RICE UNIVERSITY

All-Conjugated Block Copolymers for Organic Photovoltaic Applications

by

Kendall Allen Smith

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APPROVED, THESIS COMMITTEE

Dr. Rafael Verduzco, Chair
Louis Owen Assistant Professor

Dr. Walter G. Chapman
William W. Akers Professor

Dr. Jeffrey D. Hartgerink
Associate Professor of Chemistry and Associate Professor of Bioengineering

HOUSTON, TEXAS
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Conventional inorganic solar technologies are expensive due to the high cost of processing, while organic materials have significant cost advantages in the raw materials and ease of processing. Unfortunately, organic devices suffer from low efficiency due to difficulty in transporting charges to the electrodes. Typical devices mix the donor and acceptor components and anneal them to allow for phase separation. However, because the phase separation is uncontrolled, domains may be larger than optimal and isolated domains can be formed reducing efficiency. All-conjugated block copolymers have the potential to improve efficiency by creating an ordered structure with controlled domains and continuous pathways through self-assembly. In this work, the relationships between structure, optoelectronic properties, and processing conditions for these materials are systematically investigated using two routes to obtain the materials. In one route, functionalized catalysts are used to initiate controlled polymerizations of two different polymers. These well functionalized precursors are then joined together using copper catalyzed azide alkyne click chemistry. In a second route, a sequential polymerization route is employed where one polymer is synthesized with a well-
defined end-group. The polymer is then used as a macroleagent to end-cap a Suzuki polycondensation reaction, yielding materials with direct conjugation between the blocks. The first route yields well-defined materials, whereas the second can access a broader variety of polymers. For all these materials, processing conditions are varied and the morphology of the all-conjugated block copolymers are analyzed by a combination of grazing-incidence X-ray scattering, neutron scattering and reflectivity, atomic force microscopy, and transmission electron microscopy. Materials are found to self-assemble into thermodynamically stable structures with well-defined length scales. It is found that crystallization of either block is predominant in all block copolymers studied, but at intermediate ratios crystallization of both blocks is observed. Processing conditions such as casting temperature, annealing duration, and speed of quenching to room temperature are found to have important effects on thin film crystallinity and orientation of the π stacking direction of polymer crystallites. By varying the annealing duration and quenching speed, crystallization of either or both blocks can be obtained.
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Contents

Acknowledgments .................................................................................................................. iv

Contents .................................................................................................................................. vi

List of Figures .......................................................................................................................... x

List of Supporting Figures ....................................................................................................... xiii

List of Tables ............................................................................................................................ xvii

Introduction .............................................................................................................................. 1

Background ............................................................................................................................... 10

  2.1. Material Synthesis .......................................................................................................... 11
  2.2. Organic Photovoltaic Devices ....................................................................................... 15
  2.3. References ..................................................................................................................... 18

Synthesis and Crystallinity of Conjugated Block Copolymers prepared by Click Chemistry .............................................................................................................................. 31

  3.1. Introduction ..................................................................................................................... 33
  3.2. Results and Discussion ................................................................................................... 35
    3.2.1. Synthesis of Conjugated Diblock Copolymers via Click Chemistry ....................... 35
    3.2.2. Crystallization of Conjugated Block Copolymers .................................................... 42
  3.3. Conclusion ...................................................................................................................... 50
  3.4. Acknowledgments .......................................................................................................... 51
  3.5. Experimental .................................................................................................................. 51
    3.5.1. Instrumentation ........................................................................................................ 51
      3.5.1.1. Nuclear Magnetic Resonance Spectroscopy (NMR) .............................................. 51
      3.5.1.2. Size-Exclusion Chromatography (SEC) ............................................................... 52
      3.5.1.3. MALDI-TOF MS ............................................................................................... 53
      3.5.1.4. Differential Scanning Calorimetry (DSC) ............................................................ 53
      3.5.1.5. Grazing Incidence Small/Wide Angle X-ray Scattering (GISAXS/GIWAXS) .... 54
    3.5.2. Materials .................................................................................................................. 54
      3.5.2.1. Hydroxyl-Functionalized Poly(9,9-dioctylfluorene) (PF-OH) via Pd[PPh₃]₄-
                Catalyzed Suzuki-Miyaura Polycondensation ......................................................... 55
      3.5.2.2. 1-bromo-4-[[1,1-dimethylethyl]dimethylsilyloxy]ethyl]benzene ....................... 56
      3.5.2.3. t-Bu₃Pd[PhCH₂CH₂OSi(CH₃)₂C(CH₃)₃]Br .................................................................. 56
3.5.2.4. Hydroxyl-Functionalized Poly(9,9-dioctylfluorene) (PF-OH) via \(t\)-Bu\(_3\)Pd\([\text{PhCH}_2\text{CH}_2\text{OSi(CH}_3)_2\text{C(CH}_3)_3\text{]}\text{Br}\)-Catalyzed Suzuki-Miyaura Polymerization ................................................................. 57
3.5.2.5. Azide-Functionalized PF (PF-N\(_3\)) .............................................................. 58
3.5.2.6. P3HT-\(b\)-PF via Copper-Catalyzed Azide-Alkyne Click Coupling .......... 58
3.6. References ........................................................................................................... 59
3.7. Supporting Information ....................................................................................... 72

Conjugated Block Copolymers via Functionalized Initiators and Click Chemistry .... 78
4.1. Introduction ........................................................................................................... 80
4.2. Results and Discussion ....................................................................................... 82
4.3. Conclusions ........................................................................................................ 95
4.4. Acknowledgements ............................................................................................ 97
4.5. Experimental ...................................................................................................... 97
4.5.1. Instrumentation ............................................................................................... 97
4.5.1.1. Nuclear Magnetic Resonance Spectroscopy (NMR) ....................................... 97
4.5.1.2. Size-Exclusion Chromatography (SEC) ....................................................... 98
4.5.1.4. Differential Scanning Calorimetry (DSC) ................................................... 99
4.5.1.5. Grazing Incidence Small/Wide Angle X-ray Scattering (GISAXS/GIWAXS) 99
4.5.1.6. Transmission Electron Microscopy (TEM) .................................................. 100
4.5.2. Synthesis ......................................................................................................... 100
4.5.2.1. Materials .................................................................................................... 100
4.5.2.2. 2-(4-Bromophenyl) ethyl 4-methylbenzenesulfonate (1) ............................ 101
4.5.2.3. 2-(4-Bromophenyl) ethyl 4-methylbenzenesulfonate bis(tri-tert-butylphosphine) palladium(0) ................................................................. 101
4.5.2.4. Tosyl functionalized Poly(9,9-dioctylfluorene) (PF-tosylate) .................. 102
4.5.2.5. Azide functionalized Poly(9,9-dioctylfluorene) (PF-azide) ....................... 103
4.5.2.6. Alkyne functionalized poly(3-alkylthiophene) (P3AT-alkyne) ............... 103
4.5.2.7. Poly(3-alkylthiophene)-b-poly(9,9-dioctylfluorene) (P3AT-b-PF) ......... 104
4.6. References .......................................................................................................... 106
4.7. Supporting Information ...................................................................................... 112

Control of All-Conjugated Block Copolymer Crystallization via Thermal and Solvent Annealing ........................................................................................................ 124
5.1. Introduction ........................................................................................................ 126
5.2. Results and Discussion ........................................................................................................ 127
5.3. Conclusions .......................................................................................................................... 139
5.4. Acknowledgments ................................................................................................................ 139
5.5. References .......................................................................................................................... 140
5.6. Experimental ......................................................................................................................... 144
  5.6.1. Nuclear Magnetic Resonance Spectroscopy (NMR) ......................................................... 144
  5.6.2. Size-Exclusion Chromatography (SEC) ........................................................................... 144
  5.6.3. Differential Scanning Calorimetry (DSC) ........................................................................ 145
  5.6.4. Grazing Incidence Small/Wide Angle X-ray Scattering (GISAXS/GIWAXS) ....... 145
  5.6.5. Photoluminescence (PL) ............................................................................................... 146
  5.6.6. Materials ............................................................................................................................ 146
  5.6.7. Supporting Information .................................................................................................... 147

Effect of Thermal Processing on Crystal Orientation and Photovoltaic Performance of P3HT – block – PFTBT with Various Side Chains ................................................................. 157

6.1. Introduction ............................................................................................................................ 159
6.2. Discussion ............................................................................................................................... 161
6.3. Conclusion .............................................................................................................................. 178
6.4. References ............................................................................................................................. 179
6.5. Supporting Information .......................................................................................................... 185
  6.5.1. Instrumentation ................................................................................................................ 185
    6.5.1.1. Nuclear Magnetic Resonance Spectroscopy (NMR) ................................................... 185
    6.5.1.2. Size-Exclusion Chromatography (SEC) ................................................................. 186
    6.5.1.3. Differential Scanning Calorimetry (DSC) ................................................................. 187
    6.5.1.4. Grazing Incidence Small/Wide Angle X-ray Scattering (GISAXS/GIWAXS) .... 187
  6.5.2. Materials ........................................................................................................................... 188
  6.5.3. Organic Photovoltaic Devices .......................................................................................... 192
  6.5.4. Determination of Block Copolymer Purity ...................................................................... 193
  6.5.5. References ......................................................................................................................... 212

Further Studies of All-Conjugated Block Copolymers .............................................................. 214
  7.1. Comparison of All-Conjugated Block Copolymers and Blends by Neutron Scattering and Reflectivity ..................................................................................................... 215
7.1.1. Introduction ......................................................................................................................... 215
7.1.2. Results and Discussion .................................................................................................... 216
7.1.3. Conclusion ......................................................................................................................... 220
7.1.4. Supporting Information ..................................................................................................... 221
7.2. P3DDT-b-PFTBT Organic Photovoltaic Devices ................................................................. 222
    7.2.1. Introduction .................................................................................................................... 223
    7.2.2. Results and Discussion ................................................................................................. 224
    7.2.3. Conclusion ..................................................................................................................... 225
    7.2.4. Supporting Information ................................................................................................. 226
7.3. References ............................................................................................................................ 227

Conclusion ....................................................................................................................................... 229
List of Figures

Figure 1.1: Best Research Efficiencies from the National Renewable Energy Laboratory ................................................................. 2

Figure 1.2: Schematic of polymer:fullerene blend devices compared to block copolymer devices ..................................................... 3

Figure 2.1: Conjugated polymers used in this work .................................................. 11

Figure 2.2: Living polymerization methods for conjugated polymers $^{3,31-33}$ .... 12

Figure 2.3: Schematics of Suzuki and Stille cross coupling reactions $^{23,24}$ .... 13

Figure 2.4: Copper Catalyzed Azide-Alkyne Click (CuAAC) Reaction and Glaser Coupling reaction ............................................. 14

Figure 2.5: Various organic materials used in OPVs and their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) Energy Levels ................................................................. 15

Figure 3.1. $^1$H NMR spectra for polymeric intermediates and block copolymers .................................................................................. 39

Figure 3.2. SEC analysis of P3HT64-b-PF36 and corresponding P3HT and PF macroreagents ................................................................. 41

Figure 3.3. Differential Scanning Calorimetry (DSC) analysis for P3HT1, P3HT2, PF3, and P3HT-b-PF block copolymers ........................................ 44

Figure 3.4. GIWAXS patterns for P3HT-b-PF block copolymer films thermally annealed at 230 °C and measured at 100 °C at an incidence angle of 0.25° ..... 46

Figure 3.5. Temperature-dependent GIWAXS analysis of P3HT23-b-PF77 film at an incidence angle of 0.25° ......................................................... 48

Figure 4.1: $^1$H NMR of A) PF-tosylate and PF-azide, B) P3AT-OH and P3AT-alkyne, and C) final P3AT-b-PF product ......................................................... 85

Figure 4.2: MALDI-TOF analysis of PF1-tosylate ...................................................... 88

Figure 4.3 Size exclusion chromatography data for P3DDT2-b-PF2 ......................... 89
Figure 4.4: GIWAXS analysis of BCP films after thermal annealing at 230°C...91

Figure 4.5: Differential scanning calorimetry curves from second heating cycle of PF2, P3HT2, and P3HT2-b-PF2...92

Figure 4.6: GIWAXS analysis for P3DDT2-b-PF2 under different processing conditions...94

Figure 4.7: Comparison of AFM and TEM images for P3HT1-b-PF1...94

Figure 5.1: SEC differential refractive index trace of starting P3DDT1 and the resulting block copolymer product P3DDT-b-PF1...129

Figure 5.2: DSC results from the second heating cycle for a pure PF, P3DDT1, and P3DDT-b-PF1...131

Figure 5.3: GIWAXS images (from left to right) of films of pure P3DDT, P3DDT-b-PF1 (32% P3DDT), P3DDT-b-PF2 (8% P3DDT), and pure PF annealed at 175°C...131

Figure 5.4: P3DDT-b-PF1 cast onto silicon wafers from 12 mg ml⁻¹ chloroform (first row) and toluene (second row) solutions...133

Figure 5.5: Photoluminescence measurements using an excitation wavelength of 380nm for P3DDT-b-PF1 samples cast from 12 mg ml⁻¹ chloroform. Samples were annealed at 170 °C for 15 min (red trace) or 5 days (blue trace)...134

Figure 5.6: P3DDT-b-PF1 cast onto PEDOT:PSS coated silicon wafers from 12mg ml⁻¹ chloroform (first row) and toluene (second row) solutions...136

Figure 5.7: GIWAXS of samples annealed in the presence of chloroform vapor for 5 days...137

Figure 5.8: Schematic showing evolution of crystallites. Since no strong evidence for ordered phase segregation was found from GISAXS, thin film structure is depicted as a random intermixed network...138

Figure 6.1: Block copolymers used P3HT as the donor block and PFTBT with various side chains as the acceptor block...161

Figure 6.2: Plot of performance data from Table S6.3 as function of A) P3HT content and B) number average molecular weight...164
Figure 6.3: GISAXS extracted domain size as a function of number average molecular weight ($M_N$) for all block copolymers processed from room temperature solvent and annealed at 165°C (●), 230°C (▲), from refluxing (Hot) solvent and annealed at 165°C (■) and 230°C (▼), and solvent annealing with room temperature chloroform (♦). 165

Figure 6.4: Ternary plots of all polymers processed from room temperature solvent and annealed at 165°C (●), 230°C (▲), from refluxing (Hot) solvent and annealed at 165°C (■) and 230°C (▼), and solvent annealing with room temperature chloroform (♦). 168

Figure 6.5: Summary of GIWAXS results of in situ measurements for P3HT9-b-PF8HTBT, P3HT-b-PF8TBT, and P3HT-b-PF1EHTBT. 170

Figure 6.6: Summary of GIWAXS results of in situ measurements of P3HT-b-PF8HTBT films cooled from 165°C (A), in situ at 220°C (B) and cooled from 220°C (C) showing the change in orientation of P3HT after annealing above the melting point. 173

Figure 6.7: Comparison of device efficiency as a function of annealing temperature with DSC data for P3HT9-b-PFTBT. 175

Figure 6.8: Schematic of evolution of block copolymer film after casting. 176

Figure 7.1: Neutron Reflectivity of dP3HT-b-PF block copolymer films. 218

Figure 7.2: Preliminary fits of dP3HT/PF blends. 218

Figure 7.3 Comparison of GISAXS data in the thin film and SANS data of thick films. 219

Figure 7.4: Select IV curves for best performing devices for three different P3DDT-b-PFTBT materials. 224
List of Supporting Figures

Figure S3.1: MALDI-TOF MS spectra of PF-OH produced via Pd(PPh3)4-catalyzed Suzuki-Miyaura polycondensation (same method as PF1) prior to conversion to the azide. .......................................................... 72

Figure S3.2: MALDI-TOF MS spectra of PF-OH produced via Suzuki-Miyaura polymerization using modified Pd catalyst with t-Bu3P (same method as PF2-4) prior to conversion to the azide. .......................................................... 73

Figure S3.3: Differential refractive index (SEC-RI) and absorbance measurements (SEC-UV/VIS) for all P3HT-b-PF block copolymers and corresponding P3HT-alkyne and PF-N3 macroreagents ........................................... 74

Figure S3.4: GIWAXS of pure P3HT and pure PF films. .............................................. 75

Figure S3.5: GIWAXS linecuts along qz for selected block copolymers. P3HT crystal peak at qz = 0.36 Å⁻¹ and PF crystals at 0.48 Å⁻¹ ........................................... 76

Figure S3.6: GISAXS measurements of solvent- and thermally annealed polymer films ......................................................................................................................... 77

Figure S4.1 SEC results for all polymers ................................................................. 113

Figure S4.2: GIWAXS linecuts along qz for samples annealed at 230°C ............ 114

Figure S4.3: Differential scanning calorimetry curves from second heating cycle, baseline subtracted for easier viewing ......................................................... 115

Figure S4.4: GIWAXS data for all samples under various annealing conditions for sample cast from room temperature chloroform ........................................ 116

Figure S4.5: GIWAXS data for all samples under various annealing conditions for sample cast from refluxing chloroform ......................................................... 117

Figure S4.6: GISAXS linecuts along qy for samples annealed at A) 165°C and B) 230°C ...................................................................................................................... 118

Figure S4.7: Transmission Electron Microscopy (TEM) images of A) P3HT1-b-PF1 B) P3HT1-b-PF2 C) P3HT2-b-PF2 D) P3DDT1-b-PF1 E) P3DDT1-b-PF2 F) P3DDT2-b-PF2 annealed at 165°C for 15 minutes ........................................... 119
Figure S4.8: Elemental line scan of P3DDT1-b-PF1 showing uniform increase in both carbon and sulfur signals from light to dark regions of TEM image. .................................................. 119

Figure S4.9: A survey of AFM phase images for samples reported in this work under various processing conditions (see inset). ................................................................. 120

Figure S4.10: $^1$H NMR of P3HT1-b-PF1 ............................................................................. 121

Figure S4.11: $^1$H NMR of P3HT1-b-PF2 ............................................................................. 121

Figure S4.12 $^1$H NMR of P3HT2-b-PF2 ............................................................................. 122

Figure S4.13: $^1$H NMR of P3DDT1-b-PF1 ............................................................................. 122

Figure S4.14: $^1$H NMR of P3DDT1-b-PF2 ............................................................................. 123

Figure S4.15: $^1$H NMR of P3DDT2-b-PF2 ............................................................................. 123

Figure S5.1: $^1$H NMR of P3DDT-b-PF1 ............................................................................. 147

Figure S5.2: GPC Traces for starting polymer and final block copolymer products for P3DDT-b-PF1 and P3DDT-b-PF2................................................................. 148

Figure S5.3: GIWAXS of all P3DDT-b-PF1 silicon wafers under a variety of casting/annealing/quenching conditions. .................................................. 149

Figure S5.4: GIWAXS linecuts in qz and qy for all P3DDT-b-PF1 silicon wafers under a variety of casting/annealing/quenching conditions. ......................... 150

Figure S5.5: Photoluminescence data for selected P3DDT-b-PF1 samples cast on silicon wafers ................................................................................................. 151

Figure S5.6: Absorbance for P3DDT-b-PF1, P3DDT1, and PF samples cast on glass slides and annealed for 15 minutes then slowly cooled ..................... 151

Figure S5.7: GIWAXS of P3DDT-b-PF1 on PEDOT:PSS coated silicon wafers under a variety of casting/annealing/quenching conditions. ......................... 152

Figure S5.8: GIWAXS linecuts in qz and qy of P3DDT-b-PF1 on PEDOT:PSS coated silicon wafers under a variety of casting/annealing/quenching conditions ........................................................................ 153
Figure S5.9: GIWAXS image taken at the Advanced Photon Source, Beamline 8-ID-E for P3DDT-b-PF1 sample cast on silicon and annealed at 180°C followed by rapidly cooling ................................................................. 154

Figure S5.10: GIWAXS of P3DDT1-b-PF1 samples drop cast onto silicon wafers under a variety of casting/annealing/quenching conditions................................................................. 155

Figure S5.11: GIWAXS linecuts for all samples drop cast onto silicon wafers under a variety of casting / annealing / quenching conditions................................................................. 156

Figure S6.1: 1H NMR Spectra for block copolymers ................................................................. 185

Figure S6.2: Plot of fit SEC calibration curves with polystyrene calibration curve (black) included for reference ................................................................. 197

Figure S6.3: Plot of analysis P3HT7bPF1EHTBT1 with P3HT/PFTBT block copolymer/homopolymer curves ......................................................................................... 199

Figure S6.4: Plot of GISAXS data showing extracted q values (d-spacing is 2·π/q) ......................................................................................... 201

Figure S6.5: Plot of GIWAX (first two rows) and GISAXS (second two rows) for all homopolymer materials ......................................................................................... 202

Figure S6.6: Example chl distribution analysis showing predominantly edge-on, face-on, and isotropic distributions ................................................................. 203

Figure S6.7: Plot of fraction of edge-on, face-on, and isotropic components of the distribution as a function of the difference between the annealing temperature and the melting point (as determined using the second DSC heating cycle) ......................................................................................... 205

Figure S6.8: Heating and cooling DSC cycles for P3HT9-b-PF8TBT, P3HT2-b-PF8HTBT3, and P3HT7-b-PF1EHTBT1 used for in situ measurements ................................................................. 206

Figure S6.9: Line cuts corresponding to qz axis for all source GIWAXS images included in Chp6_P3HT2bPF8HTBT3_220C.mpg ......................................................................................... 207

