane film structure and consequently demonstrate the presence of P3HT-b-PFTBT lamellae oriented perpendicular to the substrate, as shown in the inset of Figure 4-5. Grazing incidence small-angle X-ray scattering (GISAXS) measurements shown in Figure A-2 of the Supporting Information in the Appendix A similarly suggest in-plane microdomains with roughly 16 nm spacing (\( q^* = 0.04 \ \text{Å}^{-1} \)), in reasonable agreement with the length scales extracted from RSOXS data. Consequently, RSOXS and GISAXS data demonstrate a thin-film lamellar morphology that not only establishes an equilibrium microstructure amenable for exciton dissociation but also provides pathways for electron and hole transport to the corresponding electrodes. We note that the appearance of a lamellar microstructure in P3HT-b-PFTBT films only occurs at 165 °C and not 100 °C as illustrated in Figure 4-6, and device efficiencies exhibit a roughly two-fold increase when films are annealed at 165 °C versus 100 °C (Table 4-1). Thus, we attribute the significant
improvement in photovoltaic device performance to the self-assembly of block copolymers into well-defined mesostructures in the active layer.

**Figure 4-5.** Comparison of the morphology in the active layers of optimized P3HT-\textit{b}-PFTBT and P3HT/PFTBT photovoltaic devices using RSOXS. RSOXS data were acquired at the carbon absorption edge (285.4 eV) of a P3HT-\textit{b}-PFTBT film annealed at 165 °C and a P3HT/PFTBT (1:2 by mass) blend annealed at 100 °C. RSOXS intensities are offset for clarity. Scattering data are presented as a Kratky plot of \(I(q)q^2\) vs. \(q\), where \(I(q)\) is the scattering intensity, and \(q\) is the scattering vector. RSOXS intensities \(I(q)\) as a function of \(q\) are shown in Appendix A. In optimized P3HT-\textit{b}-PFTBT samples, a well-defined primary peak, \(q^*\) (\(\sim 0.035 \text{ Å}^{-1}\)), and second-order reflection, \(2q^*\), are identified. Schematic illustration of the lamellar morphology is shown in the inset, with the average domain spacing indicated as \(d\). Data are published in Nano Letters.\(^{57}\)
Figure 4-6. RSOXS intensities of P3HT-b-PFTBT block copolymer and P3HT/PFTBT polymer blend thin films under various processing conditions. Profiles are offset for clarity. Scattering data were acquired at 285.4 eV, azimuthally integrated, and presented as a Kratky plot of $I(q)q^2$ vs $q$, where $I(q)$ is the scattering intensity, and $q$ is the scattering vector. Data are published in Nano Letters, Supporting Information.

4.2.3 Control of Crystalline Orientations in Block Copolymer Thin Films

We examined the molecular order in block copolymer thin films using conventional X-ray diffraction (XRD) and grazing-incidence wide-angle X-ray scattering (GIWAXS). Measurements were performed on P3HT-b-PFTBT films deposited on top of PEDOT:PSS-coated Si substrates and processed in an analogous manner to optimized
devices (165 °C annealing for 10 min). XRD results show that PFTBT is amorphous while P3HT forms crystalline structures in both blend and block copolymer films with the same (100) spacing as that in the pristine P3HT films (Figure 4-7a). Complementary two-dimensional GIWAXS measurements provide the preferred orientation of these crystallites through analysis of both the in-plane (along $q_y$) and out-of-plane (along $q_z$) scattering data. As shown in Figure 4-7b, the (100), (200), and (300) reflections of P3HT ($q \sim 0.4, 0.8,$ and $1.2 \, \text{Å}^{-1}$, respectively), corresponding to spacing between the polymer backbone through the alkyl side-chains, are strongly in-plane with the substrate (along $q_y$). The (010) peak ($q \sim 1.65 \, \text{Å}^{-1}$), which corresponds to $\pi-\pi$ stacking between polymer chains, is only evident in the out-of-plane direction (along $q_z$). This indicates that P3HT assumes a predominantly face-on orientation, with $\pi$-stacking between conjugated thiophene rings primarily out-of-plane or normal to the substrate. Face-on P3HT crystallites likely enhance the hole extraction efficacy because the fast charge transport direction is along the $\pi-\pi$ stacking direction (Refer to Chapter 5 for detailed discussions).

The orientation of P3HT crystals in P3HT-$b$-PFTBT block copolymer films differs qualitatively from previously reported studies on P3HT crystallization in homopolymers, polymer/fullerene mixtures or polymer/polymer blends where edge-on orientations are strongly preferred. To first order, there is no reason for the lamellar block copolymer morphology to constrain the P3HT block into either a face-on or edge-on orientation. Instead, we hypothesize that interactions between PFTBT and the substrate lead to preferred face-on orientations for the PFTBT segment at the substrate interface. Consequently, the connectivity between blocks nucleates crystals with face-on orientations within the P3HT domains.
Figure 4-7. Molecular organization in P3HT-\textit{b}-PFTBT thin films. (a) X-ray diffraction (XRD) patterns of neat P3HT, neat PFTBT, P3HT/PFTBT blend, and P3HT-\textit{b}-PFTBT block copolymer films annealed at 165 °C. (b) Two-dimensional GIWAXS pattern for thin films of P3HT-\textit{b}-PFTBT annealed at optimized conditions (165 °C) for device performance. The (100), (200), and (300) diffraction peaks of regioregular P3HT are strongly biased in the in-plane direction ($q_y$) and the (010) peak is apparent in the out-of-plane direction ($q_z$), suggesting face-on crystallites. Data are published in Nano Letters.\textsuperscript{67}
4.2.4 Covalent Control of Donor-Acceptor Interfaces in Block Copolymer Photovoltaics

The combination of our device results and structural characterization on multiple length scales demonstrates the unique strengths of block copolymer architectures for efficient organic photovoltaics. In addition to controlling the mesoscale structure, conjugated block copolymers provide control of the donor-acceptor interface and of crystallite orientations. Covalent bonding across the donor-acceptor interface has the potential to control charge separation and charge recombination rates,\textsuperscript{51, 52} opening the possibility of achieving the near unit efficiencies for charge separation from charge transfer states observed in photosynthetic systems.\textsuperscript{53} In our studies, the device performance increases when the active layer is composed of block copolymers instead of polymer blends even when the morphology is roughly invariant between the two systems; for example, after annealing at 100 °C the device efficiencies improve by 50% when block copolymers are used as active layers even though the RSOXS data and mesoscale structure are similar for block copolymer and blend films (Table 4-1 and Figure 4-6). A possible explanation for the difference in the device performance between blend and block copolymer devices is that the connectivity between blocks provides donor/acceptor interfaces within length scales of the order of chain dimensions (ca. 10 nm) and consequently promotes charge separation. The size of domains, however, in P3HT/PFTBT blends at optimum conditions is near 10-20 nm, as evident from the inflection point in the scattering data from blends shown in Figure 4-5 or the data in reference 54. Another possible explanation, changes in charge extraction efficacy, is ruled out given that the current at reverse bias scales with the short-circuit current in
Thus, we hypothesize that conjugation across the donor-acceptor interface is responsible for enhancing device performance in block copolymer devices even when the microstructure of the active layer is similar to blends, suggesting that covalent control of donor-acceptor interfaces is a route for controlling interfacial molecular order, exciton dissociation and charge recombination to enhance excitonic solar cell performance.

4.3 Conclusions

Establishing exceptional performance in P3HT-b-PFTBT solar cells provides a clear pathway for enhancing efficiencies in fully conjugated block copolymers devices. The choice of P3HT and PFTBT as constituent blocks is motivated by previous work on optimizing polymer blends composed of P3HT and PFTBT derivatives for the active layer of solar cells. As a consequence, combinations of polymer blocks with complementary absorbance could lead to significant enhancements in short-circuit currents beyond P3HT-b-PFTBT because the absorption spectra of P3HT and PFTBT overlap significantly (Figure 4-3). Broad-band light absorption can be achieved in combination with open-circuit voltages beyond 1 V with careful design of the HOMO/LUMO levels of the constituent blocks, as demonstrated with P3HT-b-PFTBT. Previous work has also demonstrated the presence of exciplex or bound charge transfer states at polymer-polymer interfaces which are unlikely to contribute to the photocurrent at room temperature. These strongly bound states are localized, in many cases intermolecularly to the benzothiadiazole group in the acceptor polymer. Nevertheless, recent photophysical studies of conjugated donor-acceptor molecules have
shown that the presence of charge transfer states and consequently the degree of recombination depends strongly on the linking chemistry. As such, fully conjugated block copolymers provide a path to achieve unprecedented combinations of light absorption, high photovoltages and control of electronic coupling at donor-acceptor interfaces in single-component active layers of organic solar cells.

4.4 Materials and Methods

Regioregular P3HT (96% H-T regioregular, Mn = 26 kg/mol, polydispersity = 2.0) was purchased from Merck. All other reagents and solvents were purchased from Sigma-Aldrich and used as received. P3HT-b-PFTBT block copolymers were synthesized using a procedure similar to that previously described and the synthesis is briefly discussed here. Br end capped P3HT ($M_w = 16.1$ kg/mol, polydispersity = 1.12, 685 mg, 0.042 mmol), 9′,9′-dioctylfluorene-2′,7′-diboronic acid ester (455 mg, 0.82 mmol), 4,7-bis-2′-(5′-bromo)-thienyl-2′,1′,3′,- benothiadiazole) (309 mg, 0.68 mmol), tetrakis(triphenylphosphine)-palladium(0) (38 mg, 0.033 mmol), 5 mL of tetraethyl ammonium hydroxide (20% in H$_2$O) and aliquat 336 (3 drops) were added to a Schlenk tube loaded with nitrogen-purged toluene (25 mL). The flask was purged with three freeze-pump-thaw cycles, backfilled with nitrogen, and stirred overnight at 90 °C. Next, 5mL bromobenzene was added and stirred at 90°C for 1 h before cooling the reaction mixture. The polymer was precipitated in cold methanol and collected by filtration. The powder was then loaded into a Soxhlet thimble and washed with acetone, hexanes, and then
chloroform to recover the polymer. The yield of block copolymer was 740 mg ($M_w = 28.5$ kg/mol, polydispersity = 1.3).

Polymer molecular weights and polydispersities (PDIs) were obtained by size-exclusion chromatography (SEC) using an Agilent 1200 module equipped with three PSS SDV columns in series (100, 1000, and 10,000 Å pore sizes), an Agilent variable wavelength UV/visible detector, and a Wyatt Technology Optilab reX RI detector. Tetrahydrofuran was used as the mobile phase at a flow rate of 1 mL/min at 40 °C. Weight average molecular weights ($M_w$) and polydispersities (PDIs) are determined relative to a set of monodisperse polystyrene standards (Astra Software Version 5.3.4). SEC-RI analysis for the P3HT macroreagent and the final P3HT-$b$-PFTBT is shown in Figure 4-8. Deconvolution of the constituent peaks in the block copolymer trace reveals 14 wt% of P3HT homopolymer impurities.

![Figure 4-8. Size-Exclusion Chromatography (SEC) analysis of P3HT macroreagent and final block copolymer product. SEC analysis shows a clear shift of the molecular weight distribution for the final P3HT-$b$-PFTBT block copolymer compared with the starting P3HT macroreagent. The shoulder in the molecular weight distribution at long times indicates that some residual P3HT macroreagent is present (14 wt%). Data are published in Nano Letters, Supporting Information.](image-url)
Photovoltaic devices were prepared with the conventional architecture of ITO/PEDOT:PSS (65 nm)/active layer (60-70 nm)/Al (75 nm). ITO-coated glass substrates (20 ohm/sq, Xin Yan Technology, Hong Kong) were cleaned by soap, followed by 20 min of sonication in acetone, then isopropanol, and finally 15 min of ultraviolet light ozonation. Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), PEDOT:PSS (Clevios P, Heraeus), was spin-coated on top of ITO at 4000 rpm for 2 min yielding a thickness of about 65 nm. The PEDOT:PSS/ITO substrates were dried for 10 min at 165 °C in air and then transferred to a nitrogen-filled glovebox. Solutions of P3HT/PFTBT mixtures (15 mg/ml, weight ratio 1:2) and P3HT-b-PFTBT (5 mg/ml) were made with anhydrous chloroform (≥ 99%, amylene as stabilizer, Sigma-Aldrich) and stirred at 95 °C for about 20-22 hrs in a tightly sealed container prior to casting in a N₂ glovebox. The active layers of P3HT/PFTBT and P3HT-b-PFTBT devices were cast onto PEDOT:PSS layers from prepared hot solutions (95 °C) at various spin speeds for 1 min to maintain thicknesses around 60-70 nm. The film thicknesses were determined on a TENCOR P-10 surface profiler. Samples were then transferred immediately onto a calibrated digital hot plate at 100 or 165 °C and dried for 5 min. The devices were completed by vacuum thermal evaporation of 75 nm aluminum at 10⁻⁶ torr on top of the active layer through a shadow mask. The device area is 16.2 mm². Integrated solar cells were further annealed at 100 or 165 °C for various annealing times.