Figure S6.10: Line cuts corresponding to qz axis for all source GIWAXS images included in Chp6_P3HT2bPF8HTBT3_165C.mpg ......................................................................................... 208

Figure S6.11: Line cuts corresponding to qz axis for all source GIWAXS images included in Chp6_P3HT9bPF8TBT_165C.mpg ......................................................................................... 209
Figure S6.12: Line cuts corresponding to qz axis for all source GIWAXS images included in Chp6_P3HT7bPF8EHTBT1_165C.mpg.................................................................210

Figure S6.13: Schematic of alternating PF8HTBT structure giving rise to lamellar domain spacing in agreement with GIWAXS data........................................211

Figure S6.14: Plot of 1:1 P3HT:PF8TBT blend annealed at 165°C for 15 minutes. A) Shows GIWAXS image at incidence angle of 0.07° and B) shows chi linecut along P3HT alkyl stacking peak (q=0.38 Å⁻¹).................................................211

Figure S7.1: SEC-RI trace of dP3HT-b-PF and starting dP3HT...............................221

Figure S7.2: Plot of block copolymer film at 150 min fit with a multilayer having thickness period on the same order as expected for block copolymer domain size. ........................................................................................................221

Figure S 7.3: ¹H NMR of dP3HT-b-PF........................................................................222

Figure S7.4: UV/VIS analysis of 0.7% efficiency P3DDT-b-PFTBT polymer ... 226
List of Tables

Table 3.1 P3HT and PF homopolymer samples prepared ........................................... 36
Table 3.2 P3HT-\textit{b}-PF conjugated block copolymer samples................................. 40
Table 4.1: Characteristics of conjugated polymer macroreagents ............................... 84
Table 4.2: Characteristics of Conjugated Block Copolymers .................................... 87
Table 5.1: List of samples ............................................................................................. 127

List of Supporting Tables

Table S4.1 MALDI-TOF analysis for P3AT polymers to determine functionality. .......................................................... 112
Table S4.2 MALDI-TOF analysis for PF polymers to determine functionality 112
Table S5.1 Table of samples/substrates of P3DDT-\textit{b}-PF1 investigated .......... 147
Table S6.1: Table of homopolymer samples ................................................................. 190
Table S6.2: Table of block copolymer samples ............................................................ 191
Table S6.3: Table of maximal performance for selected block copolymer devices .................................................................................. 192
Chapter 1

Introduction

Organic photovoltaics (OPVs) are an interesting emerging field in solar energy.\textsuperscript{1} The goal of OPVs is to provide a more cost effective solution to the collection of solar energy relative to their inorganic counterparts. This is accomplished by ease of processing and inexpensive precursor materials.\textsuperscript{2} Although there are several different classes of organic materials that are used for these types of devices, here we will be focusing on devices that have polymeric materials for at least one component. Commonly, the polymers used have direct conjugation between the repeat units giving rise to electron/hole delocalization and the ability to conduct charges along the backbone of the polymer. Unfortunately, OPVs generally suffer from low efficiency due to non-ideal morphologies among other inherent factors. Block copolymers are known to self-assemble into a variety of interesting morphologies that could help solve this problem.\textsuperscript{3–6} Here, we look at block copolymers consisting of two chemically distinct conjugated blocks.
The field of organic photovoltaic devices is generally motivated by the larger societal issues associated with finding alternative sources of energy. Solar energy is abundant and although there are practical limitations on its use since it is subject to fluctuations due to weather and day/night cycles, it can still be an important part of an energy mix. As can be seen from Figure 1.1, organic photovoltaics have enjoyed steady improvements in efficiency over recent years; however efficiencies are still significantly less than the inorganic thin film technologies that they hope to replace. An interesting addition to the chart in recent years has been that of perovskite solar cells which are already at an impressive 17.9%. However, while this technology shares some advantages with OPVs in terms of ease of processing, significant stability issues and environmental toxicity issues still need to be addressed.
Independent of other factors, OPVs do have some unique advantages that may allow them to excel in a niche application. A recent report in the field described the utilization of donor and acceptor materials that had minimal absorption in the visible range to make a device that was nearly transparent in the visual regime, but was nevertheless able to deliver a power conversion efficiency of about 4%. In some ways, this is the ideal example of the flexibility of using organic materials as photoactive materials. Because their optical properties may be readily tuned, in principle arbitrary absorbance across different wavelengths may be obtained by tuning the structure of the component materials.

Figure 1.2: Schematic of polymer:fullerene blend devices compared to block copolymer devices.

The focus of this thesis is on a subset of OPV devices known as all-polymer solar cells. As shown schematically in Figure 1.2, top performing devices typically use a polymer:fullerene architecture where the electron donor is a conjugated polymer and the electron acceptor is a C60 derivative such as phenyl-C61-butyric acid methyl ester (PCBM). Unfortunately, while PCBM is an excellent electron conducting material, it does not absorb significant sunlight, so absorption occurs
primarily in the polymer component. All-polymer devices, by contrast, hope to broaden the absorbance of the device and have both donor and acceptor materials contribute to the photocurrent. Regrettably, phase separation issues are exacerbated in polymer blends and large scale phase separation is a significant problem.\textsuperscript{10–12} Since block copolymers can be used to covalently bind the donor and acceptor materials together in these systems, we expect that this will mitigate the problems associated with bulk phase separation and allow for thermodynamically stable structures that will be more robust to processing conditions and improve overall efficiency. Chapter 2 provides additional background for relevant work in the field. The bulk of this thesis is devoted to fundamental studies on a model system of \textit{poly(3-alkythiophene)-block-poly(9,9-dioctylfluorene)} (P3AT-\textit{b}-PF) which is used to give insights into the assembly of these types of materials where the P3AT block is either \textit{poly(3-hexylthiophene)} (P3HT) or \textit{poly(3-dodecylthiophene)} (P3DDT). Each of the blocks are semi-crystalline allowing for investigation into the tradeoff of crystallization of each block. Crystallization is known to have implications for the charge transport properties of the material, so is a key metric that is investigated in these studies.\textsuperscript{13} Chapter 3 is devoted to a study of the crystallization properties of a P3HT-b-PF block copolymer as a function of block ratio where each block is separately synthesized and then joined together after polymerization. This work includes in situ measurements of crystallization showing that the melting of the P3HT block was required in order to obtain well-ordered PF crystals. A follow-on study was performed and reported in Chapter 4 where the synthesis approach was improved to utilize functionalized catalysts to initiate the
polymerization for both polymer blocks, which were then joined together post polymerization. This study expanded the scope of the P3AT block to include both P3HT and P3DDT, a polymer with a lower crystallization temperature than P3HT. Scope of the processing conditions was also expanded to include solvent annealing and thermal annealing at different temperatures. In Chapter 5, the synthesis approach is modified to use a sequential polymerization technique that provides direct conjugation between the two polymer blocks and the effects of quenching rate on crystallization are systematically investigated. This work shows that not only is the choice of annealing temperature important, but that the duration of annealing and the speed at which the films are returned to room temperature can have significant effects on the resulting crystallization patterns, which in turn has implications for block copolymer devices that depend on crystallization of both blocks for optimal charge transport.

Chapter 6 is devoted to the study of block copolymers of P3HT and poly((9,9-dialkylfluorene)-2,7-diyl-alt-[4,7-bis(3-alkyl-thiophen-5-yl)-2,1,3-benzothiadiazole]-2′,2″-diyl) (PFTBT) which have been previously used in polymer blend devices giving about 1.8% power conversion efficiency. However in the block copolymer a significant improvement in power conversion efficiency is obtained when comparing analogous blend and block copolymer devices, obtaining a best efficiency of 3.1%. In the P3HT-\textit{b}-PFTBT block copolymer, an unusual morphology is present where the usual in-plane π stacking of the thiophene rings is rotated 90° and is shown to be out-of-plane once incorporated into the block copolymer. In the work for this thesis, alkyl side chains on the PFTBT block are
varied and effects on both the morphology and performance are evaluated. It is found that the side chains on the PFTBT have relatively little effect on the orientation of the P3HT; however annealing temperature plays a significant role with the usual in-plane π stacking recovered after annealing above the P3HT melting point. The effect of P3HT orientation is also evaluated and found to have a modest effect on overall device performance of around 5-10%.

Chapter 7 is devoted to summarizing a few related works which are not yet complete and point the direction toward future work. One major limitation of many of the studies contained herein has been the lack of data on self-assembly, a critical aspect of morphology for these systems. Using grazing incidence small angle X-ray scattering (GISAXS), some materials display a very weak signal for self-assembly indicating some ordering of the material, but it is insufficient to characterize more than the average domain size. This may be due to inherently weak contrast between the blocks and/or large disparities in domain size due to the polydispersity of the materials. Likewise, while atomic force microscopy (AFM) indicates a phase separated morphology, it is only a surface probe and does not detail the bulk morphology. Transmission electron microscopy (TEM) does provide interesting insight into the materials; however, since the contrast is between the crystalline P3HT and the amorphous matrix, interpretation of these results is difficult. Hence, a study was performed using deuterated P3HT (dP3HT) and PF blends and the corresponding block copolymers (dP3HT-b-PF) using neutron scattering and reflectivity. A direct comparison of the morphologies of the blend and block copolymer systems can then be performed using the inherent neutron contrast
between the dP3HT and PF. Additionally, observations from other P3AT-b-PFTBT systems will be discussed and their implications on potential future directions for this research. Finally some concluding remarks on the implications of the work are included in Chapter 8.

References


7. efficiency_chart.jpg (JPEG Image, 4108 x 2456 pixels) - Scaled (19%). at <http://www.nrel.gov/ncpv/images/efficiency_chart.jpg>


Chapter 2

Background

The field of organic photovoltaics is expansive with diverse work on various aspects of the challenges associated with making high efficiency devices. All-polymer solar cells, of which block copolymer devices are a subset, are a fraction of the work that has been performed in this field. The goal of this section is to provide the context and backdrop for the work and inform the reader of the synthetic methods used to create these materials as well their use in device applications. The synthetic protocols related to this work and recent work in organic photovoltaic devices is reviewed. Particular emphasis is paid to recent progress in all polymer devices and previous studies of conjugated block copolymers.
2.1. Material Synthesis

Figure 2.1: Conjugated polymers used in this work.

A key feature of most semiconductive polymers is continuous conjugation along the backbone of the polymer. Figure 2.1 shows the polymers used in this work. P3HT is a very commonly used polymer in organic photovoltaic devices.\textsuperscript{1-6} P3DDT is a related polymer with a longer side chain that lowers the crystallization temperature of the polythiophene from 220°C to about 150°C.\textsuperscript{7,8} PF is a commonly used polymer in organic light emitting diodes and PFTBT is a polymer that has been used in devices with P3HT.\textsuperscript{9-19} While a variety of well controlled synthetic methods are available to synthesize non-conjugated polymers, including atom transfer radical polymerization (ATRP), reversible addition–fragmentation chain-transfer polymerization (RAFT), anionic polymerization, and ring opening polymerization, fewer methods exist for controlled polymerization for polymers with a conjugated backbone.\textsuperscript{20-22} Therefore many conjugated polymers must be synthesized by less controlled condensation polymerizations.\textsuperscript{23,24} For controlled polymerizations of aromatic compounds, there are generally some restrictions on the monomers for successful polymerization.\textsuperscript{5,25,26} However, condensation polymerizations are very
general and can access a wide variety of monomers, with solubility of the resulting product being the chief limitation on the molecular weights that can be accessed.\textsuperscript{23,24}

Synthesis of block copolymers may be done using any combination of these techniques by sequential polymerization, where a functional group allows the second polymer to be grown from the first or allows it to end-cap another polymerization. Alternatively, each polymer may be synthesized separately with functional groups that allow them to be joined together in a third reaction.\textsuperscript{27–30} For all of these cases, it is critical that the starting materials be well functionalized.

**Figure 2.2: Living polymerization methods for conjugated polymers.\textsuperscript{3,31–33}**

Relatively few living polymerization methods exist for conjugated polymers. The primary class involves nickel catalyzed polymerization of simple cyclic molecules such as thiophenes, including Grignard methathesis (GRIM)\textsuperscript{33}. According to McCullough, the reaction proceeds along a ring-walking process where the catalyst couples the growing chain end then displaces the terminal bromine for the next reaction step.\textsuperscript{25} Because the chain end is growing, it is possible to introduce a Grignard reagent as an end-capping compound for this reaction.\textsuperscript{32,34} This reaction has been also shown to be amenable to external initiation by functionalized
catalysts for a variety of applications, including growing polymer brushes from surfaces and providing functionality that can be used to couple various polymers together to make block copolymers.\textsuperscript{3,35,36} Unfortunately the monomers that can be used in GRIM are somewhat limited, so additional research is being done on other protocols. One example is the chain growth (tBu\textsubscript{3}P)Pd(Ph)Br catalyzed Suzuki-Miyaura reaction which has been used for living polymerization of polyfluorenes and polythiophenes enabling complex structures such as polymer brushes.\textsuperscript{36–38}

![Suzuki Coupling](image1)

![Stille Coupling](image2)

**Figure 2.3: Schematics of Suzuki and Stille cross coupling reactions.\textsuperscript{23,24}**

Many polymers for organic electronics are synthesized using polycondensation routes because of the relative versatility of the reagents that can be used.\textsuperscript{39–42} Figure 2.3 shows two of the more popular routes to conjugated polymers, the Suzuki and Stille cross coupling reactions. In both of these routes, aryl groups are coupled randomly in the reaction mixture and polydisperse products result. In the case of the Suzuki reaction, aryl bromine and aryl boronic acid are used in equimolar concentrations in the presence of a palladium catalyst and an aqueous base with the polymer in the organic phase. In the case of Stille, no base is required and the boronic acid compound is replaced by organostannane reagent. Because of the uncontrolled nature of these polymerizations, products are conventionally
washed with various solvents to fractionate the sample and remove low molecular weight components. In this work, we use the Suzuki coupling route to make our block copolymers by taking advantage of a terminal aryl bromide from GRIM polymerizations or by adding an excess of functionalized end-capping agents to the Suzuki reaction mixture after the reaction has proceeded for a set amount of time.

Figure 2.4: Copper Catalyzed Azide-Alkyne Click (CuAAC) Reaction and Glaser Coupling reaction.

Click chemistry generally refers to a set of highly efficient and specific reactions used in organic chemistry. As depicted in Figure 2.4, one of the more popular reactions used in polymer chemistry is the copper catalyzed azide-alkyne click (CuAAC) reaction. This reaction has been used to synthesize a wide variety of block copolymers including conjugated polymers linked to non-conjugated flexible polymers. While highly effective, CuAAC has one significant side reaction, Glaser coupling; however this can be avoided through proper selection of ligand for the copper catalyst. For our work, we have generally functionalized a polythiophene with an alkyne group and the polyfluorene with an azide group; however the choice is based on synthetic convenience and, with some changes in the protocol, the functional groups could be swapped if desired.
2.2. Organic Photovoltaic Devices

Figure 2.5: Various organic materials used in OPVs and their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) Energy Levels $^{10,50-53}$

There are several different types of organic materials that can be used to create organic electronic devices such as OPVs. These range from small molecules, through nanomaterials such as fullerenes, up to polymers.$^{54-58}$ Figure 2.5 shows some typical materials used in OPV devices. PPV derivatives are a versatile class of polymers with tuning of energy levels being accomplished through substituents.$^{59}$ P3HT and related polymers are the archetype for study due to its ease of synthesis and good solubility properties.$^{25,32,35,46,64}$ PTB7 is a broadly absorbing polymer that is of contemporary interest having made devices with efficiencies on the order of 7%.$^{52}$ PFTBT is an example of an ambipolar polymer with the ability to transport either positive or negative charges and can be made into functional devices with both P3HT where it acts as an electron transporting material and PCBM where it...
acts as a positive charge carrier. PNDIT is one of the relatively few electron transporting polymers currently synthetically available. PCBM is the most commonly used fullerene (C60) derivative used as an electron transporting material, but other derivatives such as ICMA are also used. State of the art devices are typically composed of more complicated conjugated polymers and a soluble fullerene, usually a C70 derivative such as PC71BM.

One important factor in the selection of these materials is the offset between the highest occupied molecular orbital (HOMO) of the electron acceptor and lowest unoccupied molecular orbital (LUMO) of the donor. The way these systems work is slightly different than what is typically seen in inorganic solar cells. Whereas in an inorganic system a photon will hit the active material and excite an electron into the conduction band generating free charge carriers (electrons for negative charges and holes for positive charges), the organic system has a long lived state called an "exciton" or bound electron/hole pair. This exciton must diffuse through the active material until it finds an interface between the electron conducting component (acceptor) and the hole conducting component (donor). Once the interface is found, the charges may dissociate and be conducted to one of the electrodes, if there is a continuous path. However if an interface is not found before a certain length of time, the electron in the exciton will relax and fall back to its ground state, emitting a photon. Likewise, the charge may find an interface again and recombine, emitting a photon. The length scale corresponding to this time is on the order of 10-20 nanometers; therefore there is considerable interest in manufacturing devices that have this as their characteristic length scale. Although
typical solar cells use a single donor and a single acceptor component, some reports use multiple donor materials to broaden the absorption spectrum of the device.\textsuperscript{56}

Coincident with the development of the work presented herein, all-polymer devices have enjoyed a steady increase in performance and are presently on par with some traditional polymer/fullerene devices.\textsuperscript{70} Work on the P3HT/PFTBT system has shown considerable improvement from 1.8\% in 2007 to 2.7\% efficiency in 2012 with higher molecular weight polymers driving increases in efficiency by reducing phase separation.\textsuperscript{10,71} Studies using resonant soft X-ray scattering have been performed showing optimal polymer blends with domain spacing on the average of about 7 nm.\textsuperscript{72} A copolymer based on naphthalene diimide and selenophene as the acceptor recently achieved an efficiency of 3.3\%.\textsuperscript{51} Work based on perylene diimide has resulted in an even higher efficiency device reaching 4\% in an all polymer device.\textsuperscript{61} Solvent additives have been shown to also improve performance of these devices similar to improvements in the polymer/fullerene system.\textsuperscript{73} Morphology is of critical importance in these all polymer systems and maintaining small domains requires novel approaches.\textsuperscript{70,74–76}

While there are many reports that use block copolymers as interfacial modifiers or template materials, relatively few use them as active components.\textsuperscript{6,60,77} A non-conjugated class of block copolymers of relevance includes conductive groups, such as fullerene, pendant to the polymer chain, where these are used as compatibilizers.\textsuperscript{62,78–80} In an early demonstration, an ABA triblock copolymer was used by Jenekhe and coworkers to create a microphase separated structure with
efficient energy transfer. Work by Sun and coworkers used a blocky copolymer based on PPV with a donor - bridge – acceptor motif with the bridge consisting of an insulating linker segment. The block copolymer greatly increased the open circuit voltage (from 0.1 V to 1.1 V) and short circuit current (from 0.017 mA/cm$^2$ to 0.058 mA/cm$^2$) relative to the donor/acceptor blend. An all polymer device based on a block copolymer of P3HT and poly(naphthalene bisimide) produced an efficiency of 1.3%. Block copolymers consisting of P3HT and naphthalene diimide have also been synthesized and studied. A highly relevant work on a ternary blend of P3HT/PFTBT homopolymers and its block copolymer found increased stability with increasing annealing temperature achieving similar performance for the homopolymer blend and the ternary block copolymer system. Other reports have focused on other optoelectronic properties of very pure P3HT-$b$-PFTBT and related block copolymers. Our own work on the P3HT-$b$-PFTBT system resulted in a 3% efficiency, the highest for an all-polymer device at the time. Overall, block copolymers continue to be a promising route to the control of phase separation in these block copolymer systems.

2.3. References


49. Duxbury, C. J., Cummins, D. & Heise, A. Glaser coupling of polymers: Side-reaction in Huisgens ‘click’ coupling reaction and opportunity for polymers


Chapter 3

Synthesis and Crystallinity of Conjugated Block Copolymers prepared by Click Chemistry

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Authors: Kendall A. Smith¹, Yen-Hao Lin¹, Dana B. Dement¹, Joseph Strzalka², Seth B. Darling³, Deanna L. Pickel⁵, Rafael Verduzco¹*

¹ Rice University, Department of Chemical and Biomolecular Engineering, MS-362, 6100 Main Street, Houston, Texas 77005-1892

² X-ray Science Division, Argonne National Laboratory, Argonne, Illinois 60439

³ Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439
Conjugated block copolymers have the potential to improve solution processed optoelectronic devices such as organic photovoltaics (OPVs), but significant synthetic challenges exist and systematic studies investigating structure-property relationships are lacking. We demonstrate a new route to conjugated block copolymers via copper-catalyzed click coupling and apply this method to synthesize a series of poly(3-hexylthiophene)-\textit{block}-poly(9,9-dioctylfluorene) (P3HT-\textit{b}-PF) conjugated block copolymers with varying block weight fractions. The resulting block copolymers are comprised of two conjugated polymers joined by a flexible, non-conjugated linker. The series of conjugated block copolymers prepared enables an investigation into the role of polymer block lengths and composition on crystallization and self-assembly behavior. Grazing incidence wide-angle X-ray scattering measurements indicate the formation of highly oriented P3HT and/or PF crystallites in thermally annealed block copolymer films. Crystallization of either P3HT or PF blocks is predominant in all block copolymers studied, but at intermediate ratios crystallization of both blocks is observed.
3.1. Introduction

Conjugated polymers are solution-processable materials that can serve as key components in organic electronic devices, including bulk-heterojunction organic photovoltaics (OPVs), organic thin-film transistors, and organic light-emitting diodes.\(^1\)–\(^3\) Significant effort has been devoted to understanding and directing their mesoscale and nanoscale structure in order to optimize their optoelectronic properties for use in organic electronic materials and devices.\(^4\)–\(^8\) Conjugated block copolymers contain two or more conjugated polymer blocks and may enable simplified approaches to controlling the microstructure of conjugated polymer thin films.\(^9\)–\(^13\) These materials can potentially prevent large-scale phase separation in organic semiconductor blends and define thermodynamically stable nanostructures through micro-phase segregation, providing a path to optimal active layer structures for bulk heterojunction OPVs with good long term stability. Donor-acceptor conjugated block copolymers which contain both hole-conductive (p-type) and electron-conductive (n-type) polymer blocks can be used directly in an OPV, but relatively few examples exist and limited information on the microstructure of these materials is available. Recent work has demonstrated improved performance and nanoscale self-assembly in donor-acceptor conjugated block copolymers,\(^14\),\(^15\) and crystalline nanofibers and micro-phase segregation have been observed in conjugated block copolymer systems.\(^15\)–\(^25\) However, more versatile synthetic methods are needed to access block copolymers with targeted block lengths and desired optoelectronic properties.