Photovoltaic measurements were performed in a N₂ atmosphere under simulated AM 1.5G illumination (97 mW/cm²) from a xenon lamp solar simulator (Newport Model SP92250A-1000). The illumination intensity was calibrated using an optical power meter.
and NREL certified Si reference photocell (Newport). A Keithley 2636A Sourcemeter was used to measure the current-voltage characteristics of solar cells. External quantum efficiencies (EQE) were measured in air. The photocurrents as a function of wavelength were recorded by a multifunction optical power meter (Model 70310) using 300W xenon lamp and Cornerstone monochromator (Newport Model 74100) illumination. The absorption spectra of films were measured using an ultraviolet/visible/near-infrared spectrophotometer (Beckman DU Series 500).

Samples for RSOXS, XRD, GISAXS and GIWAXS measurements were prepared on PEDOT:PSS/Si substrates in the same manner as for device fabrication. For RSOXS experiments, as-cast films were floated-off in deionized water and picked up with 5 mm × 5 mm silicon frames supporting a 1 mm × 1 mm, 100 nm thick Si₃N₄ window. Samples were then dried for 24 hrs at room temperature under vacuum and subsequently annealed on a hot plate in the N₂ glovebox.

RSOXS measurements were carried out at beam line 11.0.1.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory. Scattering was performed in the transmission geometry in vacuum at X-ray energies at the carbon absorption edge (285.4 eV) with linearly polarized X-rays. Data were corrected for dark currents and azimuthally integrated.

XRD experiments were conducted at the Materials Characterization Lab of Pennsylvania State University, on a Rigaku DMAX Rapid Microdiffractometer. The X-ray wavelength, $\lambda$, was 1.54 Å. Rocking curves were obtained by rocking the sample (±
0.5°) around the Bragg angle and images were collected with a curved image plate
detector. Data were azimuthally integrated.

GISAXS and GIWAXS measurements were carried out at Beamline 8-ID-E of the
Advanced Photon Source, Argonne National Laboratory (λ = 1.6868 Å). Scattering
data were acquired at an incident angle of 0.2°. Data are corrected for X-ray polarization,
detector sensitivity and geometrical solid-angle.

4.5 References


Chapter 5. Orientation Control of Molecular Packing in Conjugated Block Copolymer Solar Cells and Implications for Photovoltaic Performance

The electronic properties of organic semiconducting thin films are strongly influenced by the intermolecular packing of the functional materials. In the case of planar \( \pi \)-conjugated molecules, especially in crystalline materials, it follows that transport of charges exhibits anisotropic character depending on the molecular orientation in organic thin films. Consequently, the crystalline texture in the active layer may play an important role in charge transport properties and organic photovoltaic operation. Here we demonstrate orientation control of molecular packing from mostly face-on to edge-on configurations in the active layer of P3HT-\( b \)-PFTBT block copolymer photovoltaics using 1-chloronaphthalene as a solvent additive. The effect of molecular orientations in P3HT crystals on charge transport and solar cell performance is investigated. We find that the optimized photovoltaic device performance is independent of the crystalline texture in P3HT domains. Our observations provide further insights into the molecular organization required for efficient charge transport and overall device efficiencies. That is, the dominant crystal orientation, whether face-on or edge-on, is not critical to organic solar cells. Instead, a proper control of orientation distributions allowing inter-crystallite connections might be important for optimizing charge transport and photovoltaic device operation.
5.1 Introduction

Conjugated semiconducting polymers have emerged as promising functional materials for solution-processable organic photovoltaics (OPVs), with great potentials to produce large-scale, low-cost and renewable power in the form of flexible electronic devices.$^{1-3}$ Efficient power conversion in OPVs requires optimization of a series of processes related to light absorption, exciton diffusion, charge separation and charge transport; the latter three are strongly dependent on the microstructure within the active layer of organic solar cells. A common approach is to utilize a bulk heterojunction architecture, where electron donor and acceptor materials form an interpenetrating network of nanoscale domains to create a large interfacial area for exciton dissociation into charge separated states and interconnected pathways for charge transport.$^{4-6}$ Extensive efforts have been devoted to tuning the microstructure in commonly utilized polymer/fullerene mixtures, leading to great progress in organic photovoltaic performance.$^{7-9}$

In addition to control over morphology, molecular order within nanoscale domains can significantly impact organic photovoltaic device performance as well. Due to the anisotropic nature of planar $\pi$-conjugated molecules, in particular of crystalline materials, the molecular orientation in organic thin films can greatly influence the resulting optoelectronic properties and the overall device performance. For example, charge transport in poly(3-hexylthiophene-2,5-diyl) (P3HT), a commonly used donor polymer in solar cells, is strongly affected by the molecular order in the active layer.$^{10,11}$ As shown in Figure 5-1, regioregular P3HT self-organizes into a crystalline structure through $\pi-\pi$ interchain stacking of conjugated thiophene rings along $b$ axis and segregation of alkyl side chains to spaces in between the polymer backbones along $a$ axis.$^{12}$
**Figure 5-1.** Schematic illustrations of crystal structure for regioregular P3HT.  

*b* axis denotes the direction of π-π interchain stacking between conjugated thiophene rings with a periodic spacing $d_{010}$ of 0.38 nm.  

*a* axis indicates the alignment direction of alkyl side chains between polymer backbones characterized by an interchain distance $d_{100}$ of around 1.6 nm.  

c axis represents the conjugation direction along the chain backbone. The image is adapted from ref 13.

In studies of P3HT thin-film field-effect transistors (FETs), in-plane hole mobilities near 0.1 cm$^2$ V$^{-1}$ s$^{-1}$ are observed when π-π stacking occurs parallel to the substrate known as the edge-on orientation (Figure 5-2a). In contrast, when the face-on orientation (the overlap of π-orbitals is perpendicular and stacking of polymer side chains are aligned with the substrate) is dominant (Figure 5-2b), the in-plane mobility decreases by several orders of magnitude. Because charge transport is fast along the π-π stacking direction, it is generally surmised that face-on orientations are favorable for out-of-plane charge transport to the corresponding electrodes and overall device performance in the solar cell architecture.  

14-17
Figure 5-2. Two-dimensional wide-angle X-ray scattering images of spin-coated, 70-100 nm thick P3HT films with regioregularity of (a) 96% and (b) 81% on SiO2/Si substrates, respectively. The vertical axes correspond to scattering normal to the film plane, while the horizontal axes correspond to scattering parallel with the plane of the film. The scattering data demonstrate two different orientations of ordered P3HT domains with respect to the field-effect transistor (FET) substrate, namely (a) edge-on and (b) face-on orientations, as shown in the insets.10

Many reports have explored control of molecular packing towards face-on orientation through an optimization of processing conditions including choice of solvents,12 the application of solvent additives,8 thermal treatment,18 and surface modification,19, 20 or through chemical strategies such as tuning polymer regioregularity10 and side chain engineering.21 Recently, such face-on orientations have been induced in polymer/fullerene mixtures, and are perceived as contributing to the enhanced charge transport and the resulting high performance of polymer solar cells.19, 21 In most cases, however, the alignment of crystal orientation is inevitably associated with changes of the polymer/fullerene blend structures such as the degree of phase separation and domain connectivity. The inability to decouple these mesoscale morphological factors gives rise
to the challenge in directly correlating molecular organization with device performance. In addition, recent work by Rand and coworkers suggests that the orientation between donor and acceptor materials can also tune the electronic coupling across the interface and thus affect charge generation. This further complicates efforts to elucidate the role of molecular orientation, or the texturing of crystallites in the active layer of organic photovoltaics.

Here we examine the effect of crystalline texture on the photovoltaic performance of conjugated donor-acceptor block copolymer solar cells composed of 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) as the active layer. In Chapter 4, we have demonstrated that the self-assembly of P3HT-b-PFTBT block copolymers into in-plane nanoscale lamellar morphologies where interfaces are governed by the covalent junction between donor and acceptor blocks leads to power conversion efficiencies of 3%. The well-defined microstructure and covalently linked donor-acceptor heterojunctions allow us to exclusively focus on the influence of molecular packing, particularly in crystalline P3HT, on photoconversion efficiencies (PCEs) of organic solar cells. We employ solution processing with a solvent additive 1-chloronaphthalene (CN) to induce a texture change from mostly face-on to edge-on orientations in the crystalline P3HT block, while the PFTBT block remains amorphous. No distinct differences in the self-assembled structures are observed after the application of solvent additives as characterized by resonant soft X-ray scattering (RSOXS). Surprisingly, we find that the dramatic change in crystalline orientations results in very similar device performance of optimized block copolymer solar cells, implying that organic photovoltaic performance is
independent of the crystalline texture in the active layer. We hypothesize that the ubiquitous broad distribution of crystallite orientations present in polymeric semiconductors creates percolating pathways for charge transport through tie chains, even when the average orientation is not favorable for charge transport in the desired direction.

5.2 Results and Discussions

5.2.1 Orientation Control of Molecular Packing in Poly(3-hexylthiophene)-based Conjugated Block Copolymers

Previous X-ray diffraction studies (Figure 4-7a, Chapter 4) have shown that P3HT-\textit{b}-PFTBT is a crystalline-amorphous conjugated block copolymer where the PFTBT block is amorphous, while the P3HT block crystallizes with the same characteristic diffraction peaks (h00) as that in neat P3HT films. No measurable changes in the lattice spacing are found, suggesting that co-crystallization of P3HT with PFTBT does not exist to any measurable degree. Details of the crystallographic texture in the P3HT block are investigated using grazing-incidence wide-angle X-ray scattering (GIWAXS). Experiments were performed on block copolymer thin films deposited on PEDOT:PSS-coated Si substrates to simulate identical surface conditions as in the solar cell architecture and annealed in an analogous manner (165 °C) to optimized devices. Two-dimensional GIWAXS measurements probe the preferred crystal orientations through analysis of the scattering patterns in both in-plane ($q_y$) and out-of-plane ($q_z$) directions.
Figure 5.3. Two-dimensional grazing-incidence wide-angle X-ray scattering (GIWAXS) patterns with schematic illustrations for dominant molecular orientations of P3HT crystals in P3HT-\textit{b}-PFTBT block copolymer solar cells processed with 0\% (a, c) and 5\% (b, d) 1-chloronaphthalene (CN) solvent additives. All samples were annealed at 165 °C. Block copolymer films without solvent additive adopt predominant face-on orientations with π-π stacking primarily our-of-plane in P3HT domains. When the solvent additive is present, however, P3HT crystals demonstrate a dramatic change in molecular packing from face-on to edge-on orientations. The two electrodes are Al (grey) and ITO (white), respectively.

Figure 5-3 compares the GIWAXS data of P3HT-\textit{b}-PFTBT thin films spun-cast from chloroform solutions with 0\% and 5\% by volume of 1-chloronaphthalene additives. For the block copolymer films with no additives (Figure 5-3a), the (010) diffraction peak of P3HT ($q \sim 1.65$ Å$^{-1}$) associated with the π-π stacking reflection is only evident in the out-
of-plane (along \( q_z \)) direction. Meanwhile three orders of (h00) reflections (\( q \sim 0.36, 0.72 \) and 1.08 Å\(^{-1} \)), which correspond to the distance between P3HT backbones separated by the alkyl side chains, are apparent in-plane (along \( q_y \)) with the substrate. We note that the (100) peak is also visible in the surface normal direction, but with a minor population as shown in the orientation distribution of the (100) reflection (Figure 5-4a). This indicates that P3HT crystals in block copolymer films are mostly aligned face-on with \( \pi-\pi \) stacking primarily normal to the substrate or electrode as illustrated in Figure 5-3c. Indeed, such a dominating face-on packing differs from previously reported studies of P3HT crystallization in neat films or polymer mixtures where strong edge-on orientations are observed.\(^{22-24} \) Although it is currently unclear how the block copolymer is perturbing the crystal texturing of P3HT, we speculate that the observed face-on orientation could be a result of the connectivity between blocks, if the interaction of PFTBT with the substrate has a preferred face-on orientation (See Section 4.2.3 in Chapter 4 for details). After processing with 5% 1-chloronaphthalene additives, however, the crystalline texture as shown in Figure 5-3b is drastically different. The (100), (200) and (300) peaks are highly oriented out-of-plane (along \( q_z \)), while the \( \pi \)-stacking peak (010) appears exclusively parallel to the substrate (along \( q_y \)), suggesting a predominant edge-on orientation (Figure 5-3d). The dominance of the edge-on orientation is apparent in the orientation distribution of the (010) reflection as shown in Figure 5-4b. With the addition of 1-chloronaphthalene to the solution, P3HT-\( b \)-PFTBT films exhibit a significant increase of edge-on crystallites and a drastic drop in the face-on population. The mechanism for such a texture change is currently unclear. We speculate that 1-chloronaphthalene with a high boiling point may alter the effective surface interactions between the polymer and
the substrate during film deposition, allowing P3HT to form edge-on crystallites on the PEDOT:PSS substrates.\textsuperscript{19} Overall, adding a small amount of 1-chloronaphthalene into the solution state leads to a dramatic change in the texture of P3HT-\textit{b}-PFTBT block copolymer films, from a largely face-on packing without 1-chloronaphthalene to the edge-on orientation in crystalline P3HT domains when the additive is used.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{GIWAXS intensities as a function of azimuthal angle, $\phi$, at P3HT (a) (100) and (b) (010) peaks for P3HT-\textit{b}-PFTBT block copolymer thin films processed with 0\% and 5\% chloronaphthalene (CN) additives. Intensities were integrated over a $q$ window of $\pm 0.06 \text{ Å}^{-1}$ for the (100) peak and $\pm 0.10 \text{ Å}^{-1}$ range for the (010) reflection. A linear background was subtracted from the integrated data, respectively, using intensities away from the Bragg peak of interest.}
\end{figure}
5.2.2 Effect of Solvent Additives on the Active Layer Morphology from Resonant Soft X-ray Scattering

Processing with solvent additives can not only tune the crystalline orientation, but more often is applied to control mesoscale phase separation in the polymer/fullerene mixtures.\(^8\)\(^9\) Here we examine the effect of solvent additives on the self-assembled mesoscale structures in block copolymer thin films using resonant soft X-ray scattering (RSOXS). As discussed in Chapter 3, RSOXS is a powerful tool for structure characterization of polymer thin films with compositionally similar phases or in intricate multiphase systems. Differences in the absorption in the soft X-ray range enable RSOXS to explore elemental and chemical contrast between different organic materials and provide greatly enhanced scattering intensities. The enhanced contrast in RSOXS over hard X-ray scattering techniques enables transmission geometries for scattering experiments of thin films, thereby allowing us to examine the in-plane morphology.