Conjugated block copolymers have been synthesized via a macroreagent approach that utilizes two distinct polymerization reactions\(^16\),\(^26\)–\(^29\) or through sequential monomer
addition using a controlled polymerization reaction, such as Grignard metathesis (GRIM)\textsuperscript{24,30-32} or catalyst-transfer Suzuki-Miyaura polymerization.\textsuperscript{33,34} While these latter approaches have several practical advantages, the macroreagent approach has been more popular for the synthesis of donor-acceptor conjugated block copolymers\textsuperscript{14,17,28} since the preparation of donor and acceptor conjugated block copolymers typically requires distinct polymerization reactions. However, the macroreagent approach typically gives poor control over the sizes of each polymer block. Previous work by us\textsuperscript{16,35} and others\textsuperscript{14,36} has relied on a Suzuki-Miyaura or Stille polycondensation reaction, which are uncontrolled polymerization reactions and give final products with block lengths dependent on polymer solubility and reaction conditions. Furthermore, the macroreagent approach typically yields block copolymers with significant homopolymer impurities, requiring tedious purification methods to isolate pure block copolymer.\textsuperscript{16,36}

An alternative route to conjugated block copolymers is to couple two conjugated polymers, which have been independently synthesized, by an efficient chemical reaction. This gives better control over block lengths since each block is synthesized, purified, and characterized prior to coupling. Click coupling reactions, in particular copper(I) catalyzed cycloadditions, have been successfully applied as post-polymerization coupling reactions to make rod-coil block copolymers\textsuperscript{37-41} and block copolythiophenes\textsuperscript{42} but not for the preparation of donor-acceptor conjugated block copolymers. This synthetic route provides block copolymers with a non-conjugated linker, whereas most previous work has primarily focused on materials with continuous conjugation between the blocks. One example of conjugated donor/acceptor polymer jointed by a non-conjugated linker has been reported.
The sample showed co-crystallization of the constituent blocks and improved photovoltaic performance relative to blends of the corresponding homopolymers.43,44

Herein, we demonstrate a click coupling approach for the synthesis of poly(3-hexylthiophene) – block – poly(9,9-dioctylfluorene) (P3HT-b-PF) conjugated block copolymers. This method is used to prepare a series of P3HT-b-PF block copolymers with varying composition. The resulting block copolymers consist of two conjugated polymers linked by a non-conjugated segment. The microstructure of the block copolymers is characterized using a combination of differential scanning calorimetry (DSC) and grazing incidence wide/small angle X-ray scattering (GIWAXS/GISAXS) to establish qualitative relationships between block lengths and phase behavior of the materials. We find that crystallization of one block is predominant in the film microstructure for all block copolymers studied, but near 50 % weight ratios, crystallization of both blocks is achieved. Since the electronic properties of conjugated polymers are known to be correlated with crystallinity, these results suggest that conjugated block copolymers with balanced block ratios may be optimal for use in polymer OPVs.

3.2. Results and Discussion

3.2.1. Synthesis of Conjugated Diblock Copolymers via Click Chemistry

The approach used to prepare conjugated block copolymers involves copper(I) catalyzed alkyne-azide click coupling of two conjugated polymers. P3HT and PF were chosen for this study, but the general synthetic procedure can be applied to a wide range of polymers made by GRIM and Suzuki-Miyaura polycondensation. Alkyne end-functionalized
P3HT with a targeted molecular weight and relatively low polydispersity (PDI) was synthesized via GRIM using previously reported procedures (Table 3.1, P3HT1 and P3HT2). As discussed in a recent publication, these materials were found to be unstable in oxygen and were used immediately or stored under vacuum in the dark to prevent degradation.

<table>
<thead>
<tr>
<th>Name</th>
<th>Synthesis Method</th>
<th>SEC-MALLS Analysis</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w$ (kg/mol)</th>
<th>PDI</th>
<th>$^1$H NMR Analysis</th>
<th>Mass per end group (kg/mol)</th>
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</thead>
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<tr>
<td>1 PF1</td>
<td>Suzuki-Miyaura-Pd[PPh$_3$]$_4$</td>
<td>8.2</td>
<td>5.3</td>
<td>1.55</td>
<td></td>
<td>33.</td>
<td></td>
</tr>
<tr>
<td>2 PF2</td>
<td>Suzuki-Miyaura-Pd[t-Bu$_3$P]$_2$</td>
<td>7.4</td>
<td>3.6</td>
<td>2.05</td>
<td></td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>3 PF3</td>
<td>Suzuki-Miyaura-Pd[t-Bu$_3$P]$_2$</td>
<td>11.5</td>
<td>5.5</td>
<td>2.03</td>
<td></td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td>5 P3HT1</td>
<td>GRIM</td>
<td>12.</td>
<td>11.</td>
<td>1.04</td>
<td></td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>6 P3HT2</td>
<td>GRIM</td>
<td>6.9</td>
<td>6.1</td>
<td>1.12</td>
<td></td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1 P3HT and PF homopolymer samples prepared

The preparation of a series of PF polymers of varying molecular weight and controlled end-functionality is a more significant challenge. Previous studies on block copolymers that incorporate a PF block have primarily focused on short (3 kg/mol) PF blocks synthesized using Pd[PPh$_3$]$_4$ catalyst. In more recent work, Yokozawa et al. reported a chain-growth polymerization reaction for the synthesis of PF using a modified Pd catalyst with a t-Bu$_3$P ligand. This is a more active catalyst and enables the room-temperature polycondensation of poly(dialkyl fluorenes) and other monomers. Here, we use modifications of these prior strategies to prepare a series of hydroxyl-functionalized...
PFs (PF-OH). In the first approach (Scheme 3.1a), PF-OH was synthesized via Suzuki-Miyaura polycondensation in toluene using Pd[PPh₃]₄ catalyst and 4-bromobenzyl alcohol as an endcapper. As shown in Table 3.1, PF-OH produced using this method (PF1) has a broad molecular weight distribution, as expected for a Suzuki-Miyaura polycondensation reaction. ¹H NMR analysis shows the final product is end-functionalized (Figure 3.1), and as discussed below the endgroup can be modified for click coupling to P3HT-alkyne.

In the second approach, a modified Pd catalyst with protected hydroxyl functionality is prepared and used to initiate Suzuki-Miyaura polycondensation (Scheme 3.1b). This approach is similar to that reported previously by Yokozawa et al.⁴⁹ with a silane-protected hydroxyl functionality incorporated into the catalyst. The catalyst is synthesized in a one-step reaction with Pd[t-Bu₃P]₂. Due to the more active t-Bu₃P ligand, the Suzuki-Miyaura polymerization can be carried out at room temperature in the presence of a mild base. After polymerization, the silane-protecting group is removed by addition of n-tetrabutyl ammonium fluoride (TBAF) to yield PF-OH. As indicated in Table 3.1, the PF samples produced using this approach are not well-controlled with respect to polydispersity. The broad molecular weight distribution suggests that the bulky silane-protecting group or the presence of excess endcapper may interfere with the catalyst-transfer mechanism reported previously for a similar catalyst.⁴⁹ For all PF polymers produced using this method (PF2, PF3, and PF4), ¹H NMR indicates the presence of a hydroxyl endgroup.
Scheme 3.1: Preparation of PF-OH and PF-N₃. a) Preparation of PF-OH via Pd[PPh₃]₄-catalyzed Suzuki-Miyaura polymerization. 4-Bromobenzyl alcohol is added at the start of the reaction (7 mol %) then after polymerization in excess to quench the reaction. b) Preparation of PF-OH via Suzuki-Miyaura using modified Pd catalyst with t-Bu₃P ligand. c) Preparation of PF-N₃ by coupling PF-OH with azido acetic acid.

The degree of end-functionality can be assessed by comparing the molecular weight obtained from ¹H NMR with SEC-MALLS analysis, which provides an absolute molecular weight. For PF2 and PF3, ¹H NMR and SEC-MALLS indicate a high degree of functionalization since the molar content of polymer endgroups estimated by ¹H NMR is in good agreement with SEC-MALLS analysis. For PF1 and PF4, the large molecular weight estimate from NMR indicates that a significant amount of unfunctionalized PF is present, and this was also confirmed by MALDI-TOF MS analysis (see Figure S3.1 and Figure S3.2). Thus, the modified synthetic methods used for the preparation of PF-OH yield a mixture of functionalized and unfunctionalized polymer for PF1 and PF4.
Figure 3.1. $^1$H NMR spectra for polymeric intermediates and block copolymers. a) PF-OH (PF1) produced via Pd[PPh$_3$]$_4$-catalyzed Suzuki-Miyaura polycondensation. b) PF-OH (PF2-4) produced via Suzuki-Miyaura polymerization using modified Pd catalyst with t-Bu$_3$P ligand. c,d) PF-N$_3$ resulting from coupling of PF-OH with azido acetic acid. e,f) P3HT-$b$-PF conjugated block copolymers resulting from click coupling of PF-N$_3$ with alkyne-terminated P3HT.

With these limitations in mind, all four PF samples were used in the preparation of conjugated block copolymers. All PF polymers contain end groups which can be modified for click coupling. As shown in Scheme 3.1c, PF-N$_3$ is prepared by coupling PF-OH with azido acetic acid. $^1$H NMR reveals a shift of the terminal $\alpha$-hydroxy protons, indicating complete conversion of the hydroxyl end group to an azide end group (Figure 3.1c and d). Next, click coupling of P3HT-alkyne and PF-N$_3$ (Scheme 3.2) was carried out in THF in the presence of Cu(I)Br and PMDETA. An excess of the PF macrorreagent (20 mol % based on $^1$H NMR ratio of repeat unit to end group) was added to ensure full reaction of the P3HT-
alkyne and to compensate for any errors in estimates of functionalization. After the reaction was complete, typically less than 8 h or overnight, the product was run through an alumina column, precipitated in hexanes, and washed with boiling hexanes to remove unreacted PF. This was carried out with 5 different combinations of P3HT-alkyne and PF-N₃ to yield a series of P3HT-b-PF block copolymers (Table 3.2).

Scheme 3.2: Preparation of P3HT-b-PF via copper-catalyzed azide-alkyne click chemistry.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Source Polymers</th>
<th>Mass % P3HT by NMR</th>
<th>Mₜ (kg/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT79-b-PF21</td>
<td>PF2, P3HT1</td>
<td>79%</td>
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<td>1.22</td>
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<td>P3HT64-b-PF36</td>
<td>PF1, P3HT1</td>
<td>64%</td>
<td>17.</td>
<td>1.27</td>
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<tr>
<td>P3HT52-b-PF48</td>
<td>PF3, P3HT2</td>
<td>52%</td>
<td>17.</td>
<td>1.53</td>
</tr>
<tr>
<td>P3HT32-b-PF68</td>
<td>PF1, P3HT2</td>
<td>32%</td>
<td>18.</td>
<td>1.38</td>
</tr>
<tr>
<td>P3HT23-b-PF77</td>
<td>PF4, P3HT2</td>
<td>23%</td>
<td>19.</td>
<td>1.50</td>
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</tbody>
</table>

Table 3.2 P3HT-b-PF conjugated block copolymer samples

The composition, purity, and molecular weight distributions of the final block copolymer products can be determined by ¹H NMR and SEC with both MALLS and UV/VIS detection. In all cases, SEC-RI revealed a shift in the molecular weight distribution of the polymeric product relative to the starting macromonomers (see Figure 3.2a and Figure S3.3).
SEC with UV/VIS detection can be used to detect homopolymer impurities and measure the molecular weight distribution for each polymer block separately (see Experimental section for details of this analysis). A representative example of SEC-UV/VIS analysis is shown for P3HT64-b-PF36 in Figure 3.2b and Figure 3.2c, and a good match in the molecular weight distributions and at two distinct wavelengths indicates pure block copolymer product with little or no residual homopolymer. A similar shift in the UV/VIS trace at 450 nm was observed for P3HT79-b-PF21 and P3HT52-b-PF48, which indicates complete reaction of the P3HT macroreagent. As expected, block copolymers resulting from the coupling of PF2 and PF3 gave results consistent with the molecular weights of the corresponding homopolymers.

![Graph showing SEC analysis](image)

**Figure 3.2.** SEC analysis of P3HT64-b-PF36 and corresponding P3HT and PF macroreagents. a) SEC-RI analysis showing a shift in the molecular weight distribution of the final block copolymer relative to the P3HT and PF macroreagents. b) SEC-UV/VIS analysis at 450 nm showing a shift in the molecular weight distribution of the P3HT block relative to the starting P3HT macroreagent. c) SEC-UV/VIS analysis at 300 nm (corrected for the absorbance of the P3HT block) showing a shift in the molecular weight distribution of the PF block relative to starting PF1 macroreagent.

In the case of block copolymers resulting from the coupling of PF1 and PF4, the measured molecular weight of the final block copolymers is inconsistent with the
constituent homopolymers. This may due to the presence of homopolymer impurities caused by unfunctionalized PF chains in PF1 and PF4. High molecular weight homopolymer impurities might remain after solvent washing. Additionally, extensive solvent washing may bias the distribution by removing lower molecular weight block copolymer. Thus, obtaining precursor materials that have a high degree of functionality remains a significant obstacle to obtain well-defined materials via this route. However, in all cases, a clear shift is observed in the SEC-RI and corrected 300 nm UV/VIS traces, indicating the formation of block copolymer product. SEC analysis shows that block copolymer is the major product resulting from coupling, and $^1$H NMR analysis shows the P3HT content in the block copolymer series varies from 23 wt % up to 79 wt %. As a result, while residual homopolymer impurities were present in some samples, this synthetic method enables the preparation of a series of conjugated block copolymers with systematic variation of the block ratios.

3.2.2. Crystallization of Conjugated Block Copolymers

Both crystallization and chain orientation impact charge transport in conjugated polymer thin films. In the case of P3HT, larger charge mobilities are correlated with increased crystallinity due to improved $\pi$ stacking, and the highest charge mobilities are measured in the direction parallel to the $\pi$ stacking direction and along the polymer backbone. However, several polymers with exceptional performance in bulk heterojunction OPVs have been found to have a low degree of crystallinity. In some cases, thermal annealing decreases the performance of OPV devices, and the optimal performance is thought to depend on phase separation and organization at hierarchical length scales.
As a result, in conjugated block copolymers, crystallization of one or both blocks may impact performance. The series of conjugated block copolymers prepared in this study enables an investigation into the role of polymer block lengths and composition on crystallization and self-assembly behavior.

**DSC measurements (Figure 3.3)**

Figure 3.3) indicate a crystal melting transition near 230 °C for P3HT1, 200 °C for P3HT2, and 150 °C for PF polymers. P3HT-\(b\)-PF block copolymers show a peak corresponding to P3HT at either 230 °C or 200 °C, depending on the source polymer used. The temperature of the thermal transition corresponding to P3HT does not change in the block copolymers relative to the source P3HT homopolymers and is present in all P3HT-\(b\)-PF block copolymers studied. A peak corresponding to PF crystal melting is only present in block copolymers with PF as the majority block but not for block copolymers with majority P3HT. Thus, the crystallization of PF is suppressed in P3HT-\(b\)-PF when the P3HT weight fraction is greater than 52 %.
Figure 3.3. Differential Scanning Calorimetry (DSC) analysis for P3HT1, P3HT2, PF3, and P3HT-b-PF block copolymers. All PF homopolymers studied here show a crystallization transition near 150 °C.

GIWAXS analysis was carried out to examine the characteristics and orientation of crystallites present in the samples. Samples were heated at or above 230 °C to melt any crystals present and then subsequently cooled to 100 °C for measurement. Samples subjected to five days of 1,2-dichlorobenzene solvent annealing were also investigated, but did not show as strong crystallization as the thermally annealed samples. As shown in Figure 3.4, crystallites were found for all samples, with qualitatively different diffraction
patterns observed with changing block ratios. These diffraction patterns correspond to those of either pure P3HT or PF, as shown in the Supporting Information Figure S3.4 and Figure S3.5. For block copolymers that contain majority P3HT (P3HT79-b-PF21, P3HT64-b-PF36, P3HT52-b-PF48), P3HT crystallites dominate the morphology. GIWAXS reveals characteristic (100), (200), and (300) peaks oriented along the $q_z$ axis, normal to the substrate. These peaks correspond to spacing between the backbones through the alkyl side-chains, and the GIWAXS scattering pattern indicates an in-plane π-π stacking direction, typical of regioregular P3HT.\textsuperscript{51,52} PF crystallization is suppressed for P3HT79-b-PF21 and P3HT64-b-PF36, but some evidence of weak PF crystallinity can be seen for P3HT52-b-PF48. Conversely, for block copolymers with a majority PF block, P3HT32-b-PF68 and P3HT23-b-PF77, PF crystallinity is predominant. The pattern observed corresponds to the α-phase of PF previously seen in oriented PF fibers.\textsuperscript{56,57}

Some evidence for P3HT crystallinity is apparent in P3HT32-b-PF68, but exclusively PF crystallites are detected in P3HT23-b-PF77. Line cuts of the GIWAXS data, provided in Figure S3.5 confirm this observation. This indicates that thin film confinement may play a role in suppressing some P3HT crystallization, reflected by DSC measurements of all bulk samples (Figure 3.3).
Figure 3.4. GIWAXS patterns for P3HT-b-PF block copolymer films thermally annealed at 230 °C and measured at 100 °C at an incidence angle of 0.25°. Materials with high PF content show crystallinity characteristic of highly ordered PF crystallites while block copolymers with a high P3HT content show exclusively P3HT crystallites. P3HT52-b-PF48 and P3HT32-b-PF68 films show evidence for both P3HT and PF crystals.

These results indicate that competitive crystallization occurs in P3HT-b-PF. While some indication of crystallization of both blocks is seen in block copolymers with roughly balanced block weight fractions, most samples indicate the predominance of one type of crystallite. Transmission electron microscopy and X-ray diffraction studies of the α-phase of PF indicate that chains are not organized in a face-to-face packing structure,\textsuperscript{8,56} in contrast to the structure of P3HT crystallites. This mismatch between crystal structures and confinement in a thin film may explain the predominance of one type of crystallite in the samples studied. These results are consistent with previous studies of double-crystalline diblock copolymers which found that the crystallization behavior could be broadly tuned by changing the composition of the block copolymer and, in some cases, competitive crystallization occurs.\textsuperscript{58–61} These results are also consistent with previous work from our group on P3HT conjugated block copolymers with conjugation across the linker.\textsuperscript{16,35} In general, the majority block is observed to dominate crystallization or
suppress crystallization of the second block.\textsuperscript{35} In the case of P3HT-\textit{b}-PF reported here, similar behavior is observed, and crystallization of both blocks is only possible when the block weight fractions are in balance, with P3HT wt % ranging between 32 and 52. This suggests that the flexible linker has a relatively small impact on film morphology and polymer crystallization. Also, based on the good match in the peak positions for P3HT-\textit{b}-PF and pristine P3HT and PF homopolymer films, we infer that crystalline domains in the block copolymer films consist of pure P3HT or PF polymer blocks, which suggests that phase-separation between the polymer blocks occurs during crystallization.

Extensive temperature-dependent measurements were performed on P3HT\textsubscript{23}-\textit{b}-PF\textsubscript{77}, which has a majority PF block (Figure 3.5). The as-cast sample is largely featureless, but upon heating to 175 °C, above the crystallization temperature of PF but below that of P3HT, and cooling back to room temperature, only faint crystal peaks emerge. The sample was subsequently heated to 220 °C, above the crystallization temperature for both constituent polymer blocks, before cooling down to room temperature, resulting in ordered PF crystallite peaks. The sample was then heated to 230 °C to completely melt any P3HT crystals and slowly cooled while measuring at 170 °C, 160 °C, 150 °C, and 100 °C. While the final GIWAXS pattern appears to indicate only PF crystallites are present, heating the film above the crystallization temperature of P3HT is necessary to achieve well-oriented PF crystallite peaks. This suggests that, consistent with DSC measurements, some P3HT crystallites may be present in as-cast films and play a role in the PF crystallization kinetics in thin films.
Figure 3.5. Temperature-dependent GIWAXS analysis of P3HT23-b-PF77 film at an incidence angle of 0.25°. The film was measured sequentially from left to right: a) as-cast, b) heat to 175°C and c) return to room temperature. Then d) heat to 175 °C, e) continue heating to 220 °C and hold for several hours before returning to room temperature, f) heat to 230 °C allowing all crystal features to melt, and slowly cool to g) 170 °C, h) 160 °C, i) 150 °C, and j) 100 °C.

No clear evidence for micro-phase segregation was observed by GISAXS (see Figure S3.6). Samples subjected to thermal annealing and solvent annealing in the presence of 1,2-dichlorobenzene at room temperature and 150 °C failed to give any indication of an ordered nanostructure. The lack of a self-assembled mesophase may be due to the high crystallization temperatures of the polymers or the specific processing conditions chosen.

Crystallization of both blocks in double crystalline block copolymers has been previously reported for a range of non-conjugated block copolymers in both the strong
and weak segregation regimes as well as for block co-polythiophenes.\textsuperscript{15,19,22–24,31,32} P3HT based block copolymers with one non-conjugated block typically exhibit a crystalline, nanowire morphology characteristic of P3HT crystallites,\textsuperscript{41,46,63–66} and previous work with donor/acceptor conjugated block copolymers has typically found exclusive crystallization of the P3HT block.\textsuperscript{14,16} The results reported here demonstrate that crystallization of both blocks in conjugated block copolymers can be achieved by proper balance of the molecular weight ratios. This may be important for achieving optimal active layer morphology and favorable electronic properties in all-polymer OPVs and other organic electronic devices. Crystallization of P3HT is correlated with high charge carrier mobilities and improved performance in a photovoltaic device, and, depending on the second polymer block chosen, crystallization of the second polymer block may be less important.\textsuperscript{53–55} This work also highlights the challenges in achieving a self-organized structure in conjugated block copolymers. High crystallization temperatures and long relaxation times may require modification of conventional annealing procedures to achieve micro-phase segregation. Future work will focus on tailoring the properties of conjugated block copolymer films and on the development of new annealing procedures for achieving self-organization.
3.3. Conclusion

Herein, we have demonstrated a new route for synthesis of conjugated block copolymers using click chemistry. The principle advantage of this synthetic route is the ability to characterize and/or purify the starting materials fully before the coupling reaction, and a single starting polymer may be coupled with multiple different products to give a variety of materials. Obtaining precursor materials that have a high degree of chain-end functionality remains a significant obstacle to obtaining well-defined materials by this route. While we are able to obtain reasonably well-defined materials by removing the highly soluble PF impurities, not all block copolymer systems will be able to take advantage of differential solubility. We find that in P3HT-\textit{b}-PF, crystallization of the majority block is predominant at extreme block ratios, and at intermediate ratios crystallization of both blocks occurs. The resulting crystallites are highly aligned with an in-plane π stacking direction for P3HT crystallites and the observation of a PF β-phase for PF crystallites. Micro-phase segregation was not observed in any of the thermally annealed samples. The thin film structure observed is similar to that of conjugated block copolymers with conjugation across the linker, indicating that the presence of a flexible linker does not have a significant impact on film morphology or polymer crystallization.
3.4. Acknowledgments

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3.5. Experimental

3.5.1. Instrumentation

3.5.1.1. Nuclear Magnetic Resonance Spectroscopy (NMR)

Solution $^1$H NMR spectroscopy was performed on a 500 MHz Varian Inova NMR spectrometer and a Bruker 400 MHz multinuclear spectrometer. Chloroform-d
(CDCl₃, Cambridge Isotope Laboratories) was used as the solvent with TMS (0.05%) as an internal standard. Data was processed using SpinWorks 3.1.8.1.⁶⁷

3.5.1.2. Size-Exclusion Chromatography (SEC)

Polymer molecular weights and polydispersities (PDIs) were obtained by 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, a Wyatt Technology HELEOS II multi-angle laser light scattering (MALLS) detector ($\lambda$=658 nm), and a Wyatt Technology Optilab reX RI detector. This system enables SEC with simultaneous refractive index (SEC-RI), UV/VIS (SEC-UV/VIS), and MALLS (SEC-MALLS) detection. THF was used as the mobile phase at a flow rate of 1 mL/min at 40 °C. Weight average molecular weights ($M_\text{w}$) are determined by light scattering with $dn/dc$ values calculated assuming 100% mass recovery of the injected sample. Polydispersity (PDI) was determined using SEC-RI calibrated with a set of monodisperse polystyrene standards (Astra Software Version 5.3.4).

The molecular weight distributions for each polymer block and corresponding homopolymer impurities can be obtained by SEC-UV/VIS analysis at two distinct wavelengths. First, by using a wavelength specific to one polymer block, we can obtain the molecular weight distribution for one block only. In the case of P3HT-b-PF, 450 nm is specific to P3HT since PF has negligible absorbance at this wavelength. Next, SEC-UV/VIS analysis at a second wavelength sensitive to both polymer blocks can be corrected to obtain the molecular weight distribution of the second block. In the case of P3HT-b-PF, analysis at 300 nm is sensitive to both
blocks, but the contribution of P3HT to the signal is subtracted using the 450 nm SEC-UV/VIS trace and the absorbance ratio for P3HT at 450 nm relative to 300 nm, measured independently to be 5.4. The 300 nm absorbance trace presented in Figure 3.2 and Figure S3.3 is the result of this subtraction and reflects the molecular weight distribution of the PF blocks only.

3.5.1.3. MALDI-TOF MS

MALDI-TOF MS spectra were collected using a Bruker Daltonics Autoflex II mass spectrometer, which is equipped with an N₂ laser, (λ = 337 nm) operating at a frequency of 25 Hz and an accelerating voltage of 20 kV. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (>98%, TCI) was used as the matrix. Solutions of DCTB (20 mg/mL) and the analyte (10 mg/mL) were prepared in THF and then mixed in a 10:2 ratio. A volume of 1 μL was applied to the target via the dried droplet method. Mass spectra were collected in reflectron mode, and the instrument was externally calibrated with polystyrene standards.

3.5.1.4. Differential Scanning Calorimetry (DSC)

Thermograms were recorded on a TA Instruments DSC 2920 equipped with a refrigerated cooling system against an empty sealed pan as reference. In a typical run, the sample was heated to 250 ºC at 5 ºC/min, cooled to 40 ºC at 5 ºC/min, then equilibrated for 10 min before heating to 250 ºC at 5 ºC/min. Second heating cycles are reported.
3.5.1.5. Grazing Incidence Small/Wide Angle X-ray Scattering (GISAXS/GIWAXS)

Grazing incidence small/wide angle X-ray scattering measurements were carried out on Sector 8 at the Advanced Photon Source, Argonne National Laboratory.\textsuperscript{69} Beamline 8-ID-E operates at an energy of 7.35 keV and images were collected from a Pilatus 1MF camera (Dectris), with two exposures for different vertical position of the detector. After flatfield correction for detector nonuniformity, the images are combined to fill in the gaps for rows at the borders between modules, leaving dark only the columns of inactive pixels at the center. Using the GIXSGUI package for Matlab (Mathworks), data are corrected for X-ray polarization, detector sensitivity and geometrical solid-angle.\textsuperscript{70} For GIWAXS, the beam size is 200 µm (h) × 20 µm (v), and the sample detector distance is 204 mm. For GISAXS, the beam size is 100 µm (h) × 50 µm (v), and the sample detector distance is 2185 mm. Sample measurement and thermal annealing were carried out under vacuum, with the sample stage interfaced with a Lakeshore 340 unit.

3.5.2. Materials

Anhydrous tetrahydrofuran (THF), 1,3-bis(diphenylphosphino)propane]dichloronickel(II) (Ni[dppp]Cl\textsubscript{2}), isopropylmagnesium chloride (\textsuperscript{6}PrMgCl) 2M in THF, ethynylmagnesium bromide 0.5 M in THF, 9,9-diocetyl-2,7-dibromofluorene, 9,9-diocetylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, 4-bromobenzyl alchohol, phenylboronic acid, magnesium sulfate (MgSO\textsubscript{4}), copper(I) bromide (CuBr), 18-crown-6, cesium fluoride
(CsF), N,N,N’,N”’,N”’ pentamethylene-triamine (PMDETA), 4-bromophenethyl, imidazole, tetrakis(triphenylphosphine) palladium(0) (Pd[PPh₃]₄), bis(tri- tert-butylphosphine) palladium(0) (Pd[t-Bu₃P]₂), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), 4(dimethylamino) pyridine (DMAP), 1.0 M tetrabutylammonium fluoride solution in THF (TBA), and sodium azide were obtained from Aldrich and used as received. 2,5-dibromo-3-hexylthiophene, 7'-bromo-9',9'-dioctyl-fluoren-2'-yl-4,4,5,5,-tetramethyl-[1,3,2]dioxaborolane and azido acetic acid were synthesized as previously described.³¹-³³ Alkyne-terminated P3HT was synthesized by a method described elsewhere.⁴⁶

3.5.2.1. Hydroxyl-Functionalized Poly(9,9-dioctylfluorene) (PF-OH) via Pd[PPh₃]₄-Catalyzed Suzuki-Miyaura Polycondensation

In a typical procedure, 2.1 g (3.6 mmol) 7'-bromo-9',9'-dioctyl-fluoren-2-yl-4,4,5,5,-tetramethyl-[1,3,2]dioxaborolane, 46 mg (0.25 mmol) 4-bromobenzyl alcohol, and 50 mg (43 µmol) Pd[PPh₃]₄, were added to a Schlenk tube and degassed under vacuum followed by backfilling with nitrogen. A mixture of purged toluene (10 ml), water (10 ml) and aliquot 336 (a few drops) were then added by cannula. The vessel was reacted for 22 hours at 90 °C after which 0.25 g (1.3 mmol) of 4-bromobenzyl alcohol was added to quench the reaction. The reaction was allowed to proceed an additional 20 hours followed by addition of 0.27 g (2.2 mmol) of phenylboronic acid. The polymer was precipitated into methanol and washed with acetone overnight in a Soxhlet extractor followed by collection in dichloromethane to give product (1). Yield: 1.4 g :¹H NMR (CDCl₃, ppm) δ = 7.84 (d, 2 nH, Ar—H), 7.71
(d, 2nH, Ar—H), 7.68 (s, 2nH, Ar—H), 2.13 (m, 4nH, Ar—C—CH2—), 1.30-1.00 (m, 20nH, —CH2—), 0.85 (m, 4nH, —CH2—), 0.82 (t, 6nH, —CH3), 4.79 (s, 2H, Ar—CH2—OH)

3.5.2.2.

1-bromo-4-[2-[[1,1-dimethylethyl]dimethylsilyloxy]ethyl]benzene

4-bromophenethyl alcohol (2.5 g, 12.6 mmol) was dissolved in 6 mL dry DMF in a 25 mL round-bottom flask. The solution was purged with N2 before adding t-butyl dimethyl silane (2.47 g, 16.4 mmol). Imidazole (2.24 g, 32.8 mmol) was dissolved in 10 mL DMF in a separate flask. Both flasks were cooled to 0 °C in an ice bath before transferring the imidazole solution to the reaction flask by cannula. The reaction solution was stirred at r.t. for 4 hours before quenching by the addition of water and hexanes, collecting the organic layer, and drying over MgSO4. The final product was purified by column chromatography (5% ethyl acetate/hexanes) to collect 1.91 g (48 % yield) of a clear oil. 1H NMR (CDCl3, ppm) δ = 7.39 (d, 2H, Ar—H), 7.08 (d, 2H, Ar—H), 3.78 (t, 2H, Ar—CH2—CH2—O—Si), 2.76 (t, 2H, Ar—CH2—CH2—O—Si), 0.86 (s, 9H, Si—C—CH3), -0.02 (s, 6H, Si—CH3)

3.5.2.3. t-Bu3Pd[PhCH2CH2OSi(CH3)2C(CH3)3]Br

In a typical procedure, Pd[t-Bu3P]2 (21.5 mg, 0.042 mmol) was dissolved in 0.2 mL toluene in an inert atmosphere glovebox, and an excess of 1-bromo-4-[2-[[1,1-dimethylethyl]dimethylsilyloxy]ethyl] benzene (170 mg, 0.539 mmol) was
added. The solution was stirred at 75 °C for two hours and then allowed to cool to room temperature. The crude product was used without purification.

3.5.2.4. Hydroxyl-Functionalized Poly(9,9-dioctylfluorene) (PF-OH) via t-Bu3Pd[PhCH2CH2OSi(CH3)2C(CH3)3]Br-Catalyzed Suzuki-Miyaura Polymerization

7’-bromo-9’,9’-dioctyl-fluoren-2-yl-4,4,5,5,-tetramethyl-[1,3,2]dioxaborolane (0.51 g, 0.86 mmol) was dissolved in 30 mL THF along with 18-crown-6 (1.56 g, 5.9 mmol), CsF (0.4.0 g, 3.1 mmol), and 1.5 mL DI water. The monomer solution was purged with N2 for 30 minutes before adding the crude product solution from the preparation of t-Bu3Pd [PhCH2CH2OSi(CH3)2C(CH3)3]Br. The solution was stirred overnight at room temperature before quenching with 1 mL of 5M HCl. The polymer was recovered by precipitation in methanol and washed with copious amounts of acetone. To remove the silane protecting group, the solid product was re-dissolved in THF (15 mL) at room temperature and 0.2 mL TBAF was added. The solution was stirred overnight before recovering the polymeric product by precipitation in methanol to collect a light green solid. Yield: 194 mg, 52 % (2): 1H NMR (CDCl3, ppm) δ = 7.84 (d, 2 nH, Ar—H), 7.71 (d, 2 nH, Ar—H), 7.68 (s, 2 nH, Ar—H), 2.13 (m, 4 nH, Ar—C—CH2—), 1.30-1.00 (m, 20 nH, —CH2—), 0.85 (m, 4 nH, —CH2—), 0.82 (t, 6 nH, —CH3), 3.92 (t, 2H, Ar—CH2—CH2—OH), 2.95 (t, 2H, Ar—CH2—CH2—OH)
3.5.2.5. Azide-Functionalized PF (PF-N₃)

In a typical procedure, 1.4 g (0.14 mmol) of PF-OH was dissolved in dichloromethane at room temperature and 107 mg of EDC (0.54 mmol) and 21 mg (0.17 mmol) of DMAP was added followed by 136 mg of azido acetic acid (1.3 mmol). The reaction was allowed to proceed overnight at room temperature, and the resulting solution was then washed with water. The organic phase was collected and the solvent removed in a rotary evaporator. The product was recovered by precipitation in methanol and dried under vacuum.

PF-N₃ (PF1): δ = 7.84 (d, 2nH, Ar—H), 7.71 (d, 2nH, Ar—H), 7.68 (s, 2nH, Ar—H), 2.13 (b, 4nH, Ar—C—CH₂—), 1.30-1.00 (m, 20nH, —CH₂—), 0.85 (b, 4nH, —CH₂—), 0.82 (t, 6nH, —CH₃), 5.31 (s, 2H, Ar—CH₂—OOC—), 3.95 (s, 2H, Ar—CH₂—OOC—CH₂—N₃).

PF-N₃ (PF2-4): ¹H NMR (CDCl₃, ppm) δ = 7.84 (d, 2nH, Ar—H), 7.71 (d, 2nH, Ar—H), 7.68 (s, 2nH, Ar—H), 2.13 (m, 4nH, Ar—C—CH₂—), 1.30-1.00 (m, 20nH, —CH₂—), 0.85 (m, 4nH, —CH₂—), 0.82 (t, 6nH, —CH₃), 4.48 (t, 2H, Ar—CH₂—CH₂—OOC—), 3.89 (s, 2H, —CH₂—OOC—CH₂—N₃), 3.07 (t, 2H, Ar—CH₂—CH₂—COO)

3.5.2.6. P3HT-b-PF via Copper-Catalyzed Azide-Alkyne Click Coupling

PF-N₃ were reacted with alkyne-terminated P3HT in a click coupling reaction to give P3HT-b-PF. In a typical reaction, 0.15 g of P3HT (Mₙ=6 kDa, 0.025 mmoles) was reacted with an excess of PF (1.2X based on NMR determined functionality) in the presence of CuBr (14 mg, 0.1 mmol) in THF (35 mL) and 0.1 ml of N,N,N',N''-
pentamethyldiethylenetriamine. P3HT, PF, CuBr, and THF were mixed in air in a 50ml flask, purged by needle with nitrogen for 30 min before addition of the PMDETA. The reaction was allowed to proceed for at least 8 h at 40 °C. Reaction vessel contents were passed through an alumina column to remove excess copper, and the reaction products were concentrated before precipitation into hexanes. The precipitate was then collected and washed with boiling hexanes to remove excess PF.

P3HT-\textit{b}-PF (P3HT64-\textit{b}-PF36 and P3HT32-\textit{b}-PF68): \textsuperscript{1}H NMR (CDCl\textsubscript{3}, ppm) \(\delta = 7.84\) (d, 2\textit{n}H, Ar\textendash H), 7.71 (d, 2\textit{n}H, Ar\textendash H), 7.68 (s, 2\textit{n}H, Ar\textendash H), 6.98 (s, 1\textit{m}H, Ar\textendash H), 2.80 (t, 2\textit{m}H, Ar\textendash CH\textsubscript{2}―), 2.13 (b, 4\textit{n}H, Ar\textendash C\textendash CH\textsubscript{2}―), 1.50-1.00 (m, (20\textit{n}+11\textit{m})H, \textendash CH\textsubscript{2}―), 0.85 (m, 4\textit{n}H, \textendash CH\textsubscript{2}―), 0.82 (t, 6\textit{n}H, \textendash CH\textsubscript{3}), 5.33 (s, 2H, Ar\textendash CH\textsubscript{2}―OOC―), 5.29 (s, 2H, \textendash CH\textsubscript{2}―OOC―CH\textsubscript{2}―N\textsubscript{3}C\textsubscript{2}H).

P3HT-\textit{b}-PF (P3HT79-\textit{b}-PF21, P3HT52-\textit{b}-PF48, and P3HT23-\textit{b}-PF77): \textsuperscript{1}H NMR (CDCl\textsubscript{3}, ppm) \(\delta = 7.84\) (d, 2\textit{n}H, Ar\textendash H), 7.71 (d, 2\textit{n}H, Ar\textendash H), 7.68 (s, 2\textit{n}H, Ar\textendash H), 6.98 (s, 1\textit{m}H, Ar\textendash H), 2.80 (t, 2\textit{m}H, Ar\textendash CH\textsubscript{2}―), 2.13 (b, 4\textit{n}H, Ar\textendash C\textendash CH\textsubscript{2}―), 1.50-1.00 (m, 20\textit{n}+11\textit{m}H, \textendash CH\textsubscript{2}―), 0.85 (m, 4\textit{n}H, \textendash CH\textsubscript{2}―), 0.82 (t, 6\textit{n}H, \textendash CH\textsubscript{3}), 5.25 (s, 2H, \textendash OOC―CH\textsubscript{2}―N\textsubscript{3}C\textsubscript{2}H) 4.51 (t, 2H, Ar\textendash CH\textsubscript{2}―CH\textsubscript{2}―OOC), 3.06 (t, 2H, Ar\textendash CH\textsubscript{2}―CH\textsubscript{2}―OOC).

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3.7. Supporting Information

Figure S3.1: MALDI-TOF MS spectra of PF-OH produced via Pd(PPh3)4-catalyzed Suzuki-Miyaura polycondensation (same method as PF1) prior to conversion to the azide. A mixture of functionalized and unfunctionalized PF were observed, which is consistent with the larger molecular weight estimates by $^1$H NMR.
Figure S3.2: MALDI-TOF MS spectra of PF-OH produced via Suzuki-Miyaura polymerization using modified Pd catalyst with t-Bu3P (same method as PF2-4) prior to conversion to the azide. Results show approximately 50% functionality with significant amounts of TDMS protected OH groups in good agreement with $^1$H NMR for this sample.
Figure S3.3. Differential refractive index (SEC-RI) and absorbance measurements (SEC-UV/VIS) for all P3HT-b-PF block copolymers and corresponding P3HT-alkyne and PF-N3 macroreagents. All traces are normalized for clarity. SEC-UV/VIS absorbance traces for block copolymers reflect the molecular weight distribution of one polymer block only. For analysis of P3HT block, measurement at 450 nm is used. For analysis of PF block, measurement at 300 nm is used and corrected for P3HT absorbance, as described in the Experimental section. For the PF homopolymer in P3HT23-b-PF77, differential refractive index data has been replaced by the UV signal at 254 nm due to noise in the differential refractive index data.
Figure S3.4: GIWAXS of pure P3HT and pure PF films.
Figure S3.5: GIWAXS linecuts along qz for selected block copolymers. P3HT crystal peak at qz = 0.36 Å⁻¹ and PF crystal peak at 0.48 Å⁻¹.
Figure S3.6. GISAXS measurements of solvent and thermally annealed polymer films.
Chapter 4

Conjugated Block Copolymers via Functionalized Initiators and Click Chemistry


Kendall A. Smith,\textsuperscript{a} Deanna L. Pickel,\textsuperscript{b} Kevin Yager\textsuperscript{c}, Kim Kisslinger\textsuperscript{c}, and Rafael Verduzco\textsuperscript{a}

\textsuperscript{a}Rice University, Department of Chemical and Biomolecular Engineering, MS-362, 6100 Main Street, Houston, Texas 77005-1892

\textsuperscript{b}Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
Conjugated block copolymers are potentially useful for organic electronic applications and the study of interfacial charge and energy transfer processes; yet few synthetic methods are available to prepare polymers with well-defined conjugated blocks. Here, we report the synthesis and thin film morphology of a series of conjugated poly(3-hexylthiophene)-block-poly(9,9-dioctylfluorene) (P3HT-b-PF) and poly(3-dodecylthiophene)-block-poly(9,9-dioctylfluorene) (P3DDT-b-PF) block copolymers prepared by functional external initiators and click chemistry. Functional group control is quantified by proton nuclear magnetic resonance spectroscopy, size-exclusion chromatography, and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. The thin film morphology of the resulting all-conjugated block copolymers is analyzed by a combination of grazing-incidence X-ray scattering, atomic force microscopy, and transmission electron microscopy. Crystallization of the P3HT or P3DDT blocks is present in thin films for all materials studied, and P3DDT-b-PF films exhibit significant PF/P3DDT co-crystallization. Processing conditions are found to impact thin film crystallinity and orientation of the π-π stacking direction of polymer crystallites.