Figure 5-5 presents RSOXS scattering intensities as a function of in-plane scattering vector \(q\) \((q = 4\pi \sin(\theta/2)/\lambda, \lambda\) is the X-ray wavelength and \(\theta\) is the scattering angle), for thin films of P3HT-b-PFTBT block copolymers processed with 0% and 5% CN additives. RSOXS experiments were performed at the carbon absorption edge of 285.4 eV, where significant absorption contrast exists between P3HT and PFTBT (See Figure 4-4 in Chapter 4). Films were annealed at the optimal conditions (165 °C) for device performance. RSOXS data from P3HT-b-PFTBT thin films with and without 1-chloronaphthalene in the casting solvent show similar scattering patterns.
Figure 5-5. Comparison of the morphology in the active layers of P3HT-b-PFTBT photovoltaic devices processed with 0% and 5% solvent additive using RSOXS. RSOXS data were integrated azimuthally and presented as (a) $I$ vs $q$ and (b) a Kratky plot of $I(q)q^2$ vs $q$, where $I(q)$ is the scattering intensity and $q$ is the scattering vector. Scattering data were acquired at the carbon absorption edge of 285.4 eV. Thin films of P3HT-b-PFTBT with 0% and 5% solvent additives were annealed at the optimal conditions (165 °C) for the device performance. Scattering profiles are offset for comparisons. A primary scattering peak, $q^*$, and its higher-order reflections are identified for optimized P3HT-b-PFTBT samples with different concentrations of solvent additive.

For block copolymer layers without the additive, a primary scattering peak at $q^* \approx 0.035$ Å$^{-1}$ and the second order reflection at $2q^*$ are evident. Higher order reflections are outside the $q$ range for our experiments. Such scattering patterns in transmission experiments indicate an in-plane lamellar microstructure with an average domain spacing of approximately 18 nm. Each domain is approximately 9 nm in size assuming a roughly symmetric composition of P3HT and PFTBT blocks. After the addition of 5% 1-chloronaphthalene to the casting solution, scattering data from the resulting films show a
broad primary scattering feature at a slightly lower $q$ (\(\sim 0.020\) to \(0.025\,\text{Å}^{-1}\)), suggesting an increase in the structural periodicity with the domain size $d$ of roughly 12-15 nm. The peak shift is clearly demonstrated in the Kratky plot ($Iq^2$ vs $q$) of RSOXS data as shown in Figure 5-5b. A third order lamellar peak is now within the $q$ range of our experiments and is visible at $3q^*$. The second order reflection is not apparent and maybe either enveloped into the broad initial peak or may be suppressed due to interference between form and structure factors of the lamellae, as is common in block copolymers with symmetric compositions\(^{25,26}\).

Thus, RSOXS data shown in Figure 5-5 suggest that P3HT-$b$-PFTBT with and without 1-chloronaphthalene in the casting solvent form in-plane lamellae with domain sizes of roughly 9-15 nm. We attribute the increased in the lamellar spacing after adding additives to the casting solution to swelling of domains by 1-chloronaphthalene during film deposition. Even if 1-chloronaphthalene leaves the film, it is not uncommon for block copolymers to be kinetically trapped at non-equilibrium domain sizes\(^{27-30}\). In most polymer semiconductors, excitons can only diffuse a short distance $l_D$ (\(~5-10\,\text{nm}\))\(^{31}\) during their lifetime. Hence, the size of the domains should ideally be within the length scale of $2l_D$ (\(~10-20\,\text{nm}\)) in order to maximize the number of excitons that can reach the interface and undergo dissociation. Thus, the domain size (\(~9\,\text{nm}\)) is not limiting for exciton dissociation in block copolymer films cast without 1-chloronapthalene, where donor/acceptor interfaces are always within the access range. When solvent additives are used, the slight increase in the lamellar domain size (\(~12-15\,\text{nm}\)) could prevent some excitons from reaching donor/acceptor interfaces. We estimate that at most 17-33\% of excitons could be lost due to the larger than optimal domain sizes, assuming a short
exciton diffusion length of 5 nm. In addition, we do not expect significant differences in
the charge transfer process near the donor/acceptor junction when tuning the crystalline
texture in the bulk domains. The relative orientation across donor and acceptor interfaces
in conjugated P3HT-b-PFTBT block copolymers should be independent of the crystallite
texture, as it is mainly governed by the block copolymer self-assembly. Therefore, the
self-assembled microstructure of P3HT-b-PFTBT block copolymers provides an ideal
model system to examine explicitly the impact of crystallite texturing on solar cell
performance.

5.2.3 Optimized Block Copolymer Photovoltaic Performance is Independent of the
Crystalline Texture in the Active Layer

![Figure 5-6](image.png)

Figure 5-6. Average current-voltage characteristics of optimized P3HT-b-PFTBT
photovoltaic devices processed with 0% and 5% solvent additive (a) under simulated one
sun illumination and (b) in the dark environment. Data were averaged over six devices.
P3HT-b-PFTBT solar cells with different concentrations of solvent additives are both
optimized at an annealing temperature of 165 °C. Devices were measured under
simulated AM 1.5G irradiation with intensity of 95 mW/cm².
Table 5-1. Device characteristics\textsuperscript{a} of optimized P3HT-\textit{b}-PFTBT block copolymer solar cells processed with 0\% and 5\% volume fraction of 1-chloronaphthalene.

<table>
<thead>
<tr>
<th></th>
<th>efficiency (%)</th>
<th>short-circuit current (mA/cm\textsuperscript{2})</th>
<th>open-circuit voltage (V)</th>
<th>fill factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% additive</td>
<td>2.3 ± 0.2</td>
<td>5.3 ± 0.3</td>
<td>1.11 ± 0.03</td>
<td>0.38 ± 0.01</td>
</tr>
<tr>
<td>5% additive</td>
<td>2.2 ± 0.1</td>
<td>5.0 ± 0.2</td>
<td>1.04 ± 0.03</td>
<td>0.40 ± 0.01</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Under simulated AM 1.5G irradiation with intensity of 95 mW/cm\textsuperscript{2}.

Average current-voltage (\textit{J}-\textit{V}) characteristics of P3HT-\textit{b}-PFTBT block copolymer solar cells with distinct molecular orientations are compared in Figure 5-6, under simulated one sun illumination (Figure 5-6a) as well as in the dark environment (Figure 5-6b). The block copolymer active layers were solution-processed with 0\% and 5\% 1-chloronaphthalene additives, respectively, in order to control the crystalline texture of P3HT domains to mostly face-on (0\% CN) or edge-on (5\% CN) orientations (Figure 5-3). All devices were fabricated in the same architecture as ITO/PEDOT:PSS (70 nm)/P3HT-\textit{b}-PFTBT (65-85 nm)/Al and optimized at an annealing temperature of 165 °C. Regardless of whether 1-chloronaphthalene is used in the casting solution, optimized P3HT-\textit{b}-PFTBT solar cells show similar photovoltaic responses under illumination (Figure 5-6a) and diode behaviors in the dark (Figure 5-6b). Some small differences are present at forward bias beyond \textit{V}_{oc}. The device characteristics of optimal solar cell devices are summarized in Table 5-1. In block copolymer devices with face-on P3HT crystals (0\% CN), an average power conversion efficiency (PCE) of 2.3 ± 0.2\% with short-circuit currents (\textit{J}_{sc}) of 5.3 ± 0.3 mA/cm\textsuperscript{2}, high open-circuit voltages (\textit{V}_{oc}) of 1.11 ± 0.03, and fill factors of 0.38 ± 0.01 are obtained. The measured device efficiency is
slightly lower than the record of 2.7 ± 0.4% we previously reported for P3HT-\textit{b}-PFTBT photovoltaics in Chapter 4. The performance difference is mainly attributed to variations in molecular weights and relative compositions of block copolymer materials synthesized from different batches. In this study, solar cell devices were fabricated using materials from the same batch for valid comparisons. Surprisingly, when the molecular packing in P3HT-\textit{b}-PFTBT active layers changes from largely face-on (0% CN) to edge-on (5% CN) orientations, device characteristics (Table 5-1) including efficiency, $J_{sc}$ and fill factor are similar within statistical errors, except for a slight drop in the average $V_{oc}$ by about 70 mV (within 7%) in devices with edge-on P3HT crystals. Therefore, we conclude that the optimal photovoltaic performance of P3HT-\textit{b}-PFTBT block copolymer solar cells remain invariant, regardless of the predominant crystalline orientation in the active layer.

5.2.4 Differences in Thickness Dependence of Block Copolymer Photovoltaic Performance at Various Processing Conditions

Although the difference in optimum performance is not statistically significant for devices made with and without 1-chloronaphthalene, the optimum active layer thicknesses to maximize P3HT-\textit{b}-PFTBT photovoltaic device performance does differ. Face-on (0% CN) block copolymer solar cells with an average PCE of 2.3 ± 0.2% are obtained using an active layer of about 65 nm. While a thicker film around 84 nm is needed to achieve similar efficiencies of 2.2 ± 0.1% for edge-on (5% CN) P3HT-\textit{b}-PFTBT devices. The absorption spectra of different block copolymer films are compared in Figure 5-7. As
expected, optimal devices fabricated from solutions containing 5% 1-chloronapthalene exhibit slightly higher absorptivity, because the block copolymer film is thicker. Integrating the absorptivity results with an AM 1.5G solar spectrum predicts a small increase of approximately 9% in the number of absorbed photons. Thus, the similar overall performance in optimized devices shown in Figure 5-6 suggests a slight drop in the internal quantum efficiency (IQE) for P3HT-\textit{b}-PFTBT solar cells with primarily edge-on textures (5% CN). This is consistent with excitonic losses due to the larger domain size (Figure 5-5) in block copolymer films after solvent additive treatment. Perhaps more photons are absorbed in the thick active layer of additive-processed block copolymer solar cells in order to compensate for carrier losses resulting from domain swelling with the solvent additive.

![Figure 5-7](image_url)

**Figure 5-7.** Comparison of UV-Visible absorptivity for P3HT-\textit{b}-PFTBT thin films processed with 0% and 5% CN additives. Both films were annealed at 165 °C to match the optimum conditions for the device performance. Absorptivity data of block copolymer films are calculated from the absorbance data measured from UV-Visible spectroscopy.
Moreover, it is interesting that P3HT-\textit{b}-PFTBT solar cells with mostly edge-on P3HT crystals (5% CN) in a thick active layer demonstrate a similar fill factor (Table 5-1) as that of devices with thinner active layers and mostly face-on P3HT textures (0% CN). We further investigated the dependence of block copolymer photovoltaic performance on the thickness of the active layer.

\textbf{Figure 5-8.} The thickness dependence of photovoltaic performance for P3HT-\textit{b}-PFTBT block copolymer solar cells processed with 0% and 5% solvent additives. (a) Fill factor, (b) open-circuit voltage, $V_{oc}$, (c) short-circuit current, $J_{sc}$, and (d) power conversion efficiency as a function of the active layer thicknesses. All devices were optimized at an annealing temperature of 165 °C. Device characteristics were measured under simulated AM 1.5G irradiation with intensity of 95 mW/cm$^2$. 
As shown in Figure 5-8a, fill factors decrease with increasing film thicknesses in devices fabricated with and without 1-chloronapthalene additives, suggesting that for thicker active layers performance is limited by charge transport. More importantly, within the same thickness range, block copolymer solar cells show a near 30% increase in fill factors when the P3HT crystallite orientation is changing from mainly face-on (0% CN) to edge-on (5% CN). Given that PFTBT domains remain amorphous, the change in fill factors is most likely a result of the change in orientation of P3HT crystals. Therefore, our devices with mostly edge-on crystallite orientations demonstrate more efficient charge extraction than our solar cells with mainly face-on crystallites, even though we expect faster charge transport along the π-stacking direction.