**KEYWORDS** Conjugated block copolymers, click chemistry, organic photovoltaics, self-assembly, block copolymers, P3DDT, P3HT, PFO
4.1. Introduction

Conjugated block copolymers (BCPs) are comprised of two or more π-conjugated polymer blocks and are promising for use in organic electronic applications.\textsuperscript{1–4} Recent work has demonstrated the potential of conjugated BCPs for use in organic photovoltaics (OPVs), and they may also be useful for organic light-emitting diodes (OLEDs), thin film transistors, and microelectronics.\textsuperscript{5–7} Furthermore, understanding the mechanism of charge separation at the interface between donor and acceptor organic semiconductors remains a challenge for the development of OPVs, and conjugated BCPs provide a way to control this interface through the covalent linking of two conjugated polymers.\textsuperscript{8} However, further progress requires addressing both synthetic and processing challenges. Only a handful of examples of conjugated BCPs with both p-type and n-type polymer blocks have been reported, and the relationship between different processing steps and film microstructure – including polymer crystallinity and microphase segregation – remains unclear.\textsuperscript{7,9–11}

Conjugated polymers are typically made by step-growth or condensation polymerization reactions, which provide little control over the final polymer molecular weight and polydispersity. All-conjugated BCPs are typically synthesized using one or more condensation polymerization steps, making it difficult to synthesize well-defined all-conjugated BCPs. An alternative is to use a controlled polymerization method along with sequential monomer addition, but this is applicable to a limited set of monomers.\textsuperscript{12–14} Click chemistry can provide an efficient
method to couple conjugated macrorereagents and can give control over both block molecular weights independently. The application of click chemistry to synthesize conjugated BCPs has been limited due to the difficulty in obtaining functionalized materials from polycondensation reactions and removing homopolymer impurities. However, recent synthetic innovations have demonstrated improved control over the functionality of conjugated polymers through the use of functional external initiators. This method enables the preparation of well-defined macrorereagents for use in click coupling reactions to prepare conjugated BCPs.

Here, we demonstrate an efficient click coupling route for the synthesis of conjugated BCPs using functionalized initiators for both blocks, and the resulting materials are used to study the effects of processing conditions on film microstructure. A series of poly(3-hexylthiophene)-block-poly(9,9-dioctylfluorene) (P3HT-b-PF) and poly(3-dodecylthiophene)-block-poly(9,9-dioctylfluorene) (P3DDT-b-PF) BCPs are prepared, and functionality of the precursor materials is quantified by proton nuclear magnetic resonance spectroscopy (1H NMR), size-exclusion chromatography (SEC), and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). 1H NMR was used to monitor conversion of functional groups during each reaction step. The microstructure of P3DDT-b-PF and P3HT-b-PF films is analyzed by grazing-incidence X-ray scattering (GIXS) and transmission electron microscopy (TEM), and we find significant co-crystallization of both blocks for P3DDT-b-PF but predominantly P3HT crystallization for P3HT-b-PF BCPs. This may be due to a mismatch of crystal melting temperatures or of crystal lattice spacings for P3HT and PF polymer blocks.
4.2. Results and Discussion

The use of functionalized initiators has been shown to be an effective route for the synthesis of functional polythiophenes and polyfluorenes. Grignard metathesis polymerization (GRIM) initiated by a functionalized nickel catalyst results in well-defined polythiophenes with good control over the functionality.\textsuperscript{15,17} Functionalized polyfluorenes can be synthesized through catalyst-transfer Suzuki-Miyaura polymerization initiated by a functionalized Pd catalyst.\textsuperscript{13,16} Together, these chemistries provide routes to separately synthesize alkyne and azide functionalized polythiophenes and polyfluorenes which can subsequently be coupled using click chemistry. Click chemistry provides an efficient means to couple polymeric materials together, but requires that the starting materials be well functionalized in order for the final BCPs to be well defined. Thus, we extensively characterized the precursor materials described herein. Synthesis of the alkyne functionalized P3AT was recently described so this work will focus more on the synthesis of the azide functionalized PF. Characterization of both materials is more extensive than the previous report.\textsuperscript{17}
Scheme 4.1: Synthetic scheme for the preparation of P3AT-alkyne, PF-azide, and P3AT-b-PF block copolymers.

Our overall synthetic approach to prepare conjugated BCPs is shown in Scheme 4.1. Alkyne-functionalized poly(3-alkylthiophene) (P3AT) is prepared through the use of a functionalized nickel catalyst with protected hydroxyl functionality. This details of this synthesis were recently described.\textsuperscript{17} P3AT with a hydroxyl functionality is obtained after polymerization and deprotection, and the functional group is subsequently converted to an alkyne through a Steglich esterification with 5-hexynoic acid. The resulting alkyne-functionalized polythiophenes were found to have good stability, solubility, and reactivity in click reactions with azide-functionalized poly(ethylene glycol).\textsuperscript{17} This procedure was applied to the synthesis of both P3HT-alkyne and P3DDT-alkyne (Table 4.1). $^{1}H$ NMR analysis reveals the presence of a hydroxyl group after polymerization and
deprotection, and a clean shift in the peaks is observed after conversion to the alkyne (Figure 4.1A).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ MALLS (kg mol$^{-1}$)</th>
<th>PDI SEC-RI</th>
<th>DP SEC$^a$</th>
<th>DP $^1$H NMR$^b$</th>
<th>Functionalit y MALDI (%)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT1</td>
<td>11.9</td>
<td>1.23</td>
<td>72</td>
<td>88</td>
<td>62±6</td>
</tr>
<tr>
<td>P3HT2</td>
<td>7.3</td>
<td>1.20</td>
<td>44</td>
<td>41</td>
<td>71±2</td>
</tr>
<tr>
<td>P3DDT1</td>
<td>17.1</td>
<td>1.25</td>
<td>68</td>
<td>109</td>
<td>80±5</td>
</tr>
<tr>
<td>P3DDT2</td>
<td>9.2</td>
<td>1.20</td>
<td>37</td>
<td>43</td>
<td>91±3</td>
</tr>
<tr>
<td>PF1</td>
<td>4.9</td>
<td>1.49</td>
<td>13</td>
<td>13</td>
<td>96±1</td>
</tr>
<tr>
<td>PF2</td>
<td>6.2</td>
<td>1.75</td>
<td>16</td>
<td>31</td>
<td>42±0</td>
</tr>
</tbody>
</table>

Table 4.1: Characteristics of conjugated polymer macroreagents. $^a$ DP calculated from MALLS $M_n$ divided by repeat unit molecular weight. $^b$ DP calculated from the relative integrated intensities of aromatic hydrogens to polymer functional group hydrogens. $^c$ Reported percent functionality is relative abundance of all polymer species containing desired functional groups averaged over at least three mer distributions with deviation from these values.

Azide-functionalized poly(9,9-dioctyfluorene) (PF-azide) is prepared through the use of an externally added, functionalized palladium catalyst. As detailed in Scheme 4.1, the palladium catalyst Pd(t-Bu$_3$P)$_2$ is reacted with (1) using a method similar to those described by Yokozawa et al.$^{14}$ The resulting Pd complex initiates the polymerization of (2) resulting in tosylate-functionalized PF (PF-tosylate). The tosylate functional group is converted to an azide in a one-step reaction with tert-butyl ammonium fluoride (TABF) and azidotrimethylsilane in chloroform, yielding PF-azide after precipitation, filtration, and washing with methanol and acetone. This procedure was applied to synthesize two PF-azide polymers, and $^1$H NMR analysis indicates quantitative transformation of PF-tosylate to PF-azide (Figure 4.1B).
Figure 4.1: $^1$H NMR of A) PF-tosylate and PF-azide, B) P3AT-OH and P3AT-alkyne, and C) final P3AT-b-PF product
The degree of functionality can be analyzed using a combination of $^1$H NMR, SEC-MALLS, and MALDI-TOF. As shown in Figure 4.1, NMR peaks corresponding to the expected functional groups are present for hydroxyl and alkyne functionalized polythiophenes and tosylate and azide-functionalized PFs. $^1$H NMR provides an estimate of polymer molecular weight through comparison of the integrated intensities of peaks corresponding to protons on the functional group and main-chain backbone. By comparing $^1$H NMR molecular weight estimates to SEC-MALLS estimates, the degree of functionality can be estimated. The molecular weight estimates by $^1$H NMR and SEC are in good agreement for all macroreagents except for P3DDT1 and PF2 (Table 4.1). For these samples, the higher DP estimates from $^1$H NMR analysis reflects incomplete functionalization, roughly 62 % and 52 % on a molar basis for P3DDT1 and PF2, respectively. Table 4.1 also shows that higher molecular weight polymers (P3HT1, P3DDT1, and PF2) have a lower degree of functionality as compared to lower molecular weight polymers P3HT2, P3DDT2, and PF1.

MALDI-TOF MS provides an independent measurement of the degree of functionality of P3AT and PF polymers. MALDI-TOF MS indicates the desired functionalized product is the major product for all P3AT polymers, and the degree of functionality ranges from 60 – 90 %. The percent functionality is calculated based on the monoisotopic peak of each major distribution for a particular mer. As detailed in Supporting Information (Table S4.1 and Table S4.2), at least three mer distributions are chosen and an average and standard deviation is calculated. The results of this calculation are generally lower than that predicted by $^1$H NMR and
SEC-MALLS, but comparable to previous studies that have found significant variability in the degree of functionality for P3HT depending on the structure of the nickel initiator.\textsuperscript{18} The MALDI-TOF technique samples from the lower molecular weight spectrum of the polymers, therefore it is possible that MALDI-TOF reflects poor functionality only in the lower-molecular weight fraction of the polymer samples. Consistent with the measurements by \textsuperscript{1}H NMR and SEC-MALLS, MALDI-TOF measurements show a higher degree of functionality for P3DDT2 and P3HT2 compared with P3DDT1 and P3HT1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ MALLS (kg mol$^{-1}$)</th>
<th>PDI SEC-RI</th>
<th>P3AT (wt %)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT1-b-PF1</td>
<td>15.8</td>
<td>1.19</td>
<td>78</td>
</tr>
<tr>
<td>P3HT1-b-PF2</td>
<td>13.9</td>
<td>1.24</td>
<td>78</td>
</tr>
<tr>
<td>P3HT2-b-PF2</td>
<td>8.3</td>
<td>1.33</td>
<td>52</td>
</tr>
<tr>
<td>P3DDT1-b-PF1</td>
<td>25.1</td>
<td>1.27</td>
<td>84</td>
</tr>
<tr>
<td>P3DDT1-b-PF2</td>
<td>22.9</td>
<td>1.36</td>
<td>82</td>
</tr>
<tr>
<td>P3DDT2-b-PF2</td>
<td>11.9</td>
<td>1.31</td>
<td>65</td>
</tr>
</tbody>
</table>

Table 4.2: Characteristics of Conjugated Block Copolymers $^a$ P3AT wt % determined by integrating aromatic regions of BCP to obtain the relative degree of polymerization and the respective molecular weight of the P3AT and PF repeat units.

As can be seen in Table 4.12 and Figure 4.2, MALDI-TOF shows a high degree of functionality for PF1. For this polymer, the estimated DP calculated from the MALLS molecular weight is in good agreement with the DP measured by \textsuperscript{1}H NMR and in agreement with the expected DP based on the monomer to catalyst ratio. For PF2, we targeted a polymer molecular weight twice that of PF1 by adjusting the catalyst to monomer ratio, but SEC-MALLS indicates that PF2 and PF1 have comparable molecular weights. \textsuperscript{1}H NMR and SEC-MALLS indicate poor functionality, and MALDI-TOF indicates a significant amount of OH functionalized product as an
impurity (see Table S4.1 and Table S4.2 in Supporting Information). Our previous work has shown poor functionality for PF with molecular weights greater than 7 kg mol$^{-1}$. Thus, for the reaction conditions detailed herein, we obtain PF with a high degree of functionality and controlled molecular weight determined by the catalyst to monomer ratio only for polymer chains with an average molecular weight of 5 kg mol$^{-1}$.

Figure 4.2: MALDI-TOF analysis of PF1-tosylate.
Figure 4.3 Size exclusion chromatography data for P3DDT2-b-PF2. A) differential refractive index (SEC-RI), B) UV-VIS absorbance signal for P3DDT2 block (measured at 500 nm), and C) UV-VIS absorbance signal for PF2 block (measured at 300 nm and corrected for the contribution of P3DDT2).

P3AT-b-PF BCPs are synthesized using a copper-catalysed click reaction between PF-azide and P3AT-alkyne, and the resulting products are summarized in Table 4.2. Although PF1 and PF2 have similar molecular weights, they differ with respect to functionality and were both investigated in the synthesis of BCPs. The click coupling reaction is carried out in the presence of copper(I)bromide and PMDETA in a THF solution under a nitrogen atmosphere at 40°C. A modest excess of the PF reagent is utilized as this reagent is easily removed in subsequent processing by washing the BCP product with hexanes. Successful coupling is revealed through both $^1$H NMR (Figure 4.1 and Supporting Information Figure S4.10 - Figure S4.15) and SEC analysis (Figure 4.3 and Supporting Information Figure S4.1). As shown in Figure 4.3 and Figure S4.1, SEC traces of the BCP show significant shifts to shorter elution times as compared to the macroreagents by both RI detection and by UV absorbance at wavelengths selective for each block. Due to the similarities in molecular weight between PF1 and PF2, relatively small differences are observed
when comparing BCPs that only differ in the PF macroreagent used. A significant difference in the final BCP molecular weight and composition is observed for BCPs that differ in the P3HT or P3DDT macroreagent used in the synthesis. For example, the molecular weight difference between P3HT1-b-PF2 and P3HT2-b-PF2 corresponds to the molecular weight difference between P3HT1 and P3HT2, roughly 4.6 kg mol\(^{-1}\), and the P3HT content of P3HT1-b-PF2 is higher by 26 wt %.

The BCPs generally have lower molecular weights than the sum of the corresponding homopolymer, which may be due to the presence of homopolymer impurities in the final products. We expect that most of the homopolymer impurities are P3HT or P3DDT homopolymer since PF is removed by washing with hexanes.

A comparison of the film morphologies of the synthesized BCPs gives some insight into the role of polymer block ratios and the crystallization behaviour of the constituent polymer blocks. Previous work has found that P3HT crystallization typically dominates thin film morphology for BCPs with one P3HT block.\(^{19-21}\) In P3HT-b-PF all-conjugated BCPs, we determined that P3HT tends to dominate the crystallization at larger weight fractions of P3HT and likewise PF at low P3HT weight fractions, with co-crystallization being seen between about 30-50 wt % P3HT.\(^{16,22}\) With the materials presented herein, we can compare P3HT and P3DDT all-conjugated BCPs. Since P3DDT has a crystallization temperature similar to that of PF, we expect that BCPs of these materials may allow for enhanced competition between the crystallization of the P3AT and PF blocks. Additionally, the larger size of the P3DDT unit cell may be more compatible with the crystal structure of PF.
Figure 4.4: GIWAXS analysis of BCP films after thermal annealing at 230°C.

Polymer film samples were heated above 230°C then slowly cooled to room temperature. GIWAXS images in Figure 4.4 and corresponding line cuts in Figure S4.2 can be analysed to assess crystallization of each block in the block copolymer. Crystallization of each block is determined by observing the characteristic peaks at $q_z = 0.38$, $0.77$, and $1.14$ for P3HT, $q_z = 0.22$, $0.46$, $0.68$, and $1.14$ for P3DDT, and $q_z = 0.5$ for PF. While P3HT and PF have readily distinguished peaks, peaks for P3DDT and PF overlap but can be readily distinguished in the line cuts (see Supporting Information Figure S4.2). Crystallinity of the PF block is suppressed for copolymers where the P3HT is the majority block, and crystallization of both blocks is observed for a ratio near 50 wt % P3HT, similar to our previous report. However for P3DDT2-b-PF2, which is 62 % P3DDT, we see both crystal forms which suggests that the molecular weight ratio may not be the deciding factor for whether both crystals may...
be observed. A very weak PF peak can also be discerned in the line cut for P3DDT1-\textit{b}-PF2 (82% P3DDT). The lower crystallization temperature of P3DDT or the larger size of the monomer unit may be responsible for the observed co-crystallization of P3DDT and PF polymer blocks. Analysis of the polymers by DSC is detailed in Supporting Information (Figure S4.3). As an example, the DSC for P3HT2-\textit{b}-PF2 and its constituent polymers is shown in Figure 4.5. The transitions associated with the P3HT block (200-220°C) are very evident and are at temperatures similar to those of the constituent homopolymer, however there is only a broad and weak transition (see inset) spread from 105-155°C that may be attributable to PF. In general, BCPs show thermal transitions at temperatures similar to their P3AT constituents. For copolymers containing P3DDT, the location of the thermal transition for the P3DDT block (150-175°C for P3DDT1 and 120-150°C for P3DDT2) overlaps significantly with that of the PF (110-145°C) making evaluation of PF crystallization in the BCP difficult by DSC.

![Differential scanning calorimetry curves](image)

**Figure 4.5** Differential scanning calorimetry curves from second heating cycle of PF2, P3HT2, and P3HT2-\textit{b}-PF2.
A variety of annealing conditions were investigated including solvent annealing in the presence of vapor chloroform for 5 days, as well as 24 hours of annealing at 165°C. Additionally, casting conditions were varied to cast from room temperature chloroform and refluxing chloroform. Results for all these conditions may be found in Supporting Information Figure S4.4 and Figure S4.5. As detailed in Figure 4.6, casting from refluxing chloroform resulted in some randomization of the orientation of crystals evidenced in GIWAXS, particularly evident in the secondary reflections for the as cast samples. Heating to 230°C effectively erases the initial morphology and the usual out-of-plane orientation of the spacing between crystallites through alkyl-side chains is observed. As expected, this case of high temperature annealing followed by slow cooling gives rise to very good order with the π stacking peak clearly visible. Lower-temperature annealing conditions give rise to orientation distributions of the P3HT component that deviate markedly from that observed for pure P3HT thin films. This tunability of the ordering has implications for applications in organic electronics. For example the P3HT component has anisotropic hole mobility: for transistor applications one would want to emphasize the out-of-plane lamellae orientation so as to enhance in-plane conduction; whereas for photovoltaic applications one would instead want to emphasize the in-plane lamellae orientation so as to enhance out-of-plane mobility.23
Figure 4.6 GIWAXS analysis for P3DDT2-\textsubscript{b}-PF2 under different processing conditions. First row shows samples cast from room temperature chloroform while second row shows samples cast from refluxing chloroform. Columns denote as cast films, 165°C and 230°C thermally annealed films, and films annealed in presence of chloroform vapor for five days at room temperature.

Figure 4.7: Comparison of AFM and TEM images for P3HT1-\textsubscript{b}-PF1.

Assessment of GISAXS data in Supporting Information (Figure S4.6) shows a weak peak for the P3HT-\textsubscript{b}-PF, but none for P3DDT-\textsubscript{b}-PF. This may be due to the
reduced contrast between the P3DDT block and PF relative to that of P3HT. As
detailed in Figure 4.7, a comparison of TEM and AFM images of P3HT1-b-PF1
reveals that this peak may be due to scattering of regularly sized P3HT crystallites
embedded in an amorphous matrix. As detailed in Supporting Information (Figure
S4.7), no such crystallites are seen by TEM in P3DDT-b-PF although topologies
similar to those of P3HT-b-PF are seen in AFM. Uneven patches are observed in all
P3DDT-b-PF samples; however these do not appear to be macroscopic phase
separation as elemental analysis shows uniform changes in both sulfur and carbon
signals suggesting that the patterns are due to variations in film thickness and/or
density (Figure S4.8). As shown in Supporting Information Figure S4.9, an AFM
survey of other samples show similar results showing few if any differences in
topology based on the block size or processing conditions and no evidence of
ordered nanostructures. This suggests that a periodic nanostructure characteristic
of microphase segregation is not observed for these materials under any of the
processing conditions tested, and crystallization of one or both blocks is the
predominant characteristic of thin film morphology.

4.3. Conclusions

Herein, we demonstrated a synthetic route for preparing P3AT-b-PF block
copolymers using click chemistry. P3AT and PF macroreagents are prepared
through the use of functionalized, external initiators, and subsequent modification
provides PF-azide and P3AT-alkyne macroreagents. This method enabled control
over the molecular weight of the P3AT block, but only allowed for the synthesis of relatively short PF polymer blocks for incorporation into block copolymers.

The resulting P3AT-b-PF were cast from room temperature and refluxing chloroform and subjected to a variety of annealing conditions. GIWAXS showed that P3DDT-b-PF shows more significant co-crystallization of both polymer blocks compared with P3HT-b-PF. This may be due to a closer match in the crystal melting temperatures of P3DDT (140°C) and PF (130°C) compared with the higher crystal melting temperature of P3HT (220 °C). Alternatively, co-crystallization of P3DDT-b-PF may indicate a better match in crystal lattice spacings of P3DDT and PF. The casting temperature during film preparation affected the orientation of P3AT crystallites. Cast at room temperature, P3AT-b-PF films exhibit a typical out-of-plane stacking direction for spacing between polymer chains through the alkyl-side chains and an in-plane π-π stacking direction. For samples cast from refluxing chloroform, crystalline orientation exhibits no preferred orientation, but annealing at 230°C results in a crystalline orientation similar to room-temperature cast films. Analysis of samples by AFM show a microphase separated morphology with length scales on the order of tens of nanometers, but no clear ordered nanostructure. TEM images of P3HT-b-PF show P3HT crystallites distributed in an amorphous matrix. Overall, the results show polymer crystallization is the predominant feature of P3AT-b-PF films.
4.4. Acknowledgements

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4.5. Experimental

4.5.1. Instrumentation

4.5.1.1. Nuclear Magnetic Resonance Spectroscopy (NMR)

Solution $^1$H NMR spectroscopy was performed on a 500 MHz Varian Inova NMR. Chloroform-d (CDCl$_3$, Cambridge Isotope Laboratories) was used as the solvent with TMS (0.05%) as an internal standard. Data was processed using SpinWorks 3.1.8.1.$^{24}$
4.5.1.2. Size-Exclusion Chromatography (SEC)

Polymer molecular weights and polydispersities (PDIs) were obtained by 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, a Wyatt Technology HELEOS II multi-angle laser light scattering (MALLS) detector (λ=658 nm), and a Wyatt Technology Optilab reX RI detector. This system enables SEC with simultaneous refractive index (SEC-RI), UV/VIS (SEC-UV/VIS), and MALLS (SEC-MALLS) detection. THF was used as the mobile phase at a flow rate of 1 mL/min at 40 °C. Weight average molecular weights (M\text{w}) are determined by light scattering with dn/dc values calculated assuming 100% mass recovery of the injected sample. Polydispersity (PDI) was determined using SEC-RI calibrated with a set of monodisperse polystyrene standards (Astra Software Version 5.3.4).


MALDI-TOF spectra were collected using a Bruker Daltonics Autoflex II mass spectrometer, which is equipped with an N\textsubscript{2} laser (λ = 337 nm), operating at a frequency of 25 Hz and an accelerating voltage of 20 kV. trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (>98%, TCI) was used as the matrix. Solutions of DCTB (20 mg/mL) and the analyte (10 mg/mL) were prepared in THF and then mixed in a 10:2 ratio. A volume of 1 μL was applied to the target via the dried droplet method. Mass spectra were collected in
reflection mode, and the instrument was externally calibrated with polystyrene standards.

### 4.5.1.4. Differential Scanning Calorimetry (DSC)

Thermograms were recorded on a TA Instruments DSC 2920 equipped with a refrigerated cooling system against an empty sealed pan as reference. In a typical run, the sample was heated to 250 °C at 5 °C/min, cooled to 40 °C at 5 °C/min, then equilibrated for 10 min before heating to 250 °C at 5 °C/min. Second heating cycles are reported. Plots are baseline subtracted for easier viewing.

### 4.5.1.5. Grazing Incidence Small/Wide Angle X-ray Scattering (GISAXS/GIWAXS)

GIWAXS and GISAXS measurements were carried out at the X9 undulator beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. An X-ray energy of 14.0 keV was selected using a silicon monochromator, and images were collected using two area detectors: a Pilatus 300k (Dectris) for small-angle measurements (3091 mm distance) and a Photonic Sciences fiber-coupled CCD for wide-angle data (370 mm distance). Sample measurement was carried out under vacuum which is in the range of 2-3 × 10⁻⁶ bar. GIWAXS images presented herein are median filtered and processed using the GIXS GUI package for Matlab (Mathworks). Data are corrected for X-ray polarization, detector sensitivity and geometrical solid-angle.²⁶ Plots are normalized and plotted on a logarithmic scale.
4.5.1.6. Transmission Electron Microscopy (TEM)

TEM images were acquired on a JEOL JEM-1400LaB6 TEM operating at an accelerating voltage of 120 keV. All the TEM images were collected using a Gatan 2K CCD camera. Samples were prepared by casting solutions of 3mg ml\(^{-1}\) polymer solution at 1500 rpm for 30 sec onto poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) coated silicone substrates. Substrates were then placed in water to allow the PEDOT:PSS layer to dissolve and the polymer film was collected onto 300 mesh copper TEM grids with lacey carbon. Samples were then annealed at about 165°C for about 15 minutes before measurements.

4.5.2. Synthesis

4.5.2.1. Materials

Anhydrous tetrahydrofuran (THF), anhydrous toluene, dichloromethane, chloroform, tetrahydrofuran, hexanes, acetone, methanol, 1,3-bis(diphenylphosphino)propane|dichloronickel(II) (Ni[dppp]Cl\(_2\)), isopropylmagnesium chloride (\(^{t}\)PrMgCl, 2M in THF), 9,9-dioctyl-2,7-dibromofluorene, 3-hexylthiophene, 3-bromothiophene, magnesium, 1-bromododecane, copper(I) bromide (CuBr), 18-crown-6, cesium fluoride (CsF), N,N,N',N''-pentamethyldiethylene-triamine (PMDETA), poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), 4-bromophenyl ethanol, tosyl chloride, bis(tri-\(t\)-butylphosphine) palladium(0) (Pd[t-Bu\(_3\)P]\(_2\)), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), 4(dimethylamino), pyridine
(DMAP), 5-hexynoic acid, tetrabutylammonium fluoride solution in THF (TBAF, 1M in THF), tosyl chloride, and azidotrimethylsilane were obtained from commercial sources and used as received. 2,5-dibromo-3-hexylthiophene, 2,5-dibromo-3-dodecylthiophene, and 7′-bromo-9′,9′-diocetyl-fluoren-2′-yl-4,4,5,5,5-tetramethyl-[1,3,2]dioxaborolane (2) were synthesized as previously described.\textsuperscript{27-31}

4.5.2.2. 2-(4-Bromophenyl) ethyl 4-methylbenzenesulfonate (1)

4-Bromophenyl ethanol (1.96g 9.75 mmol) was dissolved in dichloromethane (8 ml) at 0°C. Tosyl chloride (2.34g, 12.2 mmol) and pyridine (1.4 ml) were added, and the reaction was allowed to warm to room temperature. The reaction was stirred at room temperature for at least 48 hours and the reaction mixture was washed with water, extracted with dichloromethane, and dried over sodium sulfate. Solvent was removed by rotary evaporation, and the product was collected as a white solid.

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, \(\delta\)): 7.68-7.62 (d, 2H, Ar—H), 7.38-7.32 (d, 2H, Ar—H), 7.31-7.25 (d, 2H, Ar—H), 7.0-6.94 (d, 2H, Ar—H), 4.23-4.17 (t, 2H, CH\textsubscript{2}), 2.95-2.88 (t, 2H, CH\textsubscript{2}), 2.47-2.43 (s, 3H, Ar—CH\textsubscript{3}),

4.5.2.3. 2-(4-Bromophenyl) ethyl 4-methylbenzenesulfonate bis(tri-tert-butylphosphine) palladium(0)

Similar to previously reported synthesis, (1) (0.25 g 0.87 mmoles) and bis(tri-tert-butylphosphine)palladium(0) (82 mg, 0.16 mmol) were dissolved in 3ml
of anhydrous toluene in an inert atmosphere and heated to 70 °C for 3 hours. The material was used without further purification.

4.5.2.4. Tosyl functionalized Poly(9,9-dioctylfluorene) (PF-tosylate)

Similar to previously reported synthesis, 7'-bromo-9,9'-dioctyl-fluoren-2-yl-4,4,5,5,-tetramethyl-[1,3,2]dioxaborolane (2) (1.23 g, 2.07 mmol) was dissolved in 110 mL THF along with 18-crown-6 (6.61 g, 25.3 mmol), CsF (1.6 g, 12.6 mmol), and 5 mL water. The monomer solution was purged with N₂ for 30 minutes before adding the crude product solution from the preparation of 2-(4-bromophenyl) ethyl 4-methylbenzenesulfonate bis(tri-tert-butylphosphine) palladium(0). The solution was stirred overnight at room temperature before quenching with 1 mL 5M HCl. The polymer was recovered by precipitation in methanol and washed with copious amounts of acetone to collect a light yellow/green solid. Yield: 394 mg, 49 %:

PF1: \(^1\)H NMR (500 MHz, CDCl₃, \(\delta\)): 8.0-7.5 (m, 81H, Ar—H), 2.31-1.91 (m, 52H, Ar—C—CH₂—), 1.39-0.97 (m, 276H, —CH₂—), 0.97-0.50 (m, 135H, —CH₂—), 4.34-4.21 (t, 2H, Ar—CH₂—CH₂—OTs), 3.11-2.96 (t, 2H, Ar—CH₂—CH₂—OTs), 3.11-2.96 (t, 3H, —SO₂—Ph—CH₃)

PF2: \(^1\)H NMR (500 MHz, CDCl₃, \(\delta\)): 8.0-7.5 (m, 188H, Ar—H), 2.31-1.91 (m, 128H, Ar—C—CH₂—), 1.39-0.97 (m, 661H, —CH₂—), 0.97-0.50 (m, 317H, —CH₂—), 4.34-4.21 (t, 2H, Ar—CH₂—CH₂—OTs), 3.11-2.96 (t, 2H, Ar—CH₂—CH₂—OTs), 3.11-2.96 (t, 3H, —SO₂—Ph—CH₃)
4.5.2.5. Azide functionalized Poly(9,9-dioctylfluorene) (PF-azide)

Azide functionalized poly(9,9-dioctylfluorene) was prepared by dissolving PF—tosylate (0.32 g, 0.64 mmole) in 5 ml of anhydrous THF followed by the addition of azidotrimethylsilane (0.2 ml, 1.5 mmol) and 1M tert-butyl ammonium fluoride solution (1.5 ml, 1.5 mmol). The reaction was allowed to proceed overnight and the product was isolated by precipitation into methanol, followed by washed with acetone.

PF1: $^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 8.0-7.5 (m, 80H, Ar—H), 2.31-1.91 (m, 53H, Ar—C—CH$_2$—), 1.39-0.97 (m, 283H, —CH$_2$—), 0.97-0.50 (m, 136H, —CH$_2$—), 3.63-3.55 (t, 2H, Ar—CH$_2$—CH$_2$—N$_3$), 3.01-2.91 (t, 2H, Ar—CH$_2$—CH$_2$—N$_3$)

PF2: $^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 8.0-7.5 (m, 185H, Ar—H), 2.31-1.91 (m, 131H, Ar—C—CH$_2$—), 1.39-0.97 (m, 698H, —CH$_2$—), 0.97-0.50 (m, 330H, —CH$_2$—), 3.63-3.55 (t, 2H, Ar—CH$_2$—CH$_2$—N$_3$), 3.01-2.91 (t, 2H, Ar—CH$_2$—CH$_2$—N$_3$)

4.5.2.6. Alkyne functionalized poly(3-alkylthiophene) (P3AT-alkyne)

Alkyne functionalized poly(3-alkylthiophene) was prepared using a general procedure described elsewhere.$^{17}$

P3HT1: $^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 7.13-6.64 (s, 88H, Ar—H), 3.09-2.37 (t, 176H, Ar—CH$_2$—), 2.08-1.09 (m, 845H, —CH$_2$—), 1.09-0.60 (m, 265H, —CH$_3$), 4.52-4.41 (t, 2H, Ar—CH$_2$—CH$_2$—O—CO—), 4.27-4.18 (t, 2 H, Ar—CH$_2$—CH$_2$—O—CO—)
P3HT2: $^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 7.13-6.64 (s, 41H, Ar—H), 3.09-2.37 (t, 84H, Ar—CH$_2$—), 2.08-1.09 (m, 442H, —CH$_2$—), 1.09-0.60 (m, 124H, —CH$_3$), 4.52-4.41 (t, 2H, Ar—CH$_2$—CH$_2$—O—CO—), 4.27-4.18 (t, 2H, Ar—CH$_2$—CH$_2$—O—CO—)

P3DDT1: $^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 7.13-6.64 (s, 109H, Ar—H), 3.09-2.37 (t, 230H, Ar—CH$_2$—), 2.08-1.09 (m, 2332H, —CH$_2$—), 1.09-0.60 (m, 352H, —CH$_3$), 4.52-4.41 (t, 2H, Ar—CH$_2$—CH$_2$—O—CO—), 4.27-4.18 (t, 2H, Ar—CH$_2$—CH$_2$—O—CO—)

P3DDT2: $^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 7.13-6.64 (s, 43H, Ar—H), 3.09-2.37 (t, 85H, Ar—CH$_2$—), 2.08-1.09 (m, 881H, —CH$_2$—), 1.09-0.60 (m, 130H, —CH$_3$), 4.52-4.41 (t, 2H, Ar—CH$_2$—CH$_2$—O—CO—), 4.27-4.18 (t, 2H, Ar—CH$_2$—CH$_2$—O—CO—)

4.5.2.7. Poly(3-alkylthiophene)-b-poly(9,9-dioctylfluorene) (P3AT-b-PF)

Poly(3-alkylthiophene)-b-poly(9,9-dioctylfluorene) was synthesized using a procedure described elsewhere.$^{16}$ In a typical reaction, PF-azide (4) (106 mg, 9.6 mmol), P3AT-alkyne (5) (128 mg, 8.53 mmol), and copper(I) bromide (8.8mg, 61.5 mmol) were added to a dry 50 ml round bottom flask and purged with nitrogen. Anhydrous THF (9ml) was added by syringe and the reaction was purged via needle while $N,N,N',N''-pentamethyldiethylenetriamine (0.1 ml, 0.48 mmol) was added. The reaction was allowed to proceed overnight at 40 °C. The reaction mixture was passed through a short basic alumina column followed by copious amounts of THF. Product was concentrated in a rotary evaporator, and then precipitated into
hexanes, collected by filtration, and washed with boiling hexanes. Full \(^1\)H NMR spectra for BCPs synthesized are included in the Supporting Information Figures S4.10 – S4.15.

P3HT1-b-PF1: \(^1\)H NMR (500 MHz, CDCl\(_3\), \(\delta\)): 8.10-7.41 (m, 67H, Ar—\(H\)), 7.15-6.88 (s, 92H, Ar—\(H\)), 3.01-2.35 (t, 199H, Ar—\(CH_2\)—), 2.35-1.88 (m, 46H, —\(CH_2\)—), 1.88-1.01 (m, 1032H, —\(CH_2\)—), 1.01-0.50 (m, 397H, —\(CH_3\)), 4.49-4.39 (t, 2.00H, Ar—\(CH_2—CH_2—O—CO—\), 4.24-4.12 (t, 1.98H, Ar—\(CH_2—CH_2—O—CO—\), 4.65-4.55 (t, 2.05H, Ar—\(CH_2—CH_2—N_3C_2H—\)), 3.34-3.17 (t, 2.51H, Ar—\(CH_2—CH_2—N_3C_2H—\))

P3HT1-b-PF2: \(^1\)H NMR (500 MHz, CDCl\(_3\), \(\delta\)): 8.10-7.41 (m, 63H, Ar—\(H\)), 7.15-6.88 (s, 86H, Ar—\(H\)), 3.01-2.35 (t, 187H, Ar—\(CH_2\)—), 2.35-1.88 (m, 41H, —\(CH_2\)—), 1.88-1.01 (m, 981H, —\(CH_2\)—), 1.01-0.50 (m, 373H, —\(CH_3\)), 4.49-4.39 (t, 2.00H, Ar—\(CH_2—CH_2—O—CO—\), 4.24-4.12 (t, 1.92H, Ar—\(CH_2—CH_2—O—CO—\), 4.65-4.55 (t, 1.86H, Ar—\(CH_2—CH_2—N_3C_2H—\)), 3.34-3.17 (t, 2.72H, Ar—\(CH_2—CH_2—N_3C_2H—\))

P3HT2-b-PF2: \(^1\)H NMR (500 MHz, CDCl\(_3\), \(\delta\)): 8.10-7.41 (m, 97H, Ar—\(H\)), 7.15-6.88 (s, 42H, Ar—\(H\)), 3.01-2.35 (t, 102H, Ar—\(CH_2\)—), 2.35-1.88 (m, 79H, —\(CH_2\)—), 1.88-1.01 (m, 797H, —\(CH_2\)—), 1.01-0.50 (m, 290H, —\(CH_3\)), 4.49-4.39 (t, 2.00H, Ar—\(CH_2—CH_2—O—CO—\), 4.24-4.12 (t, 1.90H, Ar—\(CH_2—CH_2—O—CO—\), 4.65-4.55 (t, 1.93H, Ar—\(CH_2—CH_2—N_3C_2H—\)), 3.34-3.17 (t, 1.83H, Ar—\(CH_2—CH_2—N_3C_2H—\))

P3DDT1-b-PF1: \(^1\)H NMR (500 MHz, CDCl\(_3\), \(\delta\)): 8.10-7.41 (m, 49H, Ar—\(H\)), 7.15-6.88 (s, 69H, Ar—\(H\)), 3.01-2.35 (t, 149H, Ar—\(CH_2\)—), 2.35-1.88 (m, 37H, —\(CH_2—\)), 1.88-1.01 (m, 1642H, —\(CH_2—\)), 1.01-0.50 (m, 296H, —\(CH_3\)), 4.49-4.39 (t,
2.00H, Ar—CH₂—CH₂—O—CO—), 4.24-4.12 (t, 2.08H, Ar—CH₂—CH₂—O—CO—),
4.65-4.55 (t, 1.86H, Ar—CH₂—CH₂—N₃C₂H—), 3.34-3.17 (t, 1.48H, Ar—CH₂—CH₂—
N₃C₂H—)

P3DDT1-b-PF2: ¹H NMR (500 MHz, CDCl₃, δ): 8.10-7.41 (m, 89H, Ar—H),
7.15-6.88 (s, 108H, Ar—H), 3.01-2.35 (t, 228H, Ar—CH₂—), 2.35-1.88 (m, 58H, —
CH₂—), 1.88-1.01 (m, 2600H, —CH₂—), 1.01-0.50 (m, 476H, —CH₃), 4.49-4.39 (t,
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4.65-4.55 (t, 1.30H, Ar—CH₂—CH₂—N₃C₂H—), 3.34-3.17 (t, 1.94H, Ar—CH₂—CH₂—
N₃C₂H—)

P3DDT2-b-PF2: ¹H NMR (500 MHz, CDCl₃, δ): 8.10-7.41 (m, 83H, Ar—H),
7.15-6.88 (s, 39H, Ar—H), 3.01-2.35 (t, 90H, Ar—CH₂—), 2.35-1.88 (m, 61H, —CH-
₂—), 1.88-1.01 (m, 1359H, —CH₂—), 1.01-0.50 (m, 251H, —CH₃), 4.49-4.39 (t,
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4.65-4.55 (t, 1.61H, Ar—CH₂—CH₂—N₃C₂H—), 3.34-3.17 (t, 1.75H, Ar—CH₂—CH₂—
N₃C₂H—)

4.6. References

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(2) Darling, S. B. Block Copolymers for Photovoltaics. Energy & 
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(21) Li, Z.; Ono, R. J.; Wu, Z.-Q.; Bielawski, C. W. Synthesis and Self-Assembly of poly(3-Hexylthiophene)-Block-Poly(acrylic Acid). *Chemical Communications* 2011, 47, 197.


# 4.7. Supporting Information

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Table S4.1 MALDI-TOF analysis for P3AT polymers to determine functionality.