The dependence of the overall power conversion efficiency with active layer thicknesses is consistent with more efficient charge extraction from devices with predominantly edge-on P3HT crystallites (5% 1-chloronapthalene). We observe little changes (~10%) in open-circuit voltages ($V_{oc}$) with variations in the active layer thickness as shown in Figure 5-8b. Thus, changes in the device efficiency with the film thickness are mostly a result of the interplay between short-circuit currents ($J_{sc}$) and fill factors. For face-on (0% CN) P3HT-$b$-PFTBT cells, the short-circuit currents (Figure 5-8c) and device efficiencies (Figure 5-8d) increase initially with the active layer thickness likely due to improved light absorption. The efficiency peaks around 2.3% at a film thickness near 65 nm, where a maximum short-circuit current is also found. Beyond this optimum thickness, limitations in charge transport and charge collection, reflected in reduced fill factors (Figure 5-8a), lead to an immediate drop in both short-circuit currents and overall efficiencies. In the case of edge-on (5% CN) block copolymer solar cells,
however, device efficiencies continue to increase with increasing active layer thickness until about 84 nm. Consequently, enhanced charge extraction in block copolymer solar cells with predominantly edge-on crystals (5% CN) enables thicker active layers for efficient photovoltaic operation. In this way, more photons are absorbed to offset losses due to the larger domain size of films cast with 5% 1-chloronaphthalene as we have discussed previously. As a result, P3HT-b-PFTBT solar cells with mostly edge-on P3HT crystallites demonstrate similar photovoltaic performance of 2.2% as that of block copolymer devices with mostly face-on crystals.

Our findings contradict an established hypothesis in organic photovoltaics, that face-on orientations are important to improve vertical charge transport and extraction and thereby maximize overall device performance. We propose that the dominant orientation of crystallites, either face-on or edge-on, is not crucial for the bulk transport properties in organic solar cells. Instead, a complete picture of the distribution in crystallite orientations might be important for efficient device operation. In solar cells fabricated from 5% 1-chloronaphthalene solutions, P3HT crystals are predominantly edge-on but also have a wide distribution of orientations. As shown in the azimuthal distribution of the (100) intensities in Figure 5-4a, a single Gaussian-like distribution is present with a full width at half maximum (FWHM) near 20 degrees. The wide distribution of crystallite orientations in P3HT-based electronic devices is ubiquitous.22-24 A broad distribution of predominantly edge-on crystals but with gradually tilted crystallites could be sufficient to form interconnected pathways for charge transport throughout the active layer. A small deflection angle of 5 degrees for a two micrometer fiber (common for P3HT in polymer mixtures33) would provide a pathway for charges to vertically traverse
a film that is 170 nm thick. Our hypothesis that the broad distribution of crystallites leads
to percolating pathways is consistent with high fill factors of 0.6 and above obtained in
devices comprised of polymer/fullerene mixtures with preferential edge-on orientations. 23

For solar cells cast from solutions without solvent additives, a variety of possibilities
could explain why it appears that charge extraction is less efficient in our devices with
predominantly face-on P3HT crystallites (0% CN) in the active layer. 1-
chloronapthalene has been shown to increase the crystallinity of polymers, 8, 9 and as such,
devices cast from solutions containing 5% 1-chloronapthalene may have higher
 crystallinity and more efficient charge transport. However, because of the dramatic
change in crystalline orientations of P3HT-b-PFTBT films, comparison of the relative
crystallinity from rocking scans can be erroneous. In addition, devices without solvent
additive treatment (0% CN) exhibit a majority of face-on crystallites and a significant
amount of edge-on P3HT crystals, as reflected in the distinct dual populations near 0 and
90 degrees (Figure 5-4a). It is possible that a random arrangement of face-on and edge-
on orientations in the film may result in considerable grain boundaries with large
misorientations between neighboring crystallites, such that high-angle grain boundaries
serve as defects or barriers for transport. Further, the inter-crystalline connectivity plays
 a crucial role in transport in polymeric semiconductors. 34, 35 Thus, the distinct
populations of face-on and edge-on crystallites in films spun-cast without 1-
chloronaphthalene may either disrupt the formation of tie chains between crystallites or
transport through tie chains, thereby decreasing the charge mobility within the P3HT
domains.
5.3 Conclusions

In conclusion, we have investigated the role of crystalline orientations in organic photovoltaics using a crystalline-amorphous block copolymer P3HT-b-PFTBT as a model system. We control the orientation of P3HT crystals from mostly face-on to edge-on packing through the application of 1-chloronaphthalene as a solvent additive. Meanwhile, the self-assembled microstructures of block copolymer films remain largely invariant regardless of the addition of 1-chloronaphthalene. With separate control of chain orientation and the active layer morphology, we are able to examine the role of crystallite texturing on photovoltaic device performance. We find that the optimum performance of P3HT-b-PFTBT solar cells is independent of the predominant crystalline texture adopted in the active layer. Our results suggest that face-on crystallite orientations are not critical for photovoltaic applications. Instead, we propose that proper control of the distribution of crystallite orientations and inter-crystal connections may be important for optimizing charge transport and photovoltaic device operation.

5.4 Materials and Methods

P3HT-b-PFTBT block copolymers were synthesized using a procedure similar to that previously described in Chapter 4, Section 4.4.

Photovoltaic devices were prepared with the conventional architecture of ITO/PEDOT:PSS (70 nm)/active layer (65-85 nm)/Al (75 nm). ITO-coated glass substrates (20 ohm/sq, Xin Yan Technology, Hong Kong) were cleaned by soap, followed by 20 min of sonication in acetone, then isopropanol, and finally 15 min of
ultraviolet light ozonation. Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), PEDOT:PSS (Clevios P, Heraeus), was spin-coated on top of ITO at 4000 rpm for 2 min yielding a thickness of about 70 nm. The PEDOT:PSS/ITO substrates were dried for 10 min at 165 °C in air and then transferred to a nitrogen-filled glovebox. Solutions of P3HT-b-PFTBT (5 mg/ml) were made with anhydrous chloroform (≥ 99%, amylenes as stabilizer, Sigma-Aldrich) and stirred at 95 °C for about 20 hrs in a tightly sealed container in the N₂ glovebox. Solutions were filtrated with a 0.2 µm filter and stirred for another 2 hrs at 95 °C prior to casting. The active layers of P3HT-b-PFTBT devices were spin-cast onto PEDOT:PSS layers from prepared hot solutions (95 °C) at various spin speeds for 1 min to yield thicknesses around 65-85 nm. The film thicknesses were determined on a TENCOR P-10 surface profiler. Samples were then transferred immediately onto a calibrated digital hot plate at 165 °C and dried for 5 min. The devices were completed by vacuum thermal evaporation of 75 nm aluminum at 10⁻⁶ torr on top of the active layer through a shadow mask. The device area is 16.2 mm². Integrated solar cells were further annealed at 165 °C for various annealing times until the maximum device performance was recorded.

Photovoltaic measurements were performed in a N₂-filled atmosphere under simulated AM 1.5G illumination (95 mW/cm²) from a xenon lamp solar simulator (Newport Model SP92250A-1000). The illumination intensity was calibrated using an optical power meter and NREL certified Si reference photocell (Newport). A Keithley 2636A Sourcemeter was used to measure the current-voltage characteristics of solar cells. The absorption spectra of films were measured using an ultraviolet/visible/near-infrared spectrophotometer (Beckman DU Series 500).
Samples for RSOXS and GIWAXS measurements were prepared on PEDOT:PSS/Si substrates in the same manner as for device fabrication. For RSOXS experiments, as-cast films were floated-off in deionized water and picked up with 5 mm × 5 mm silicon frames supporting a 1 mm × 1 mm, 100 nm thick Si$_3$N$_4$ window. Samples were then dried for 24 hrs at room temperature under vacuum and subsequently annealed on a hot plate in the N$_2$ glovebox.

RSOXS measurements were carried out at beam line 11.0.1.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory. Scattering was performed in the transmission geometry in vacuum at X-ray energies at the carbon absorption edge (285.4 eV) with linearly polarized X-rays. Data were corrected for dark currents and azimuthally integrated.

GIWAXS measurements were carried out at Beamline 8-ID-E of the Advanced Photon Source, Argonne National Laboratory ($\lambda = 1.6868$ Å). Scattering data were acquired at an incident angle of 0.2°. Data are corrected for X-ray polarization, detector sensitivity and geometrical solid-angle. GIWAXS intensities are integrated over a $q$ window of ± 0.06 Å$^{-1}$ around the (100) peak at 0.36 Å$^{-1}$ and ± 0.10 Å$^{-1}$ range around the (010) reflection at 1.65 Å$^{-1}$. A linear background was subtracted from the integrated data, respectively, using intensities away from the Bragg peak of interest.
5.5 References


Improving the performance of organic photovoltaic devices depends on exploiting and understanding the complex nanostructures formed in the photoactive layer. Current imaging methods based on energy-filtered transmission electron microscopy (EFTEM), however, provides limited chemical sensitivity to organic materials and thus is not applicable for compositionally similar phases or complicated multicomponent systems. Here we introduce a novel contrast generation mechanism in monochromated EFTEM imaging at low energy-loss range to characterize the structure formation in organic thin films. At low-loss regions of electron energy-loss spectrum, electronic fingerprints that correspond to inter-band excitations in organic semiconductors can be utilized to generate significant spectral contrast between phases. Based on differences in chemical bonding of organic materials, high-contrast micrographs are obtained to reveal the phase separation of polymer/fullerene mixtures. Through principle component analysis of the spectroscopic image series, further details about phase compositions and local electronic transitions in the active layer of organic solar cells are probed.
6.1 Introduction

Solution-processable organic semiconductors have emerged as a promising alternative to inorganic materials in solar cell applications.1-3 In recent years, power conversion efficiencies (PCEs) of organic solar cells have improved rapidly with increasing efforts on design of high-performance materials4, 5 and optimization of the active layer morphology.6-8 Efficient organic photovoltaics (OPVs) rely on mesoscale phase separation of electron donor and electron acceptor materials to create a large interfacial area for charge photogeneration and a interpenetrating network of bicontinuous phases for charge transport.9-11 An extensively studied model system is blends of poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). Optimization of the nanostructure in P3HT/PCBM mixtures has been implemented through a variety of processing approaches,7, 12-14 resulting in greatly enhanced device performance with an PCE over 4%.14 To further improve the device performance, a better understanding of the processing-structure-property relationship is essential. Therefore, efforts in developing efficient organic solar cells must confront the challenge in characterizing the complex morphology formed in these organic functional layers.

Techniques to analyze the phase separation in organic thin films are currently lacking. Transmission electron microscopy (TEM) is often used to probe the volume-averaged structural information about the in-plane morphology of thin films.14-17 Nevertheless, organic phases that comprise the photoactive layer show inherently low contrast in typical bright-field (BF) TEM images due to their similarities in mass densities. Several reports have applied TEM imaging with a defocused objective lens to enhance phase
Strong defocus, however, degrades the intrinsic spatial resolution in the TEM, and thus obscures structural details at smaller length scales especially in poorly-ordered systems. In addition, the origin of visible contrast in BF images is not clear. It is thus difficult to distinguish domains that correspond to distinct material compositions in the nanoscale network.

Spectroscopic imaging through Energy-filtered TEM (EFTEM) provides an alternative mechanism for contrast generation between organic materials by imaging with inelastically scattered electrons. With in-focus EFTEM imaging, the image contrast originates from the intrinsic differences in chemistry or electronic structures between organic phases. For example, energy-filtered imaging at ionization edges (100-300 eV) characteristic of the constituent atoms in organic materials can map the elemental distributions in different phases. Kozub et al. have examined the morphological evolution in P3HT/PCBM mixtures via core-loss elemental mapping. Given the large differences in sulfur and carbon densities between materials, high-contrast EFTEM images have visualized the formation of P3HT fibers and structure coarsening in blend films during thermal annealing process. Recent work by Herzing et al. and Drummy et al. also reports on spectral imaging at plasmon loss energies (~ 20-30 eV) to characterize the nanostructure in P3HT/PCBM blend films. Discriminating plasmon peaks resulting from differences in electronic structures between organic materials provide complementary material contrast to image the fibrillar network in P3HT/PCBM mixtures. However, plasmon resonances are spectrally broad, and often overlap or vary little between different organic materials. Also, elemental mapping is only effective when there are significant differences in elemental compositions between the materials. As a
result, spectral imaging based on inner shell ionizations or plasmon loss excitations is still limited for compositionally similar phases or complex multicomponent systems.

In this chapter, we present a novel contrast mechanism in EFTEM imaging with high chemical sensitivity to characterize the structure formation in the active layer of organic solar cells. Using high-resolution electron energy-loss spectroscopy (EELS), characteristic inter-band transitions of organic semiconductors can be identified at low electron energy-loss regions. Significant material contrast can thus be derived from spectral differences of band excitations and enable chemical imaging of organic materials. We demonstrate the application of low-loss EFTEM imaging to characterize the phase separation of widely studied P3HT/PCBM mixtures as a model system. By applying principle component analysis of the acquired EFTEM image series, we identify different phases that can be attributed to distinctive material compositions.

6.2 Results and Discussions


Measurements of electron energy-loss spectroscopy (EELS) examine the transfer of energy between a high-energy (i.e. 100 or 200 keV) incident beam and materials. In principle, EELS can be used to measure the available excitations, or electronic density of states, of semiconductors by measuring energy losses near the band gap.\textsuperscript{24, 25} Unfortunately, the spread in energy of the incident electron beam, near 1 eV for field emission sources, creates a large background which makes the extraction of the electron
absorption spectra challenging. However, with the development of monochromatic sources, which can achieve energy dispersions of approximately 0.1 eV, the study of electronic absorption spectra for low band-gap semiconductor materials through EELS becomes possible.

Figure 6-1. (a) Raw electron energy-loss spectra (EELS) with zero-loss peaks (ZLPs) of rr-P3HT, PCBM, and PGeBTBT neat films at low energy-loss regions. rr-P3HT films were annealed at 150 °C for 12 hrs to highlight crystalline properties. The upturn at low energy losses (< 2.5 eV) is due to the energy spread of the incident beam. Distinct spectral features down to 1.5 eV can be identified from ZLPs. (b) ZLP-subtracted EELS spectra of rr-P3HT, PCBM and PGeBTBT neat films. EELS data are normalized by the incident intensity and the film thickness accordingly, and scaled with the maximum intensity of the PGeBTBT spectrum for comparison.
For example, we can utilize a monochromated TEM to examine the electron absorption spectra (low-loss EELS) of organic photovoltaic materials as shown in Figure 6-1a. The small energy spread of the incident beam leads to clear peaks corresponding to π-π* transitions in the raw data, such that subtraction of the elastic background is unambiguous. The background due to the zero-loss peak is modeled as a third-order power law and subtracted from the EELS data as presented in Figure 6-1b. Data in Figure 6-1b are normalized by the incident intensity and the film thickness accordingly, and scaled with the maximum intensity of the PGeBTBT spectrum for comparison.

We can identify specific features associated with the optoelectronic properties, such as the band-gap of regioregular poly(3-hexylthiophene-2,5-diyl) (rr-P3HT, 1.7 eV), [6,6]-phenyl-C61-butyric acid methyl ester (PCBM, 2.0 eV), and poly[(4,4’-bis(2-ethylhexyl)dithieno[3,2-b:2’,3’-d]germole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl] (PGeBTBT, 1.3 eV) from the low-loss EELS data in Figure 6-1b. The absorption edges in electron energy-loss spectra are consistent with the band-gap energies deduced from UV-Visible absorption data for organic materials discussed here (Figure B-1, Supporting Information in Appendix B). Furthermore, observed electronic states can be attributed to inter-band transitions of organic semiconductors, and compared to peaks measured in optical absorption experiments. For example, the π to π* transition in P3HT occurs around 2.6 eV, while multiple fine structures of the π to π* absorption in PCBM are found at 3.7, 4.8 and 6.5 eV. For PGeBTBT samples, spectral transitions down to 1.7 (a small shoulder) and 1.9 eV are also identified. The EELS spectra are similar to UV-Visible spectra, with the exception of a blue shift in the EELS data of 0 to 0.25 eV (Figure B-1 and Table B-1, Supporting Information in Appendix B). Although this could
partly be a result of the spectral changes caused by electron beam damage, we show below that it cannot fully explain the discrepancy between the EELS and UV-vis spectra. Nevertheless, characteristic electronic features resulting from band transitions at low energy-loss regions can be used as unique spectral signatures of materials, and thus provide a mechanism to generate imaging contrast for structural characterization in thin films of organic materials, as we will show.

6.2.2 Degradation of Electronic Structures in Organic Materials upon Electron Radiation

The electronic structure of organic materials becomes degraded upon electron radiation, which inevitably gives rise to changes in spectral responses and the material contrast.\textsuperscript{25-27} To investigate this, electron energy-loss spectra measured under various exposure doses for rr-P3HT, PCBM and PGeBTBT neat films are shown in Figure 6-2 a-c, respectively. Decreases in peak intensities with increasing electron dose are observed for all samples in the low electron energy-loss range. In addition, rr-P3HT and PGeBTBT exhibit a blue shift of spectral peaks towards higher energies with increasing beam damage, while the spectral features in PCBM remain the same energies.

To quantitatively describe the effect of electron beam damage, the EELS intensities in the low-loss range have been integrated and are presented as a function of electron dose for various organic materials. The integration is performed up to 4 eV for rr-P3HT (Figure 6-2d), 8.5 eV for PCBM (Figure 6-2e), and 2.6 eV for PGeBTBT (Figure 6-2f), i.e. in energy ranges where degradation of spectral features is evident. The peak
positions for rr-P3HT have been extracted from Gaussian fits to the EELS spectra and are added to Figure 6-2d. Whereas broadening of spectral features in PGeBTBT samples gives rise to the challenge in extracting the peak positions. While for PCBM an exponential decay of integrated EELS intensities is observed (Figure 6-2e), for rr-P3HT (Figure 6-2d), the integrated intensities initially decay exponentially and then level off after a dose of about 4000 electron/nm². For increasing electron dose, the \( \pi \) to \( \pi^* \) transition of rr-P3HT gradually shifts from 2.6 eV to around 3.2 eV, which is similar to the band transition energy observed in amorphous regiorandom P3HT (rra-P3HT) (Figure B-1b and Figure B-2 c-d, Supporting Information in Appendix B). We hypothesize that the initial spectral degradation is primarily attributed to the rapid destruction of long range order in crystalline rr-P3HT, after which the sample temporarily stabilizes in the amorphous state before further degradation at higher electron doses. We extrapolate that the electronic absorption peak for rr-P3HT at zero electron dose is 2.54 eV. Compared to the absorption feature at 2.37 eV measured in optical experiments (Figure B-1 and Table B-1, Supporting Information in Appendix B), a blue shift of 0.17 eV in extrapolated zero-dose EELS peak is found. We surmise that this offset reflects a fundamental difference between photon- and electron-induced excitation mechanisms.
Figure 6-2. EELS data at various radiation exposures and integrated EELS intensities at low energy-loss regions as a function of electron dose for (a, d) rr-P3HT, (b, e) PCBM, and (c, f) PGeBTBT neat films. EELS Data of different materials were measured from the same sample area. ZLP-subtracted EELS intensities are integrated up to 4 eV for rr-P3HT, 8.5 eV for PCBM, and 2.6 eV for PGeBTBT. The solid lines represent data fits to an exponential decay. The peak positions of rr-P3HT are extracted from Gaussian fits to EELS spectra and plotted versus electron dose in (d).
By fitting exponential decay curves to the integrated EELS intensities (solid lines in Figure 6-2 d-f), the corresponding decay rate, $\lambda$, can be extracted. The maximum acceptable dose, $D_c$, in units of electron/nm$^2$ defined as $1/\lambda$ can then be calculated, and is a measure of the sensitivity of materials to electron radiation.\textsuperscript{25} In Table 6-1 the decay rates and critical doses for various organic semiconductors calculated from the degradation of low-loss spectral features are summarized. The critical doses for crystalline rr-P3HT and PCBM are determined to be approximately 3,600 and 83,000 electron/nm$^2$, respectively. PCBM is significantly more stable under irradiation than rr-P3HT, likely due to the stable $\pi$-electron system in spherical fullerenes and the lack of C-H bonds.\textsuperscript{26} These critical doses indicating the material radiation sensitivity help to determine an optimum acquisition scheme to minimize the beam damage effect on high-contrast imaging.

**Table 6-1.** Summary of decay rates and critical doses for EELS degradation of various organic semiconductors at the low-loss range.

<table>
<thead>
<tr>
<th></th>
<th>rr-P3HT</th>
<th>rra-P3HT</th>
<th>PCBM</th>
<th>PGeBTBT</th>
</tr>
</thead>
<tbody>
<tr>
<td>decay rate $\lambda$ (nm$^2$/e$^-$)</td>
<td>overall 0.00028</td>
<td>subtracted 0.00059</td>
<td>0.00036</td>
<td>0.000012</td>
</tr>
<tr>
<td>critical dose $D_c$ (e$^-$/nm$^2$)</td>
<td>3600</td>
<td>1700</td>
<td>2800</td>
<td>83000</td>
</tr>
</tbody>
</table>
6.2.3 Low Energy-loss Spectral Imaging of P3HT/PCBM Mixtures

Energy-filtered TEM micrographs from low-loss spectrum-imaging of P3HT/PCBM mixtures (weight ratio of 1:1) are shown in Figure 6-3. We acquired a series of spectral images across the low-loss range between 3 and 8 eV with an energy step size of 0.5 eV. Given that the electronic features of rr-P3HT (between 2 and 3.5 eV) degrade relatively rapidly compared to those of PCBM (which are found between 3.5 and 8 eV) as shown in Figure 6-2, the EFTEM image series were acquired in the direction of increasing energy-loss. In this way, the impact of beam damage on spectrum imaging is minimized. These radiation damage effects are investigated in more details below. EFTEM slices at 3, 4, 5 and 6 eV are selected from the image data set and shown in Figure 6-3 a-d. We note that the spectrum imaging below 3 eV was strongly affected by the tail of the zero-loss peak. Hence in the following we focus on the analysis of the data acquired at energy losses of 3 eV and higher.

The EFTEM slices at 3 and 4 eV shown in Figure 6-3 a-b reveal elongated fibers distributed within a matrix. At 5 eV the fibrous structures are less apparent, and vanish at 6 eV where PCBM exhibits strong absorption. We speculate that P3HT dominates inelastic scattering intensities at low energy losses, such that the contrast between P3HT and PCBM diminishes when the electron absorption increases in PCBM but decreases in P3HT at higher energies (between 4-6 eV) as shown in Figure 6-1. Hence we assign the bright fibers to P3HT domains, while the dark regions correspond to PCBM (or PCBM-rich) domains. This morphology is consistent with the sulfur map shown in Figure B-3 of the Supporting Information in Appendix B or Figure 3-4 in Chapter 3, and previously reported elemental maps.21 Nevertheless, the intensity of elemental maps is limited by
the low cross section of inelastic electron scattering at ionization edges of constituent atoms in organic materials. Long exposure time typically beyond 1 min is necessary to collect enough signals. As a result, beam damage and significant sample drift during the image acquisition could obscure the material contrast. Low energy-loss EFTEM imaging, in contrast, provides enhanced electron scattering intensities within short exposure time (15 s) to reduce the exposure dose and sample drift for acquisition of high-contrast micrographs.

![Figure 6-3.](image)

Figure 6-3. Low energy-loss energy-filtered imaging of a P3HT/PCBM blend with a 1:1 weight ratio annealed at 190 °C for 30 min at (a-d) 3, 4, 5, and 6 eV with the slit width of 1.5 eV. Scale bar is 100 nm.
The phase compositions and local electronic transitions in P3HT/PCBM mixtures can be probed further by performing statistical analysis on the low-loss spectrum-images acquired. A spectrum-image dataset is effectively a 3D data cube with two spatial axes and an energy axis, since it is composed of a series of EFTEM images acquired at consecutive energy-losses. Thus for each pixel in the image an energy spectrum has been collected and as such the dataset contains a large amount of information requiring an efficient method of analysis. A convenient method for the analysis of spectrum-image datasets is the multivariate statistical technique known as principal component analysis (PCA).\(^{20}\) PCA allows one to identify the various elemental/chemical/electronic phases in the specimen as well as the random noise components in the dataset, which can then be subtracted out before further analysis is performed.

**Figure 6-4.** Component energy-loss spectra corresponding to P3HT- and PCBM-rich domains extracted from the spectral image series for P3HT/PCBM blend films annealed at 190 °C for 30 min. (a) Energy-filtered TEM image at 4 eV for P3HT/PCBM mixtures presenting bright fibers and a dark matrix. Scale bar is 100 nm. (b) Component spectra 1 and 2 that correspond to fibrous and matrix phases, respectively. Spectral data were extracted from the acquired EFTEM image stack from 3 to 8 eV. Spectral intensities are normalized to 1.
Performing PCA on the low-loss spectrum-image dataset for the P3HT/PCBM blend, we are able to distinguish the two polymer phases present based on differences in their low-loss spectral signatures, as shown in Figure 6-4. Comparing with the EELS spectra of Figure 6-1, where we see that P3HT exhibits stronger inelastic scattering at lower energies compared to PCBM, we assign the spectral signature extracted for the fibrous structures to P3HT-rich domains and the matrix to PCBM-rich domains as indicated in Figure 6-4b. The energy-loss spectrum extracted for each phase can then be used for multiple linear least-squared fitting to the noise-reduced spectrum-image dataset to generate chemical maps showing the distributions of P3HT- and PCBM-rich domains in the blend. These phase maps are shown in Figure 6-5 a-b, and the composite two-phase chemical map presenting P3HT-rich domains in red and PCBM-rich domains in green is shown in Figure 6-5c.