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Table S4.2 MALDI-TOF analysis for PF polymers to determine functionality.
Figure S4.1 SEC results for all polymers. First column show differential refractive index (SEC-RI), second column is UV absorbance signal for P3AT (negligible absorbance of PF at 500 nm for block copolymer), and third column is UV absorbance signal for PF (block copolymer trace is corrected for the presence of a P3AT signal by subtracting the contribution of P3AT using the signal at 500 nm and the ratio of absorbance of pure P3AT at 300 nm and 500 nm).
Figure S4.2: GIWAXS linecuts along $q_z$ for samples annealed at 230°C. Crystalline peaks at $q_z = 0.38, 0.77, 1.14$ are associated with P3HT, $q_z = 0.5$ with PF, and $q_z = 0.23, 0.46, 0.68, 0.91, 1.14$ with P3DDT.
Figure S4.3: Differential scanning calorimetry curves from second heating cycle, baseline subtracted for easier viewing. Transition temperatures are PF1 (109°C,128°C), PF2 (127°C), P3HT1 (230°C, 244°C), P3HT2 (216°C), P3HT1-b-PF1 (227°C, 242°C), P3HT1-b-PF2 (227°C, 242°C), P3HT2-b-PF2 (206°C, 214°C), P3DDT1 (155°C, 162°C, 169°C), P3DDT2 (135°C, 144°C), P3DDT1-b-PF1 (154°C, 160°C, 167°C), P3DDT1-b-PF2 (156°C, 160°C, 168°C), and P3DDT2-b-PF2 (141°C, 146°C). Very weak and broad transitions for P3HT-b-PF, particularly for P3HT2-b-PF2, are observed in the range of 110-150°C which may indicate PF crystallization.
Figure S4.4: GIWAXS data for all samples under various annealing conditions for samples cast from room temperature chloroform. First column is films as cast, second column shows samples annealed for 5 days at room temperature in the presence of a chloroform vapor followed by thermal annealing at 165°C and 230°C in columns three and four respectively.
Figure S4.5: GIWAXS data for all samples under various annealing conditions for samples cast from refluxing chloroform. First column is films as cast, second column shows samples annealed for 5 days at room temperature in the presence of a chloroform vapor followed by thermal annealing at 165°C and 230°C in columns three and four respectively.
Figure S4.6: GISAXS linecuts along $q_y$ for samples annealed at A) 165°C and B) 230°C. Broad and weak peaks are present in P3HT-b-PF samples between 0.02-0.03 Å$^{-1}$ corresponding to length scales of about 21-31 nanometers.
Figure S4.7: Transmission Electron Microscopy (TEM) images of A) P3HT1-b-PF1 B) P3HT1-b-PF2 C) P3HT2-b-PF2 D) P3DDT1-b-PF1 E) P3DDT1-b-PF2 F) P3DDT2-b-PF2 annealed at 165°C for 15 minutes.

Figure S4.8: Elemental line scan of P3DDT1-b-PF1 showing uniform increase in both carbon and sulfur signals from light to dark regions of TEM image.
Figure S4.9: A survey of AFM phase images for samples reported in this section under various processing conditions (see inset). All images are 1 μm x 1 μm. RT Cast indicates casting from room temperature chloroform and Hot Cast indicates casting from refluxing chloroform. Annealing conditions are CHCL3 for chloroform annealing for 5 days, 165°C and 230°C for thermal annealing at those respective temperatures.
Figure S4.10: $^1$H NMR of P3HT1-b-PF1

Figure S4.11: $^1$H NMR of P3HT1-b-PF2
Figure S4.12 $^1$H NMR of P3HT2-\textit{b}-PF2

Figure S4.13: $^1$H NMR of P3DDT1-\textit{b}-PF1
Figure S4.14: $^1$H NMR of P3DDT1-\textit{b}-PF2

Figure S4.15: $^1$H NMR of P3DDT2-\textit{b}-PF2
Control of All-Conjugated Block Copolymer Crystallization via Thermal and Solvent Annealing


The following was accepted in the Journal of Polymer Science B: Polymer Physics.

Kendall A. Smith¹, Bridget Stewart¹, Kevin G. Yager², Joseph Strzalka³, and Rafael Verduzco¹

¹Rice University, 6100 Main St., Houston, TX, USA, 77005

²Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973
Control of the crystallization of conjugated polymers is of critical importance to the performance of organic electronics, such as organic photovoltaic devices, due to the effect on charge separation and transport, particularly for all-polymer devices. The block copolymer poly(3-dodecylthiophene)-block-poly(9,9-dioctylfluorene) (P3DDT-b-PF), which has matched crystallization temperatures for each block, is used to study the effects of processing history on resulting crystallization. For longer annealing times and rapid quenching to room temperature, P3DDT crystals are preferred whereas for shorter annealing times and slower quenching, PF crystals are preferred. Both crystal forms are evidenced for long annealing time and slow quenching. Additionally, for room temperature annealing in the presence of a chloroform vapor, PF crystals are found in the PF $\beta$ phase with the predominant crystal peak oriented perpendicular to the thermally annealed case. These results will provide guidance for optimizing annealing strategies for future donor/acceptor block copolymer photovoltaic devices.

**KEYWORDS:** poly(3-alkylthiophene), P3AT, poly(3-dodecylthiophene), P3DDT, poly(9,9-dioctylfluorene), PF, block copolymers, organic photovoltaics, crystallization, and rod-rod polymers.
5.1. Introduction

Conjugated polymers show great promise as functional materials in organic electronics such as organic photovoltaic (OPV) devices.\textsuperscript{1,2} Crystallization plays an important role in the electronic properties of some conjugated polymers, and thermal annealing is routinely performed on organic photovoltaic devices in order to improve their performance.\textsuperscript{3} Block copolymers consisting of covalently joined conjugated polymers for both the donor and acceptor materials may form nanostructures by microphase separation that can be favorable for charge separation and transport.\textsuperscript{4} Recently we reported on a block copolymer consisting of poly(3-hexylthiophene) (P3HT) and poly((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2′,2″-diyl) (PFTBT) achieving a 3% power conversion efficiency without a fullerene acceptor.\textsuperscript{5} Optimization of these devices is non-trivial and processing conditions that produce optimal devices for the homopolymer constituents are a poor guide for the block copolymer devices. Relatively few reports discuss the interplay between crystallization of the constituent blocks in these types of rod-rod block copolymers.\textsuperscript{6–9} Additional research is needed to understand the relationship between processing, morphology, and optoelectronic properties in these systems.

Herein, we investigate the processing-dependent morphology of poly(3-dodecyl thiophene)-\textit{block}-poly(9,9-dioctylfluorene) (P3DDT-\textit{b}-PF) all-conjugated block copolymers. P3DDT has a crystal melting temperature comparable to that of PF, and as a result P3DDT-\textit{b}-PF block copolymers exhibit a rich, processing-
dependent morphology in which both polymer blocks can crystallize. By varying the processing conditions and observing the effects on crystallization using grazing incidence X-ray scattering, we find that we are able to induce or inhibit crystallization of either or both blocks. We show that the processing history influences the film optical properties. These results provide fundamental insight into the crystallization dynamics of this class of polymers and provide guidance on different annealing strategies that may be employed to optimize all-conjugated block copolymer organic photovoltaic devices.

5.2. Results and Discussion

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Table 5.1: List of samples used in this work. Weight % P3DDT determined by $^1$H NMR (see Supporting Figure S5.1) $M_W$, $M_n$, PDI determined relative to monodisperse polystyrene standards.

In this work, we systematically investigate the effect of processing conditions on film morphology by varying casting temperature, substrate, annealing time, and quenching rate. The P3DDT-b-PF system is ideally suited for this type of investigation due to the similar crystallization temperatures of both polymer blocks. Materials used in this work were synthesized using procedures detailed elsewhere.$^{10}$ Briefly, we utilize Grignard metathesis polymerization with lithium
chloride as an additive in order to obtain P3DDT that is functionalized with bromine. This macroreagent is then used as an end-capping reagent in a Suzuki polycondensation reaction (as detailed in reaction Scheme S1 in supporting information).\textsuperscript{10} The molecular weights and compositions of P3DDT, PF, and P3DDT-\textit{b}-PF polymers synthesized are detailed in Table 5.1. Size exclusion chromatography (SEC) data show a shift to shorter elution time from the original starting material as seen in Figure 5.1. Although the presence of some homopolymer cannot be excluded due to the overlap in the distributions, block copolymer is clearly the majority product. Additional characterization of these materials using SEC-UV/VIS absorption is included in supporting information (Figure S5.2).

Previous studies of all-conjugated block copolymers has found crystallization of one or both polymer blocks.\textsuperscript{10–12} For P3HT containing block copolymers, crystallization of the second block tends to be suppressed on account of the high crystallization temperature of P3HT.\textsuperscript{13} For block copolymers of two different poly(alkylthiophenes), co-crystallization can occur when side chains differ by only two carbons, but generally phase separation and separate crystal structures are observed.\textsuperscript{14} In a previous study with P3DDT-\textit{b}-PF containing short PF blocks, we found significant crystallization of both blocks in solvent cast and thermally annealed films.\textsuperscript{15}
Figure 5.1: SEC differential refractive index trace of starting P3DDT1 and the resulting block copolymer product P3DDT-b-PF1.

As shown in Figure 5.2, the polymer blocks have matched crystallization temperatures (145-170°C for P3DDT and 135-155°C for PF). The data show a slight depression in the thermal transition for P3DDT upon incorporation into the block copolymer. The transition for pure PF is very similar to that of the P3DDT block, so it is difficult to determine if there is evidence of PF crystallization; however a broad feature is present around 100-140°C which may be due to PF as it is not present in the starting P3DDT. The similar crystallization temperature of these two polymers allows us to investigate the kinetic aspects of crystallization, since both blocks will be crystallizing during the quenching process.
Samples cast from 10 mg ml\(^{-1}\) chloroform solutions were annealed overnight in a nitrogen glove box (<10 ppm O\(_2\)) at 175°C (above the crystallization temperature of P3DDT) and slowly cooled to room temperature. As seen in Figure 5.3, we observe both P3DDT and PF crystal patterns at 32 wt % P3DDT, while P3DDT crystallization is suppressed at 8 wt % P3DDT. This contrasts with our previous result which shows P3HT crystallization was almost completely suppressed in P3HT-\(b\)-PF with only 32 wt % P3HT.\(^{10,12}\) This indicates a broader range where both crystal forms may be observed for P3DDT-\(b\)-PF block copolymers. We note that the pure materials both crystallize with a preferential orientation with respect to the substrate, as evidenced by the sharp diffraction peaks (as opposed to broad arcs or rings expected for isotropically-oriented materials). The block copolymer samples evidently retain the preferential orientations of the pure materials.
Figure 5.2: DSC results from the second heating cycle for a pure PF, P3DDT1, and P3DDT-b-PF1.

Figure 5.3: GIWAXS images (from left to right) of films of pure P3DDT, P3DDT-b-PF1 (32% P3DDT), P3DDT-b-PF2 (8% P3DDT), and pure PF annealed at 175°C.

Substrates investigated in this work are bare silicon and PEDOT:PSS coated silicon. Samples were cast from chloroform, toluene, and dichlorobenzene at
concentrations of 6 mg ml\(^{-1}\) and 12 mg ml\(^{-1}\), in order to achieve different film thicknesses. Samples cast from room temperature dichlorobenzene generally produced poor quality films at these concentrations. These results are not extensively discussed here, but are included in supporting information for reference. Our previous study with block copolymer OPVs based on P3HT-\(b\)-PFTBT indicated improved performance when casting from hot solvents.\(^5\) To understand the effect of hot solvent casting, samples were cast from room temperature solvent and solvent heated at 90°C (refluxing for chloroform, near boiling for toluene, below the boiling point of dichlorobenzene). Finally, samples were also drop cast from chloroform, toluene, and dichlorobenzene to form very thick samples.

Annealing conditions were examined parametrically for varying casting solvents, annealing temperature, and cooling rate (see Supporting Information Table S5.1 for a table of cases tested). Samples were annealed at 170°C (slightly above the crystallization temperature) for 5 days or 15 minutes. Samples were quenched either by turning off the hot plate and allowing the samples to come to room temperature slowly over the course of 30 minutes to an hour, or by removing from the hot plate and immediately placing on a heat sink to rapidly bring the sample to room temperature. Special care was made to ensure good thermal contact for all samples by first adhering them to a thin aluminum plate with thermal paste and rapidly transferring to the heat sink in order to ensure that all samples experienced the same thermal environment. All thermal annealing was carried out in a nitrogen glove box (<10 ppm O\(_2\)). Additionally, samples were annealed at room temperature in the presence of a chloroform vapor for 5 days.
Figure 5.4: P3DDT-b-PF1 cast onto silicon wafers from 12 mg ml\(^{-1}\) chloroform (first row) and toluene (second row) solutions. Annealing condition is indicated in heading. Samples were cast from either room temperature (RT) or hot (90°C) solvent, annealed at 170 °C for either 15 min or 5 days, and cooled either by placing on a heat sink (Rapid) or by turning off the hot plate and allowing to come to room temperature over the course of 30-60 min (Slow).

For the samples deposited on silicon (Figure 5.4 and Supporting Figure S5.3 for images and Figure S5.4 for linecuts), we see structures dominated by PF crystallization. Annealing for 15 minutes and rapidly cooling the samples results in neither block crystallizing. However, samples annealed for a longer duration show P3DDT crystals (evidenced by alkyl chain stacking reflections at \(q_z = 0.22\) Å\(^{-1}\), \(0.44\) Å\(^{-1}\), and \(0.66\) Å\(^{-1}\)) and those allowed to cool slowly show PF crystals (\(q_z = 0.5\) Å\(^{-1}\)).

For the samples annealed for 15 minutes and cooled slowly, it is interesting to note the striking similarities in crystal structure between the sample cast from room temperature chloroform and the sample cast from 90°C toluene. Since both of these samples are cast from solvents about 20°C below their boiling points, it suggests some optimum in terms of the choice of solvent temperature to obtain well-ordered
crystals. By contrast, the sample cast from 90°C chloroform (above its boiling point) shows some orientational disorder due to the rapid evaporation of the solvent during casting. Both P3DDT and PF crystal forms are observed in both the 90°C cast toluene and chloroform samples that are annealed for 5 days and slowly cooled. This suggests that P3DDT may need a longer annealing duration in order to form well-ordered crystals relative to PF.

Figure 5.5: Photoluminescence measurements using an excitation wavelength of 380nm for P3DDT-b-PF1 samples cast from 12 mg ml⁻¹ chloroform. Samples were annealed at 170 °C for 15 min (red trace) or 5 days (blue trace).

As can be seen in Figure 5.5 and Figure S5.5, effects can also be seen in photoluminescence. By exciting at 380nm (a wavelength preferentially absorbed by PF) we can see prominent emission peaks at around 450 nm associated with PF for samples that have good PF crystals but no P3DDT crystals. Conversely, when P3DDT
crystals are present, the emission intensity near 450 nm is reduced and a strong emission peak at 540 nm appears. Regrettably, both amorphous P3DDT and defects in the PF film can give rise to the emission peak at 550 nm, so clear assignment of this emission to either P3DDT or PF is not possible.\textsuperscript{16-18} Nevertheless, the results bear a striking resemblance to those of Schref and coworkers who observed similar behavior for the P3HT-\textit{b}-PF system where P3HT photoluminescence was quenched when the polymer was dissolved in a mixed solvent preferential to PF.\textsuperscript{19} Photoluminescence of these films under a variety of processing conditions is presented in the Supporting Information Figure S5.5, and exhibit similar features with varying relative emission intensities at 450 nm and 540 nm depending on the processing conditions. Absorbance spectra are included in Figure S5.6 for P3DDT-\textit{b}-PF1, P3DDT1, and PF on glass substrates.

Qualitatively, some of the trends for the PEDOT:PSS substrates shown in Figure 5.6 and Supporting Figure S5.7 (images) and Figure S5.8 (linecuts) are similar to those found in the bare silicon cases of Figure 5.4. Similar to the previous case, we see negligible crystallinity for the samples that are annealed for 15 minutes and rapidly cooled. However for the samples that are annealed for 5 days and then rapidly cooled we see PF crystals rather than the weak P3DDT crystals seen in the bare silicon case. As before, the samples cast from 90°C solvent and then annealed for 15 minutes and slowly cooled show PF crystals, but with more disorder than in the former case of room temperature solvent and bare silicon. Finally, samples that were annealed for 5 days and slowly cooled show results in good agreement with those cast on bare silicon. While it is not clear why these samples display different
results for the case of annealing for 5 days and rapidly cooling, it may be that the presence of the PEDOT:PSS layer has an influence on the crystallization kinetics of the two polymer blocks. It is also possible that minor differences in the cooling rate can have a significant impact on crystallization. As shown in Figure S5.9, a slightly higher temperature might favor PF crystals. Results are consistent across all samples tested under similar annealing conditions with no significant dependence on film thickness or solvent choice (see supporting Figure S5.7 for images and Figure S5.8 for linecuts).

![Figure 5.6: P3DDT-b-PF1 cast onto PEDOT:PSS coated silicon wafers from 12mg ml⁻¹-chloroform (first row) and toluene (second row) solutions. Annealing condition is indicated in heading. Samples were cast from either room temperature (RT) solvent or solvent heated at 90°C for either 15 min or 5 days and cooled either by placing on a heat sink (Rapid) or by turning off the hot plate and allowing to come to room temperature over the course of 30-60 min (Slow).](image)

As seen in Figure 5.7 and Supporting Figure S5.3 (images, top row), Figure S5.4 (corresponding linecuts for Figure S5.3), Figure S5.10 (images of drop cast samples), & Figure S5.11 (corresponding linecuts for Figure S5.10), samples that
were annealed in the presence of a chloroform vapor showed a slightly different morphology. The usual P3DDT crystal form was present with a prominent alkyl stacking peak present at $q_x = 0.22$. The solvent induced $\beta$ form of PF is also present with the prominent peak at $q_y = 0.5\text{Å}^{-1}$. The presence of the $\beta$ form of PF is consistent across several different samples, though a thickness effect is apparent as the 12 mg ml$^{-1}$ toluene sample show reduced amounts of this crystal structure relative to the thicker chloroform samples and neither of the 6 mg ml$^{-1}$ samples showed any significant crystallization.

Figure 5.7: GIWAXS of samples annealed in the presence of chloroform vapor for 5 days. First column shows samples spin coated from 12mg ml$^{-1}$ room temperature solutions while second column shows drop cast samples. First row used chloroform as the solvent for spin coating / drop casting while toluene was used for samples in the second row.
Figure 5.8: Schematic showing evolution of crystallites. Since no strong evidence for ordered phase segregation was found from GISAXS, thin film structure is depicted as a random intermixed network. For long annealing times, P3DDT crystals are able to organize. If rapidly quenched, the PF phase remains amorphous, but with slower quenching times, both phases are present. Conversely, for short annealing times, P3DDT crystals do not have a chance to organize. If rapidly quenched, neither P3DDT nor PF crystals are present; however if slowly cooled, PF crystals are observed.

As illustrated in Figure 5.8, we generally find that longer annealing time favors the formation of P3DDT crystallites, while slow quenching to room temperature favors the formation of PF crystals. Thus, we can preferentially obtain PF crystal patterns for samples that are annealed for a short time and slowly quenched to room temperature whereas P3DDT crystals are obtained for longer annealing times and more rapid quenching to room temperature. Additionally, chloroform solvent annealing at room temperature shows both PF and P3DDT crystallization but with PF crystals in the β phase with the predominant crystal peak oriented perpendicularly to that found in the thermally annealed case.
5.3. Conclusions

In general, for thin film samples on silicon substrates, thermal annealing followed by rapid quenching suppressed crystallization of both blocks. For samples cast on silicon, weak P3DDT crystals were observed for samples cast from room temperature solvent that were subjected to long term thermal annealing whereas PF crystals were observed for samples with shorter annealing times and slower quenching to room temperature.

These results will provide guidance on annealing strategies for similar rod-rod block copolymer systems where crystallization of each block is important. For practical applications, annealing at both low and high temperatures could be performed to tune the relative crystallization of both blocks.

5.4. Acknowledgments

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National Synchrotron Light Source and Center for Functional Nanomaterials, Brookhaven National Laboratory, were supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

### 5.5. References


5.6. Experimental

5.6.1. Nuclear Magnetic Resonance Spectroscopy (NMR)

Solution $^1$H NMR spectroscopy was performed on a 500 MHz Varian Inova NMR. Chloroform-d (CDCl$_3$, Cambridge Isotope Laboratories) was used as the solvent with TMS (0.05%) as an internal standard. Data was processed using SpinWorks 3.1.8.1.$^{22}$ For block copolymers, the % P3DDT was determined by integration of the respective aromatic regions of each polymer block (see Supporting Information Figure S5.1).

5.6.2. Size-Exclusion Chromatography (SEC)

Polymer molecular weights and polydispersities (PDIs) were obtained by 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, a Wyatt Technology HELEOS II multi-angle laser light scattering (MALLS) detector ($\lambda=658$ nm), and a Wyatt Technology Optilab reX RI detector. This system
enables SEC with simultaneous refractive index (SEC-RI), UV/VIS (SEC-UV/VIS), and MALLS (SEC-MALLS) detection. THF was used as the mobile phase at a flow rate of 1 mL/min at 40 °C. Weight average molecular weights ($M_w$) and polydispersity index (PDI) were determined using SEC-RI calibrated with a set of monodisperse polystyrene standards (Astra Software Version 5.3.4).

5.6.3. Differential Scanning Calorimetry (DSC)

Thermograms were recorded on a TA Instruments DSC Q20-2255 equipped with a refrigerated cooling system against an empty sealed pan as reference. In a typical run, the sample was heated to 200 °C at 5 °C/min, and equilibrated for 3 min before being cooled to 0 °C at 5 °C/min, then equilibrated for 3 min before heating to 200 °C at 5 °C/min. Second heating cycles are reported.