Figure 6-5. (a-b) Phase maps deconvoluted through principle component analysis for P3HT/PCBM blends annealed at 190 °C for 30 min. Phase maps (a) and (b) illustrate spatial distributions of the component spectra 1 and 2 in Figure 6-4b, respectively. Image (a) highlights P3HT fibers in bright regions, while image (b) shows inverted contrast with bright areas corresponding to PCBM-rich domains. (c) Composite image created by combining component images (a) and (b), demonstrating P3HT fibers (red) and a PCBM-rich matrix (green). Scale bar is 100 nm.
We note that the differences between the low-loss spectra extracted from the spectrum-image dataset for the P3HT- and PCBM-rich phases (Figure 6-4b) are less prominent than those revealed in the EELS acquisitions of reference homopolymer samples (Figure 6-1). In the spectrum-imaging case, the spectral resolution is defined by the slit width selected for the acquisition (1.5 eV), whereas for the EELS acquisition the resolution is much better as defined by the monochromator settings (0.1–0.15 eV). Therefore, it is expected that the spectra extracted from the spectrum image will be more smeared out. However, beam damage and the presence of mixed phases will also play a role. For the EFTEM images shown in Figure 6-3, a cumulative dose of about 4x10^3 electron/nm^2 was required to image up to 4 eV, while imaging up to 6 eV would have accumulated a dose over 10^4 electron/nm^2. Thus while the does is well below the critical dose for PCBM, it is close to the critical level for rr-P3HT degradation (Table 6-1). Moreover, our previous work in Chapter 3 has indicated that the PCBM-rich matrix contains a significant amount of P3HT (43% volume fraction). Therefore the spectrum extracted for the matrix phase from the spectrum-image contains contributions from both P3HT and PCBM.

We have thus demonstrated that phase separation in P3HT/PCBM mixtures can be mapped based on differences in electronic band structures using low-loss EFTEM-imaging near the band-gap energies of organic materials. Previous efforts have focused on bulk-plasmon energy-loss imaging to characterize the structure formation in thin films of polymer blends based on differences in valence electron configurations.\textsuperscript{20, 22} For polymer/fullerene mixtures, the bulk-plasmon resonances for P3HT and PCBM have peak maxima at ~ 21.5 and 25 eV, respectively, and can thus be conveniently used to generate contrast between the polymer phases by performing spectral imaging in the
range of ~18 to 30 eV.\textsuperscript{28} However, since the bulk-plasmon resonances of organic materials are inherently broad, the chemical sensitivity of plasmon-loss imaging is limited, impeding the application of this technique for multicomponent systems that have similar plasmon features. In addition, elemental mapping is not applicable for systems that do not possess strong elemental contrast. Therefore, low electron energy-loss EFTEM imaging, which generates material contrast from the differences in electron absorption near 2 eV presents a much-needed alternative phase-mapping approach.

6.3 Conclusions

In conclusion, we have demonstrated the application of EFTEM imaging at low energy-loss ranges that correspond to inter-band transitions of organic semiconductors to characterize the structure formation in the active layer of organic solar cells. Electronic fingerprints resulting from band excitations reflect distinct chemical structures of organic materials, and thus provide high contrast in low-loss image series. Through optimization of the data acquisition conditions, significant spectral differences can be used to distinguish compositionally similar organic phases. In addition, the energy-filtered image series acquired across the low-loss spectral range enables direct extraction of local electronic states in organic films and validates the use of multivariate statistical methods for composition analysis. In this work, we have demonstrated the applicability of this low-loss EFTEM spectrum-imaging technique by using it to map the constituent phases of a two-phase P3HT/PCBM mixture, revealing P3HT fibers distributed in a PCBM-rich matrix. More importantly, the low electron energy-loss EFTEM technique presented here
is extendable to various combinations of organic materials or complicated multicomponent systems, in which differences in electronic band structures between each of the multiple components are present.

6.4 Materials and Methods

Solutions of regioregular P3HT (96 % H-T regioregular, $M_n = 26$ kg/mol, polydispersity = 2.0, Merck) and PCBM (>99.5%, Nano-C) with a 1:1 weight ratio were made with anhydrous chlorobenzene (Sigma-Aldrich) in a nitrogen-filled glovebox. Solutions were stirred for a minimum of 10 hrs and heated to 90 °C for 10 seconds prior to use to ensure dissolution.

For transmission electron microscopy (TEM) experiments, thin films (70 ± 10 nm thickness) of P3HT/PCBM blends were spin-cast from 15 mg/mL solutions onto poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), PEDOT:PSS, (Clevios P, H.C. Starck) films (~65 nm) deposited on silicon wafers. Silicon wafers were cleaned through sonication for 20 min in acetone and then in isopropanol for 20 min followed by 10 min of ultraviolet light ozonation. Film deposition was done in the N$_2$ glovebox. The film thicknesses were determined on a TENCOR P-10 surface profiler. As-cast films were floated-off in deionized water in the air and picked up with copper TEM grids. Samples were then dried for 24 hrs at room temperature under vacuum and subsequently annealed at 190 °C for 30 min on a calibrated digital hot plate in the N$_2$ glovebox.

Energy-filtered TEM experiments were performed at the National Center for Electron Microscopy, Lawrence Berkeley National Laboratory on the TEAM 0.5 STEM/TEM
operating at 80 kV, and equipped with a gun monochromator and a high-resolution GIF Tridiem energy-filter. High-resolution (~ 0.1-0.15 eV) EELS data were carried out in the spectroscopy mode with a total electron dose controlled below 300 electron/nm². The incident electron dose was estimated at vacuum regions outside the sample area. Experiments of EELS degradation were measured at the same sample spot under various exposure times to electron irradiation. Energy-filtered imaging was performed at focus, which was adjusted on an adjacent area several µm away from the imaged area. EFTEM spectral imaging was performed using an energy slit width of 1.5 eV for signal collection and an energy increment step of 0.5 eV. A series of spectral images were acquired across the low energy-loss regions from 3-8 eV with exposure time of 15 s for P3HT/PCBM samples. Data acquisition was conducted from low-high energy-losses in order to minimize the effect of spectral degradation upon electron irradiation. Zero-loss images, core-loss elemental maps at carbon and sulfur absorption edges, and thickness maps were also captured from the same sample area after low-loss spectral imaging. The electron dose conditions for spectral imaging are estimated from unfiltered images acquired for generation of thickness maps.

6.5 References


Chapter 7. Summary and Future Outlook

7.1 Summary

The key to high-performance organic solar cells lies in the development of novel strategies for structural control in the photoactive layer to create a large interfacial area for charge photogeneration and networks of bicontinuous phases for charge transport. A prerequisite for such full control over morphology is to establish effective characterization techniques to analyze the complex nanostructure formed in these organic functional layers.

Resonant soft X-ray scattering (RSOXS) is a powerful tool for characterizing the structure formation in polymer thin films with little mass contrast or complicated multiphase systems. The strong resonant absorption of organic materials in the soft X-ray regime enables RSOXS to provide high material contrast with elemental selectivity and chemical sensitivity. We examine the structural evolution in commonly studied poly(3-hexylthiophene-2,5-diyl) (P3HT) and phenyl-C_{61}-butyric acid methyl ester (PCBM) mixtures by tuning the X-rays to resonant absorption energies of constituent carbon and oxygen atoms. Our studies reveal that the energy dependence of RSOXS scattering profiles indicates the multiphase formation in P3HT/PCBM mixtures, which is consistent with the domain composition analysis of elemental maps obtained through energy-filtered transmission electron microscopy (EFTEM). Using P3HT/PCBM mixtures as a model system, we demonstrate that the energy tuning in RSOXS is able to modulate the scattering contrast between multiple phases, and thus probe structure information about different domains formed in the active layer of organic solar cells.
Complementary to reciprocal space methods, direct imaging in transmission electron microscopy (TEM) is often used to qualitatively characterize the in-plane film morphology, but is not applicable for compositionally similar phases in organic systems. We introduce a novel contrast generation mechanism in energy-filtered TEM imaging to characterize the nanostructure in organic thin films with greatly enhanced chemical sensitivity. Through analyzing high-resolution electron energy-loss spectroscopy (EELS), electronic fingerprints that correspond to characteristic inter-band transitions of different organic materials are identified at low energy-loss ranges. Significant material contrast is derived from intrinsic differences in optoelectronic properties and enables chemical imaging of organic materials. We demonstrate the application of low-loss EFTEM imaging to characterize the phase separation of P3HT/PCBM mixtures as a model system. Considering spectral contrast between materials and spectral degradation upon electron radiation, an optimal scheme is determined for acquisition of high-contrast EFTEM images. Through a principle component analysis of the acquired EFTEM image set, we identify a two-phase system composed of P3HT fibers distributed in a PCBM-rich matrix, which is in agreement with previous composition analysis through elemental mapping at core-loss edges of constituent atoms.

Combining RSOXS and low-loss EFTEM imaging allows us to build up a better understanding of structure-property relationships to guide further efforts in developing high-performance organic photovoltaics. State-of-the-art organic solar cells rely on kinetically-trapped, partially phase-separated structures of electron donor and acceptor mixtures, but suffer from structural disorder at interfaces of different organic materials, and morphological instability and degradation. Here we demonstrate that microphase-
separated block copolymers can address many of the current challenges in morphology and interfacial structure control for efficient photovoltaic operation. We design and synthesize a fully conjugated donor-acceptor block copolymer P3HT-\textit{b}-PFTBT, which incorporates the electronic functionalities with self-assembly properties. When utilized as the active layer of photovoltaic cells, P3HT-\textit{b}-PFTBT block copolymer devices show significantly improved photoconversion efficiencies and thermal stabilities, well beyond devices comprised of P3HT/PFTBT polymer blends. Without the use of fullerene derivatives, we obtain efficiencies near 3\% with remarkable open-circuit voltages of 1.2 V from single-component block copolymer solar cells. Morphological characterization from RSOXS reveals that the remarkable performance of P3HT-\textit{b}-PFTBT devices is due to self-assembly into nanoscale in-plane lamellar morphology, which not only establishes an equilibrium microstructure amenable for exciton dissociation but also provides pathways for efficient charge transport to the corresponding electrodes. In addition, the photovoltaic performance improves when the active layer is composed of block copolymers instead of polymer blends even when the morphology is roughly invariant between the two systems, suggesting that covalent control of donor-acceptor heterojunctions in the block copolymer architecture is a potential route to promote charge separation at interfaces and optimize the photoconversion process.

With well-controlled lamellar morphology and covalently linked donor-acceptor interfaces, P3HT-\textit{b}-PFTBT block copolymer solar cells serve as an excellent model to exclusively study the effect of molecular packing in the active layer on charge transport properties and photovoltaic performance. Through solvent additive processing, a texture change from mostly face-on to edge-on orientations is induced in the crystalline P3HT
domains, while PFTBT domains remain amorphous. Surprisingly, we find that such a dramatic change in crystalline orientations results in very similar device performance of optimized P3HT-b-PFTBT solar cells. Our results provide further insights into the molecular organization required for efficient charge transport and overall device efficiencies. That is, the dominant crystal orientation, whether face-on or edge-on, is not critical to organic solar cells. Instead, a proper control of orientation distributions allowing inter-crystallite connections might be important for optimizing charge transport and photovoltaic device operation.

In general, we demonstrate that conjugated block copolymers represent a paradigm shift for morphology and interfacial structure control in the photovoltaic active layer, and are a promising building block for next-generation high-performing organic solar cells.

7.2 Further Optimization of Block Copolymer Solar Cells

7.2.1 Development of Long-range Order in Self-assembly Structures of Block Copolymer Thin Films

Broadening of the primary peak and the weak higher order peaks in RSOXS data of P3HT-b-PFTBT thin films (Chapter 4 Section 4.2.2) suggest the formation of a defective in-plane lamellar morphology in the active layer of block copolymer solar cells. As illustrated in Figure 7-1, the lack of long-range order implies the presence of a large amount of disordered regions with poorly-defined interfaces, which could facilitate recombination of charges and impair charge extraction in solar cell operation. Therefore, we speculate that further improvement of conjugated block copolymer
photovoltaics, beyond the 3% efficiency record, is possible by reducing structural disorder during the self-assembly process.

![Figure 7-1](image)

**Figure 7-1.** Schematics of short-range (left) and long-range (right) order formation in block copolymer thin films. Self-assembled block copolymers with short-range order implies a large amount of structural disorder with poorly-defined interfaces. Block copolymer thin films with long-range order present less disorder and sharper interfaces.

Alignment of block copolymers towards long-range order has been reported through the use of external fields.\(^1\)\(^-\)\(^5\) For example, electric fields have been used to orient nanoscale lamellar or cylindrical domains in coil-coil block copolymer films.\(^1\)\(^-\)\(^3\) For systems that contain two blocks with different dielectric constants, the electric field couples to the anisotropic shape of lamellar or cylindrical microdomains and induces orientation of the internal interfaces parallel to the field direction.\(^1\)\(^,\)\(^3\)\(^,\)\(^4\) As shown in Figure 7-2, using polystyrene-\textit{block}-poly(methyl methacrylate) (PS-\textit{b}-PMMA) diblock copolymers as a test bed, the formed lamellar plane (Panel a) or cylindrical (Panel b) axis is well aligned along the applied electric field direction.
Figure 7-2. (a) TEM image of an polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) diblock copolymer samples after electric field alignment.\textsuperscript{1} The lamellar slice is parallel with the applied electric field, $E_0$, in the film plane. (b) Cross-sectional TEM image of 700 nm thick PS-b-PMMA films after annealing at 185 ± 5 °C under a $\sim$40 V/µm electric field for 16 hrs. Scale bar is 100 nm.\textsuperscript{2} A vertically oriented cylindrical structure is aligned along the applied field direction.

Recent efforts have also demonstrated magnetic field induced alignment of microphase-separated block copolymers containing liquid crystalline or semicrystalline components.\textsuperscript{4, 5} Structure alignment in this case is caused by the anisotropic molecular structure in liquid crystalline phases or polymer crystals, which gives rise to the orientation-dependent susceptibility to the external magnetic field.\textsuperscript{4} Figure 7-3 shows an example of magnetic field alignment on lithium ion conducting Poly(ethylene oxide-block-6-(4'-cyanobiphenyl-4-yl-oxy)-hexyl methacrylate) (PEO-b-PMA/CB) block copolymer membranes.\textsuperscript{5} The smectic phase formed by cyanobiphenyl mesogen induces anisotropic diamagnetic susceptibility, thus allowing cylindrical domains aligned uniformly in the magnetic field direction.
In solar cell applications, the relatively low dielectric constants of organic semiconductors and subtle differences in dielectric properties may limit the application of electrical field on structure alignment in the active layer. But magnetic field could be a preferential option for promoting long-range order in conjugated P3HT-\textit{b}-PFTBT block copolymers, as the crystalline P3HT block engenders anisotropic susceptibility that permits orientation alignment by the external magnetic field.
7.2.2 Chemical Tuning of Optoelectronic Properties of Block Copolymer Semiconductors

Although P3HT-\textit{b}-PFTBT block copolymer devices can achieve remarkable efficiencies of 3%, further improvements are possible through engineering the light absorption properties of the constituent blocks. As shown in Figure 4-3a in Chapter 4, the absorption spectra of P3HT and PFTBT overlap significantly, and the resultant P3HT-\textit{b}-PFTBT block copolymers only absorb photons up to around 650 nm. A large portion of solar energy in near-infrared regions (700-1400 nm) is not captured. To address this issue, proper combinations of polymer blocks with complementary absorbance can achieve broad-band light absorption and lead to significant enhanced current generation beyond P3HT-\textit{b}-PFTBT block copolymers.

Excitingly, great synthetic efforts in developing low bandgap polymer semiconductors\textsuperscript{6, 7} offer us a giant material database for future research on designing high-performance block copolymers for efficient photovoltaic operation. Figure 7-4 presents several examples of low bandgap polymer donors (Panel a)\textsuperscript{8-11} and polymer acceptors (Panel b),\textsuperscript{10, 12} respectively. Incorporating these polymers to form block copolymer macromolecules using established synthetic chemistries, can lead to strong absorption (> $10^5$ cm\textsuperscript{-1}) over a broad range of wavelengths (400-900 nm).
Figure 7-4. Chemical structures of selected (a) polymer donors such as PTB7, PCPDTBT, PSEHTT, and PTQ1, and (b) naphthalene diimide (NDI)-based polymer acceptors including P(NDI2OD-T2), PNDIS-HD, and P(NDI-TCPDTT).

A specific material system of PSEHTT as donor and PNDIS-HD as acceptor has been studied in polymer blend solar cells with improved light absorption up to 800 nm. Despite the large domain size of 200-500 nm observed in the blend structure, a remarkable power conversion efficiency of 3.3% with short-circuit current density of 7.78 mA/cm² and external quantum efficiency near 50% is achieved. Thus, significant improvement in photovoltaic properties of this particular material combination can be expected from further studies on morphology control through design and synthesis of...
microphase-separated PSEHTT-\textit{b}-PNDIS-HD block copolymers. However, the energy difference between the donor HOMO level and the acceptor LUMO level limits the maximum voltage below 0.8 eV, which is inferior to the high open circuit voltage of 1.1-1.2 V in P3HT-\textit{b}-PFTBT system. Thus, to achieve broad-band light absorption while maintaining high open-circuit voltages requires careful design of the HOMO/LUMO levels of the constituent polymer segments in novel block copolymers.

Also, block copolymer architectures enable chemical control of donor-acceptor heterojunctions. For example, end-group functionalization of P3HT allows inclusion of a variety of conjugated or non-conjugated moieties between the constituent blocks to tune donor-acceptor interfaces and suppress recombination. Recent work has demonstrated that interactions between the strong electron-accepting benzothiadiazole moiety and P3HT can lead to localized charge-transfer states and promote recombination. Thus, it is critical to link P3HT directly with the fluorene unit in PFTBT but not the benzothiadiazole moiety. One approach directed at tuning the linking chemistry in conjugated block copolymers is to systematically replace fluorene with carbazole and dithieno silole moieties, which exhibit different extent of electron delocalization.

### 7.2.3 Multicomponent Block Copolymer Photovoltaics Capable of Broad Light Absorption

Another potential strategy for increasing the absorption breadth of organic solar cells and consequently the short-circuit currents ($J_{sc}$) is to incorporate multiple materials with complementary absorption properties to form multi-functional triblock copolymers. As a
preliminary illustration, we can consider bulk heterojunction and ordered block copolymer solar cells as being composed of many nanoscopic devices connected in parallel as shown in Figure 7-5. Given that excitons can only diffuse ~ 10 nm, we crudely approximate that small regions of the active layer near a heterojunction are independent from the rest of the active layer. Thus, the open-circuit voltage ($V_{oc}$) may be limited by the smallest $V_{oc}$ of various donor-acceptor pairs, while the short-circuit current ($J_{sc}$) is the sum of all contributions from the active layer. Therefore, in the multicomponent solar cell architecture (Figure 7-5b), various donor-acceptor pairs in parallel with complementary absorption ranges can significantly enhance current photogeneration towards 10-15 mA/cm$^2$. Interestingly, recent work on ternary blend bulk heterojunction solar cells have shown tunable $V_{oc}$ depending on the blend compositions.\textsuperscript{14} This brings into question our preliminary hypothesis about the limited voltage to the smallest value among all material combinations. On the other hand, this finding suggests that multicomponent solar cells are not necessarily contrained in voltage generation and thus provide a potential route for maximizing the $J_{sc}V_{oc}$ product and device performance beyond binary devices. Therefore, with unprecedented combinations of broad light absorption, high photovoltages, and control of morphology and interfaces, triblock copolymer photovoltaics are promising candidates for the next generation of organic solar cells, although further studies on origin of open circuit voltages are necessary in such multicomponent block copolymer systems (which may differ from that in ternary blend solar cells).
A primary challenge of building multicomponent block copolymer solar cells lies in selecting the proper combination of materials. In addition to complementary light absorption characteristics, the selection of materials must consider proper alignment of HOMO/LUMO energy levels between donor and acceptor in order for efficient charge transfer at interfaces and high voltage generation across the device. Figure 7-6 illustrates...
several hypothetical combinations of three materials showing different situations of energy level alignment.

**Figure 7-6.** Energy level diagrams and corresponding design of self-assembled triblock copolymers for multicomponent organic solar cells. (a) Material system containing one donor and two acceptors, where the HOMO/LUMO levels of acceptor 3 lie within the bandgap of acceptor 2. Significant charge recombination can occur unless phase 3 is physically isolated from phase 2 in the active layer. (b) System composed of two donors and one acceptor with the energy levels of donor 3 inserted in the bandgap of donor 1. (c) A cascade-like energy level arrangement, with which charge transfer can occur at any donor-acceptor interfaces.

As shown in Figure 7-6a, the HOMO/LUMO levels of one semiconductor lie within the band gap of another material. It is thus energetically favorable for both electrons and holes to transfer from phase 2 to phase 3, where significant charge recombination can occur. Then phase 3 would need to be physically isolated from phase 2 in order for
efficient current generation. It’s extremely challenging to implement such morphology requirements in complicated and disordered polymer mixtures. In contrast, microphase-separated triblock copolymers provide an easier pathway to achieve the required structure through design of a macromolecule where acceptor components 2 and 3 are connected separately to each side of the donor block 1 in the middle. Figure 7-6c presents a more robust material combination, in which the HOMO/LUMO levels of three materials form a “cascade” configuration. In this way, electrons and holes are less likely to recombine in a single phase due to the favorable energetics for charge separation at any interfaces. Thus, less constraints are imposed on design of morphology for ternary photovoltaic devices. However, it should be noted that when component 2 is in contact with both components 1 and 3, the electron and hole transferred from donor phase 1 and acceptor phase 3, respectively, could still recombine in phase 2. Therefore, a suitable strategy of block copolymer design for this case would be to avoid using polymer 2 as the middle block as shown in Figure 7-6c.

Multicomponent block copolymer photovoltaics can be developed based on established knowledge of high-performing diblock copolyemr semiconductors. For example, it would be beneficial to start with the material combination of P3HT donor and PFTBT acceptor. Promising candidates as the third component in combination with P3HT and PFTBT include polymer donor PSEHTT (Figure 7-4, material 3), with the energy level arrangement similar to that in Figure 7-6b and polymer acceptor P(NDI2OD-T2), of which the energy level diagram resembles the scenario in Figure 7-6c.
7.3 Study of Donor-Acceptor Interfacial Structure via Polarized RSOXS

In Chapter 3 and 4, we have shown that resonant soft X-ray scattering (RSOXS) is a powerful tool for charactering phase separation in polymer thin films with compositionally similar phases such as P3HT and PFTBT lamellar domains, or in complicated multiphase systems as observed in P3HT/PCBM mixtures. In particular, RSOXS can exploit subtle differences in absorption between multiple phases by tuning the X-ray energy to one or more resonance peaks of the constituent organic materials.

More interestingly, resonant scattering can be performed with polarized soft X-rays, known as polarized RSOXS to explore differences in molecular orientations between organic domains. The interaction of soft X-rays with a material near an absorption edge is characterized by the material’s complex refractive index $n(\lambda)=1-\delta(\lambda)+i\beta(\lambda)$, which is composed of an energy-dependent dispersive component $\delta(\lambda)$ and an absorptive component $\beta(\lambda)$. In organic materials, electronic transitions into anisotropic molecular orbitals upon absorption of X-rays will have dipole moments along specific directions. For example, the orientation of C 1s to $\pi^*$ transition dipole moment of a $\pi$-conjugated material such as pentacene (Figure 7-7a) is normal to the aromatic plane. Near such a resonant transition, the complex index of refraction, in particular the absorption component $\beta(\lambda)$, is thus dependent on the molecular orientation as shown in Figure 7-7b. Probing the molecule with a polarized electric field at the resonant energy will then reveal its local orientation.
Figure 7-7. (a) Schematic of orientation of the C 1s to π* transition dipole moment of the pentacene molecule, normal to the aromatic plane. (b) Components of the optical constants (real, δ(λ), and imaginary, β(λ), part) for pentacene, derived from domains whose average transition dipole moments, that is the aromatic plane normal directions, are preferentially aligned parallel or perpendicular to the incident electric field. β(λ) is measured from transmission spectroscopy, whereas δ(λ) is calculated from β(λ) using a Kramers-Kronig transformation.15

In polarized RSOXS as illustrated in Figure 7-8, the incident X-rays can be polarized in the plane perpendicular to the X-ray propagating direction, with horizontally or vertically oscillated electric field. In the case of crystalline materials such as regioregular P3HT, the carbon 1s to π* transition dipole moment is along the π orbital direction normal to the conjugated backbone. When the polarized electric field is perpendicular to the π-π stacking direction, absorption at the resonant transition energy is strongly suppressed. Otherwise, when the incident electric field is parallel with the π-stacking direction, absorption of P3HT is significantly enhanced. As a consequence, differences in molecular orientations between domains provide additional scattering contrast at resonant absorption energies and generate anisotropic scattering patterns (that is, intensity
variations along azimuthal directions) which contain information about molecular ordering.

**Figure 7-8.** (Left) Incident soft X-rays can be polarized in the plane normal to the propagation direction producing horizontally or vertically oscillated electric field E. The energy of a polarized X-ray beam is tuned to be resonant with the characteristic 1s to π* transition of carbon atoms in crystalline P3HT (right), making the scattering intensities sensitive to the molecular orientation. Absorption of P3HT can vary depending on the alignment of π-stacking direction with respect to the polarized electric field E.

Figure 7-9 shows the RSOXS scattering patterns of P3HT-b-PFTBT block copolymer thin films with horizontally (0°) and vertically (90°) polarized X-rays at 285.4 eV near the carbon absorption edge. The two-dimensional RSOXS image in Figure 7-9a is divided into six sectors along the azimuthal direction. Scattering intensities are integrated along azimuth, φ, within each sector and presented as a function of scattering vector, q, as compared in Figure 7-9 b-c. Scattering anisotropy characterized by an orientation dependence of scattering intensities is observed with both horizontally (Figure 7-9b) and vertically (Figure 7-9c) polarized RSOXS experiments. Remarkably, the anisotropic RSOXS intensities only occurs near the scattering vector, q around 0.03 Å⁻¹, which corresponds to the interdomain periodicity of P3HT-b-PFTBT lamellae (See details in Chapter 4). This finding suggests that contrast between molecular orientations
that gives rise to the observed anisotropic scattering is generated between domains or across interfaces. Given that the lamellar domain size (~ 10 nm) in P3HT-b-PFTBT block copolymers is within length scales of chain dimensions, the orientational contrast across donor-acceptor interfaces observed in polarized RSOXS is instructive for studying electronic coupling and charge separation processes. Therefore, RSOXS is a powerful tool for characterizing the morphology and interfacial structure in block copolymer photovoltaics.

**Figure 7-9.** (a) 2D RSOXS scattering image with symmetric azimuthal sectors from 0 to 90° for P3HT-b-PFTBT block copolymer thin films annealed at 165 °C. Data were obtained with horizontally (0°) polarized X-rays at 285.4 eV near the carbon absorption edge. Anisotropic scattering patterns revealed by (b) horizontally (0°) and (c) vertically (90°) polarized X-ray beam. The highest scattering intensity always occurs in the direction parallel to the polarized electric field.

Analyzing the polarization dependence in Figure 7-9, we find that the highest scattering intensity always occurs in the direction parallel to the polarized electric field, suggesting that absorption contrast between P3HT and PFTBT domains is enhanced parallel to the beam polarization direction. By reverse studies of the possible molecular
configurations that can generate the observed anisotropic scattering pattern, we would be able to obtain information about the orientational organizations near the donor-acceptor interface. Further quantitative analysis of the molecular orientations is also possible, which requires a comprehensive understanding of the origin for the orientation-, energy-, and $q$ (structural length scales)-dependent scattering intensities.

7.4 References


Appendix A. Supporting Information for Chapter 4: High-performance Conjugated Block Copolymer Photovoltaics through Microphase Separation

A.1 Morphological Characterization through RSOXS and GISAXS

*Figure A-1.* RSOXS intensities of P3HT-b-PFTBT and P3HT/PFTBT thin films under various processing conditions. (a) \( I \) vs. \( q \) and (b) \( Iq^2 \) vs. \( q \), where \( I \) is the scattering intensity, and \( q \) is the scattering vector. Profiles are offset for clarity. Scattering data were acquired at 285.4 eV, azimuthally integrated in a, and presented as a Kratky plot of \( I(q)q^2 \) vs. \( q \) in b.

Figure A-1 presents resonant soft X-ray scattering (RSOXS) profiles of P3HT/PFTBT and P3HT-b-PFTBT thin films at various annealing conditions. Scattering data are acquired at 285.4 eV and offset for clarity. Figure A-1a shows the RSOXS scattering data as \( I \) vs. \( q \), where \( I \) is the scattering intensity and \( q \) is the scattering vector. Figure A-
1b shows the data as Kratky plots of $Iq^2$ vs $q$. The broad peak or shoulder in the RSOXS data for blends or the block copolymer annealed at 100 °C is similar to the scattering data obtained from P3HT mixtures with fullerene derivatives, suggesting that this scattering feature corresponds to the spacing between P3HT fibrils. Annealing P3HT/PFTBT blends at 165 °C instead of 100 °C leads to a shift of the scattering shoulder to lower $q$, suggesting that the microstructure coarsens upon annealing at higher temperatures. In contrast, a well-defined primary peak at 0.035 Å$^{-1}$ and its second-order reflection are identified only in block copolymer films annealed at 165 °C, suggesting the existence of alternating lamellar microdomains on a length scale of around 10 nm.

![Figure A-2](image.png)

**Figure A-2.** GISAXS intensities vs in-plane scattering vector, $q_y$, for a P3HT-$b$-PFTBT film annealed at 165 °C.
Grazing-incidence small-angle X-ray scattering (GISAXS) experiments were performed to characterize the morphology in block copolymer thin films annealed at 165 °C, as shown in Figure A-2. Scattering data were acquired at an incident angle of 0.2°. Using the GIXSGUI package\textsuperscript{2} for Matlab (Mathworks), data were corrected for X-ray polarization, detector sensitivity and geometrical solid-angle. A line cut along the in-plane direction was used to present scattering data as a function of the in-plane scattering vector, $q_y$. The GISAXS data clearly show that a periodic structure is present with an average domain spacing of around 16 nm, consistent with RSOXS results (Figure 4-5 and Figure 4-6 of Chapter 4, and Figure A-1). No such structure is evident from the out-of-plane GISAXS scattering data (data not shown).

A.2 References

Appendix B. Supporting Information for Chapter 6: Probing Nanoscale Morphology and Local Electronic Transitions in Organic Semiconductors through Low-loss Spectral Imaging in Transmission Electron Microscopy

B.1 Comparison of EELS and UV-Visible Absorption Data

Figure B-1 compares electron energy-loss spectra (EELS) and UV-Visible absorption spectra for various organic semiconductors. The background due to the zero-loss peak (ZLP) is modeled as a third-order power law and subtracted from the EELS data. ZLP-subtracted EELS data are normalized by the incident intensities and the film thicknesses accordingly. UV-Visible absorption data are corrected for the substrate background and normalized by the film thicknesses, respectively. The absorption edges in electron energy-loss spectra are in well agreement with the band-gap energies deduced from the UV-Visible absorption data for organic materials discussed here. Furthermore, observed electronic states in EELS data are also comparable to peaks measured in optical absorption experiments in general, and can be attributed to inter-band transitions of organic semiconductors.

We note that EELS and UV-Visible data are consistent for PCBM. For other polymer semiconductors, however, a blue shift of spectral features by about 0.08 to 0.25 eV is observed in EELS data with respect to optical absorption spectra. This could be partly a result of the spectral changes caused by electron beam damage as shown in Figure 6-2 part a and c of Chapter 6.
Figure B-1. Comparison of electron energy loss spectra (EELS) and UV-Visible absorption data for (a) rr-P3HT, (b) rra-P3HT, (c) PGeBTBT and (d) PCBM neat films. Zero-loss peaks are subtracted using third order power law. EELS data are normalized by the incident intensities and the film thicknesses accordingly. UV-Visible absorption data are normalized by the film thicknesses.

Peak positions extracted from EELS and UV-Visible spectra for various organic materials are compared in Table B-1. The spectral peak of rr-P3HT at zero dose is extrapolated to be 2.54 eV through exponential fitting of EELS peak positions at low-dose (Figure 6-2d of Chapter 6). Compared to the absorption feature at 2.37 eV measured in optical experiments, a blue shift of 0.17 eV in the peak absorption is present in EELS data even at the limit of zero dose. We speculate that a difference exists between photoexcitations and material excitations by electrons.
Table B-1. Peak positions in EELS data compared to UV-Vis absorption spectra for various semiconductor polymers and a fullerene derivative.

<table>
<thead>
<tr>
<th></th>
<th>rr-P3HT</th>
<th>rra-P3HT</th>
<th>PGeBTBT 1&lt;sup&gt;st&lt;/sup&gt;</th>
<th>PGeBTBT 2&lt;sup&gt;nd&lt;/sup&gt;</th>
<th>PC60BM</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-Vis (eV)</td>
<td>2.37</td>
<td>2.77</td>
<td>1.60</td>
<td>1.74</td>
<td>3.70</td>
</tr>
<tr>
<td>EELS (eV)</td>
<td>2.54&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.92&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.68</td>
<td>1.84</td>
<td>3.69</td>
</tr>
<tr>
<td>Peak shift (eV)</td>
<td>0.17</td>
<td>0.15</td>
<td>0.08</td>
<td>0.10</td>
<td>0.01</td>
</tr>
</tbody>
</table>

<sup>a</sup> Extrapolated to zero electron dose.

B.2 Spectral Degradation of Organic Semiconductors upon Electron Radiation

The electronic structures of organic materials degrade upon electron radiation, reflected in changes of spectral responses in EELS measurements. Figure B-2 shows degradation of electron energy-loss spectra under various exposure doses for rr- and rra-P3HT supplementary to Figure 6-2 of Chapter 6.
Figure B-2. EELS data at various radiation exposures and integrated EELS intensities as a function of electron dose for (a-b) crystalline rr-P3HT, and (c-d) amorphous rra-P3HT. For rr-P3HT, EELS data at exposure dose beyond 4000 e-/nm² are subtracted as an amorphous background from EELS spectra at lower dose. The subtracted EELS intensities are integrated to 4 eV and presented in (b). EELS intensities are integrated up to 4 eV for rra-P3HT. Solid lines are data fits to the exponential decay. Spectral peak positions of rr- and rra-P3HT are extracted from Gaussian fits to the EELS spectra and plotted in (b) and (d), respectively.

EELS intensities at low energy-loss ranges drop with increasing electron dose for all samples. In addition, EELS data exhibit a blue shift of spectral peaks towards higher energies with increasing beam damage, which is particularly evident in rr-P3HT. Spectral peak positions of rr- and rra-P3HT are extracted from Gaussian fits to the EELS spectra and compared at different dose conditions in Figure B-2 b and d, respectively. Quantitatively, EELS intensities are integrated at low-loss regions up to 4 eV for rr- and
rra-P3HT, where degradation of spectral features is evident. For rr-P3HT (Figure B-2a), little changes are observed in EELS spectra at exposure dose beyond 4000 e-/nm². This is consistent with our observation that intensity integrals in Figure 6-2d of Chapter 6 decrease initially and level off at higher electron doses. Meantime, spectral peak positions shift towards higher energy around 3.2 eV with increasing electron dose, which is similar to the band excitation energy observed in amorphous rra-P3HT in Figure B-2 c-d. Based on these findings, we hypothesize that the initial spectral degradation is primarily attributed to the rapid destruction of long range order in crystalline rr-P3HT, after which the sample temporarily stabilizes in amorphous states and exhibits similar electronic transitions as that in rra-P3HT. Therefore, EELS spectra of rr-P3HT beyond 4000 e-/nm² can be modeled as the amorphous background and subtracted from EELS data at lower doses. Figure B-2b presents the intensity integrals of background-subtracted EELS data at various electron radiation doses.

We fit the integrated EELS intensities to an exponential decay as shown by the solid lines in Figures B-2 part b and d. A decay rate, $\lambda$, is extracted from data fitting and the corresponding critical dose, $D_c$, in units of electron/nm² is defined as $1/\lambda$. The decay rates and critical doses for spectral degradation of crystalline rr-P3HT (after background subtraction), and amorphous rra-P3HT are summarized in Table 6-1 of Chapter 6 together with other organic semiconductors.
B.3 Core-loss Elemental Maps of P3HT/PCBM Mixtures

**Sulfur**

![Image of sulfur map](image)

**Figure B-3.** Sulfur map of P3HT/PCBM mixtures with a weight ratio of 1:1 annealed at 190 °C for 30 min. Scale bar is 100 nm.

A sulfur map of P3HT/PCBM mixtures annealed at 190 °C for 30 min is obtained through energy-filtered TEM at the sulfur absorption edge of 165 eV as shown in Figure B-3. The sulfur map was taken from the same sample area as low-loss spectral imaging in Figure 6-3 of Chapter 6. The intensity of the elemental map is proportional to the local elemental concentration. Given that sulfur is only present in P3HT but no PCBM, bright fibers of higher intensities correspond to P3HT-rich domains, while dark matrix of lower intensities corresponds to PCBM-rich domains. The characterized morphology in sulfur map is consistent with low energy-loss EFTEM imaging near the band-gap of organic semiconductors.
B.4 References


VITA
Changhe Guo

Education
Doctor of Philosophy in Chemical Engineering (August 2010 – December 2014)
The Pennsylvania State University, University Park, Pennsylvania, USA. GPA 3.95/4.0
Bachelor in Chemical Engineering (August 2006 – July 2010)
Tsinghua University, Beijing, China. GPA 85.2/100

Publications


Honors and Awards

- Personal Excellence Award, Best Presentation at Chemical Engineering Symposium, The Pennsylvania State University, 2013.
- Best Candidacy Exam Award, Chemical Engineering, The Pennsylvania State University, 2011.
- Hitachi Chemical Student Fellowship, Tsinghua University, China, 2008.