5.6.4. Grazing Incidence Small/Wide Angle X-ray Scattering (GISAXS/GIWAXS)

GIWAXS and GISAXS measurements were carried out at the X9 undulator beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. An X-ray energy of 14.0 keV was selected using a silicon monochromator, and images were collected using two area detectors: a Pilatus 300k (Dectris) for small-angle measurements (3091 mm distance) and a Photonic Sciences fiber-coupled CCD for wide-angle data (370 mm distance). Sample measurement was carried out under vacuum which is in the range of 2-3 × 10⁻⁶ bar. GIWAXS images presented herein are median filtered and processed using the
GIXSGUI package for Matlab (Mathworks). Data are corrected for X-ray polarization, detector sensitivity and geometrical solid-angle.\textsuperscript{23} Plots are normalized and plotted on a logarithmic scale. Data presented for bare silicon cases was collected with an incident angle of $0.10^\circ$ whereas an incident angle of $0.07^\circ$ was used for PEDOT:PSS coated substrates to preclude any influence of the underlying PEDOT:PSS layer.

5.6.5. Photoluminescence (PL)

Photoluminescence measurements were taken on a Photon Technology International (PTI) Fluorescence Master Systems.

5.6.6. Materials

Anhydrous tetrahydrofuran (THF), chloroform, tetrahydrofuran, hexanes, acetone, methanol, isopropylmagnesium chloride ($^3$PrMgCl, 2M in THF), 3-bromothiophene, magnesium, 1-bromododecane, Aliquat® 336, 9,9-dioctyl-2,7-dibromofluorene, 9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), 1,3-bis(diphenylphosphino)propane)dichloronickel(II) ($\text{Ni[dppp]Cl}_2$), and tetrakis(triphenylphosphine) palladium(0) ($\text{Pd[PPh}_3\text{]}_4$), were obtained from commercial sources and used as received. 2,5-dibromo-3-dodecylthiophene was synthesized as previously described.\textsuperscript{24–26}

P3DDT and P3DDT-\textit{b}-PF were synthesized via general procedures described elsewhere.\textsuperscript{10}
5.6.7. Supporting Information

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Table S5.1 Table of samples/substrates of P3DDT-b-PF1 investigated. First two columns show samples that were thermally annealed for 15 minutes and then quenched slowly by turning off the hot plate and allowing the samples to cool slowly over 30-60 minutes. Rapidly quenched samples were quenched by placing on a heat sink. The next two columns indicate samples that were thermally annealed for 5 days. The final column shows samples that were annealed in the presence of chloroform vapor for 5 days. Rows show samples that were cast at room temperature, 90°C, and drop cast respectively. For each row/column combination, Si indicates samples that were prepared on silicon wafers and PEDOT indicates samples that were prepared on PEDOT:PSS coated silicon wafers.

![Figure S5.1: 1H NMR of P3DDT-b-PF1.](image)

Figure S5.1: 1H NMR of P3DDT-b-PF1.
Scheme S5.1: Reaction scheme for P3DDT-b-PF block copolymers.

![Reaction scheme for P3DDT-b-PF block copolymers.](image)

Figure S5.2: GPC traces for starting polymer and final block copolymer products for P3DDT-b-PF1 and P3DDT-b-PF2. Top row shows differential refractive index, while bottom row show UV/VIS absorption for the polymers showing data at 500 nm (sensitive only to P3DDT) and 300 nm which has been corrected for the presence of P3DDT by using the data at 500nm and the ratio of absorbance of P3DDT at 500nm and 300 nm (e.g. PF absorbance at 300nm = absorbance at 300 nm - absorbance at 500nm * P3DDT homopolymer absorbance at 300 nm over P3DDT homopolymer absorbance at 500 nm).
Figure S5.3: GIWAXS of all P3DDT-b-PF1 silicon wafers under a variety of casting/annealing/quenching conditions. First two columns show samples cast from chloroform at 6 mg/ml and 12 mg/ml. Similarly, the next two columns show samples cast from toluene and the final two columns samples cast from dichlorobenzene. Rows show samples that were thermally annealed for 15 min, thermally annealed for 5 days, or chloroform annealed for 5 days and subsequently quenched slowly or rapidly. Casting conditions were room temperature (RT) or 90°C solvent (90°C). The chloroform annealed 6 mg/ml toluene cast sample was lost.
Figure S5.4: GIWAXS linecuts in $q_z$ and $q_y$ for all P3DDT-b-PF1 silicon wafers under a variety of casting/annealing/quenching conditions. First two columns show samples cast from chloroform at 6 mg/ml and 12 mg/ml. Similarly, the next two columns show samples cast from toluene and the final two columns samples cast from dichlorobenzene. Rows show samples that were thermally annealed for 15 min, thermally annealed for 5 days, or chloroform annealed for 5 days and subsequently quenched slowly or rapidly. Casting conditions were room temperature (RT) or 90°C solvent (90°C). The chloroform annealed 6 mg/ml toluene cast sample was lost.
Figure S5.5: Photoluminescence data for selected P3DDT-b-PF1 samples cast on silicon wafers.

Figure S5.6: Absorbance for P3DDT-b-PF1, P3DDT1, and PF samples cast on glass slides and annealed for 15 minutes then slowly cooled.
Figure S5.7: GIWAXS of P3DDT-b-PF1 on PEDOT:PSS coated silicon wafers under a variety of casting/annealing/quenching conditions. First two columns show samples cast from chloroform at 6 mg/ml and 12 mg/ml. Similarly, the next two columns show samples cast from toluene and the final two columns samples cast from dichlorobenzene. Rows show samples that were thermally annealed for 15 min or thermally annealed for 5 days and subsequently quenched slowly or rapidly. Casting conditions were room temperature (RT) or 90°C solvent (90°C). The 5 day annealed rapidly quenched sample cast from room temperature 12 mg/ml dichlorobenzene was lost.
Figure S5.8: GIWAXS linecuts in $q_z$ and $q_y$ of P3DDT-$b$-PF1 on PEDOT:PSS coated silicon wafers under a variety of casting/annealing/quenching conditions. First two columns show samples cast from chloroform at 6 mg/ml and 12 mg/ml. Similarly, the next two columns show samples cast from toluene and the final two columns samples cast from dichlorobenzene. Rows show samples that were thermally annealed for 15 min or thermally annealed for 5 days and subsequently quenched slowly or rapidly. Casting conditions were room temperature (RT) or 90°C solvent (90°C). The 5 day annealed rapidly quenched sample cast from room temperature 12 mg/ml dichlorobenzene was lost.
Figure S5.9: GIWAXS image taken at the Advanced Photon Source, Beamline 8-ID-E for P3DDT-b-PF1 sample cast on silicon and annealed at 180°C followed by rapidly cooling.
Figure S5.10: GIWAXS of P3DDT1-b-PF1 samples drop cast onto silicon wafers under a variety of casting/annealing/quenching conditions. Rows show samples that were drop cast from chloroform, toluene and dichlorobenzene. Columns show samples that were thermally annealed for 15 min and subsequently quenched slowly or rapidly or were annealed for 5 days in the presence of chloroform vapor.
Figure S5.11: GIWAXS linecuts for all samples drop cast onto silicon wafers under a variety of casting / annealing / quenching conditions. Rows show samples that were drop cast from chloroform, toluene and dichlorobenzene. Columns show samples that were thermally annealed for 15 min and subsequently quenched slowly or rapidly or were annealed for 5 days in the presence of chloroform vapor.

The following is intended for submission to the journal Macromolecules.

Kendall A. Smith\textsuperscript{1}, Yen-Hao Lin\textsuperscript{1}, Kevin G. Yager\textsuperscript{2}, Joe Strzalka\textsuperscript{3}, Wanyi Nie\textsuperscript{4}, Aditya Mohite\textsuperscript{4}, and Rafael Verduzco\textsuperscript{1}.

\textsuperscript{1}Rice University, 6100 Main St., Houston, TX, USA, 77005

\textsuperscript{2}Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973

\textsuperscript{3}X-ray Science Division, Argonne National Laboratory, Argonne, Illinois 60439
All-conjugated block copolymers may be an effective route to solution processed photovoltaic devices, but we lack information on the relationship between molecular characteristics and photovoltaic performance. Here, we synthesize a library of poly(3-hexylthiophene) (P3HT) block poly((9,9-dialkylfluorene)-2,7-diyI-alt-[4,7-bis(alkylthiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (PFTBT) donor-block-acceptor all-conjugated block copolymers and investigate the effect of side-chains and processing conditions on crystal orientation and device performance. The orientation of P3HT crystallites is robust to various alkyl side chains on the PFTBT and is dependent only on annealing temperature, with edge-on and face-on orientations observed for annealing temperatures above and below the P3HT melting transition, respectively. However, we find that crystal orientation has only a modest effect on performance while the addition of side-chains is detrimental to performance for a wide range of side-chain types and polymer molecular weights.
6.1. Introduction

Organic photovoltaic devices (OPVs) have potential to be a low cost method of collecting solar energy and are attractive due to their ease of processing.\(^1\) All-conjugated block copolymers are a potentially useful method to stabilize polymer phase separation in all-polymer devices; however little is understood about the factors affecting the morphology of these systems.\(^2\)\(^-\)\(^5\) Recently, we reported on the block copolymer poly(3-hexylthiophene)-\textit{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}-PF8TBT) which achieved a performance of 3%, significantly above that of the corresponding homopolymer blend device.\(^6\)\(^-\)\(^8\) In order to make further progress in the development of all-conjugated block copolymer OPVs, we require more information on the relationship between molecular structure, processing history, morphology, and photovoltaic performance.

Since our previous report, significant progress has been made in all-polymer solar cells and reported efficiencies of all-polymer blend devices.\(^2\)\(^,\)\(^9\)\(^-\)\(^{13}\) Particularly relevant for our work, a similar P3HT/PFTBT blend system has been shown to have efficiencies as high as 2.7% with very high molecular weight PFTBT.\(^{14}\) Control of morphology and phase separation is a potential problem in polymer blend systems, and all-conjugated block copolymers can prevent large-scale phase separation through a covalent linkage. However, synthetic challenges continue to limit work with all-conjugated block copolymer OPVs, and there are only a few reports of other all-conjugated block copolymer systems being studied with energy levels capable of
producing workable devices.\textsuperscript{15–18} It is worth noting that thus far many polymers selected for use in block copolymer devices have been based on polymers that have performed reasonably well in polymer blends, and in some cases the performance of block copolymers is inferior to that of corresponding homopolymer blends.\textsuperscript{13,18,19} However, since the covalent linkage precludes large scale phase separation and homopolymers that perform well in blends generally do so because they have inherently limited phase separation, a better approach may be to utilize polymers that have stronger phase separation. A better understanding of the characteristics of all-conjugated block copolymers that contribute to enhanced photovoltaic properties is needed to advance work with these materials.

A significant feature of the P3HT-\textit{b}-PF8TBT system is the atypical face-on (out-of-plane $\pi$ stacking) of the P3HT crystallites as opposed to the typical edge-on (in-plane $\pi$ stacking).\textsuperscript{20} This surprising behavior is not observed in many other block copolymers of P3HT and only a few homopolymers have similar behavior.\textsuperscript{15,21–23} The goals of this study are to understand the influence of PFTBT side chains and processing conditions on the resulting orientation of P3HT crystallites and the related performance impact. We assess the performance of organic solar cell devices and perform grazing incidence small/wide angle X-ray scattering (GISAXS/GIWAXS) on a series of block copolymers of P3HT-\textit{b}-PFTBT where the alkyl side chains of the PFTBT are systematically varied. Since altering side chains affects solubility and packing of the PFTBT block, we expect that the side chains might influence P3HT crystal orientation, the degree of phase separation in the block copolymer, and the photovoltaic performance of the material. We show that the addition of side chains
has some negative consequences on performance, which may be due to increased miscibility between the blocks and reduced domain sizes. We find that the crystal orientation of these block copolymers appears robust to various alkyl side chains but does have a strong dependence on annealing temperature. Further, we establish that the orientation of the P3HT crystals has a modest effect on photovoltaic performance.

6.2. Discussion

Figure 6.1: Block copolymers used P3HT as the donor block and PFTBT with various side chains as the acceptor block. Side chains on the fluorene unit (R1) were methyl, hexyl, and octyl and are denoted as F1, F6, and F8, respectively and hexyl and ethyl-hexyl side chains on the dithiophene-benzothiadiazole unit (R2), are denoted HTBT and EHTBT respectively. Photovoltaic performance of polymers similar to that reported previously without side chains on the dithiophene-benzothiadiazole unit (R1=C8H17, R2=H, P3HT-b-PF8TBT) are also included.5

In this work, we use block copolymers consisting of P3HT-b-PFTBT where the side-chains on the PFTBT block are systematically varied as shown in Figure 6.1. The side chains chosen here were selected to provide a range of different alkyl side
chains and improve solubility of the final block copolymer. The goal was to investigate the impact on the morphology and performance of these materials while not significantly altering the optoelectronic properties of the backbone. Synthesis of these block copolymers was performed by a sequential Grignard Metathesis (GRIM) polymerization followed by an end-capping Suzuki reaction approach that has been reported previously. Block copolymers were then purified by washing with acetone and boiling hexanes to remove PFTBT oligomers and homopolymer impurities. Homopolymers of each of the PFTBT blocks were also made and full characteristics of homopolymers and block copolymers are provided in Supporting Information (Table S6.1 & Table S6.2). Due to the lack of significant differential solubility between P3HT and PFTBT (low molecular weight PFTBT is soluble in hexanes), extensive evaluation of the purity of these samples was performed to quantify the amounts of homopolymer impurities. Our analysis also provides an estimate of the relative amounts of P3HT-\text{-}b\text{-}PFTBT diblock copolymer and P3HT-\text{-}b\text{-}PFTBT-\text{-}b\text{-}P3HT triblock copolymer in each sample. In brief, to perform this analysis we use the size exclusion chromatography with ultraviolet/visible (UV/Vis) detection combined with $^1$H NMR data (Figure S6.1, Table S6.2) for the relative mass of each polymer block at each elution time. We then utilize a standard optimization method to solve simultaneously for molecular weight distributions of PFTBT homopolymer, PFTBT in diblock and triblock block copolymers, the relative mass fractions of block copolymers and homopolymers, and the molecular weight as a function of elution time. In order to resolve a uniqueness issue in the optimization, the molecular weight of a P3HT homopolymer is fixed to the value determined by
multi-angle light scattering. Although this analysis is straightforward, the authors are not aware of a similar method being used for determining the purity of block copolymer samples thus full details of the analysis are provided in Supporting Information ("Determination of Block Copolymer Purity", Figure S6.2 & Figure S6.3) along with characteristics of all block copolymers synthesized for this work (Table S6.2). In general, we find that all samples are majority block copolymer with a mixture of diblock P3HT-b-PFTBT and triblock P3HT-b-PFTBT-b-P3HT.

Performance of most block copolymer materials are included in Supporting Information Table S6.3; however surprisingly, the best performance we obtained for the materials with hexyl or ethyl-hexyl side chains on the thiophene rings was less than 0.1%. For comparison, we have included in Table S6.3, three materials without side chains on the thiophene rings of the PFTBT block (P3HT-b-PF8TBT): the previously reported 3% materials and two similar block copolymers which differ in P3HT content and molecular weight. As can be readily seen in Figure 6.2, the P3HT-b-PF8TBT materials uniformly outperform the materials here with added side chains. This makes the poor performance of the materials with the additional side chains quite striking and may indicate that these side chains are responsible for increased mixing or disrupt conjugation along the backbone, either of which could result in decreased performance. Trends among our materials suggests that higher P3HT content (around 65%) and/or higher molecular weights may yield improved performance. Among the three P3HT-b-PF8TBT block copolymers, the higher performance of one sample may be due to the more balanced P3HT content (56%
compared with 42% and 75%) or lower polydispersity (1.30 compared with 1.91 and 1.49).

Figure 6.2: Plot of performance data from Table S6.3 as function of A) P3HT content and B) number average molecular weight. Samples that have the same starting P3HT are connected with lines.
Figure 6.3: GISAXS extracted domain size as a function of number average molecular weight ($M_N$) for all block copolymers processed from room temperature solvent and annealed at 165°C (●), 230°C (▲), from refluxing (Hot) solvent and annealed at 165°C (■) and 230°C (▼), and solvent annealing with room temperature chloroform (◇). Alkyl chain lengths of 8, 6, and 1 on the fluorene unit of PFTBT are indicated by blue, red, and green respectively. Side chains on the thiophene units of PFTBT are indicated by closed symbols (hexyl) and open symbols (ethyl-hexyl).

In order to understand the difference in photovoltaic performance among the block copolymer samples studies, we look to GISAXS to assess domain sizes. Unlike the well-defined phase separation present in the prior report, most polymers used in this study did not have strong enough phase separation to be able to observe a
domain size in GISAXS under the conditions tested. In order to extract the domain size from the GISAXS data, we perform a linecut along q_y and convert the q value at the peak position to a domain spacing using d = 2\pi / q. As detailed in Figure 6.3, the domain sizes that we are able to extract from GISAXS (Figure S6.4) for points plotted as a function of molecular weight are significantly smaller (6-10 nm) than those observed in the previously reported high performance polymer (18 nm). Since the individual domain size for each polymer block are approximately half of the domain spacing, this implies domain sizes on the order of 3-5 nm, significantly smaller than the exciton diffusion length. The small domain size is a concern since small domains may favor charge recombination in the film which would be detrimental to device performance. Hence, we expect that the small domain sized evidenced in our materials is primarily responsible for their poor photovoltaic performance.

While the literature is replete with examples of side chains having unexpected effects due to subtle differences in packing and excessive phase separation, in our case, the phase separation appears inadequate and suggests that future work focus on utilization of side chains that increase the degree of phase separation.

Next, we focus our attention on the crystal orientation aspect of these materials and the effect of that orientation on performance. While the various PFTBT homopolymers are not the focus of this manuscript, these have not been reported extensively before; therefore we make some reference observations about features present in GIWAXS/GISAXS data (Supporting Information Figure S6.5). Well defined crystal structures are not present in the homopolymer data; however diffuse arcs are present at 1.3-1.6 Å⁻¹ and 0.34-0.36 Å⁻¹ distance. A second arc is
present in the PF6HTBT homopolymer at 0.22 Å⁻¹. In contrast to a prior report, these homopolymers, in general, do not show a preferred orientation but are nearly isotropic.\textsuperscript{20} This may be a molecular weight effect as these polymers are generally much smaller than those in the prior report. One exception is the PF6EHTBT which shows a slight orientation preference for a face-on configuration (out-of-plane π stacking). Additionally, the PF6EHTBT showed a lamellar pattern (d = 13 nm) in GISAXS which is somewhat unusual for homopolymer samples. Other homopolymers show a characteristic aggregate size in the GISAXS data but no ordered structures. GIWAXS analysis of solution processed regioregular P3HT films has already been reported extensively and shows a preference for edge-on orientation.\textsuperscript{27,28}

For our analysis, we are assuming that polymers are oriented in a predominantly edge-on (π stacking in-plane, alkyl stacking out-of-plane), face-on (π stacking out-of-plane, alkyl stacking in-plane), or isotropic orientation and neglect the potential for the unlikely end-on configuration (π stacking and alkyl stacking in-plane and polymer ends out-of-plane).\textsuperscript{29,30} In order to assess the amount of material that has edge-on versus face-on, the P3HT alkyl stacking peak at q = 0.38 Å⁻¹ is used in favor of the π stacking peak at 1.6 Å⁻¹ since it has a better signal to noise ratio. A detailed discussion of how this analysis was performed and a plot showing example analysis for predominantly edge-on, face-on, and isotropic distributions is included in Supporting Information (Figure S6.6).
Figure 6.4: Ternary plots of all polymers processed from room temperature solvent and annealed at 165°C (●), 230°C (▲), from refluxing (Hot) solvent and annealed at 165°C (■) and 230°C (▼), and solvent annealing with room temperature chloroform (♦). Alkyl chain lengths of 8, 6, and 1 on the fluorene unit of PFTBT are indicated by blue, red, and green respectively. Side chains on the thiophene units of PFTBT are indicated by closed symbols (hexyl) and open symbols (ethyl-hexyl). GIWAXS images of predominantly edge-on, face-on, and isotropic distributions are included for reference. (A) Shows all the data in a single ternary plot, while (B), (C), and (D) show 165°C, 230°C and room temperature chloroform annealed cases respectively.

Figure 6.4 shows a ternary plot summarizing the resulting distribution of P3HT crystal orientation as a function of processing conditions and side chain architecture. Figure 6.4A shows all the data where it can be seen that the data generally clusters near the isotropic or edge-on axis with few points in the center of the plot or near the face-on axis. Since these regions correspond to data points with
near zero amounts of edge-on or face-on orientations we can ascertain that most samples show orientations that are split between the isotropic and either a face-on or edge-on orientation. The lack of data points in the upper corner (greater than 80% face-on) is likely due to an unavoidable systemic bias as described in Supporting Information. As can readily be seen by comparing Figure 6.4B with Figure 6.4C, we can see the effect of annealing at 165°C (generally below the melting temperature of P3HT in the block copolymer) and 230°C (generally above the melting temperature of P3HT in the block copolymer). This trend is confirmed when plotting the data as a function of the difference between the annealing temperature and melting point for each block copolymer as shown in Figure S6.7. Figure 6.4D shows the effect of room temperature solvent annealing. Here we see very little of the edge-on orientation; however it should be noted that the chloroform annealed samples generally have poorer crystallization compared to the thermally annealed samples. In general, we find that the P3HT orientation is primarily driven by the annealing temperature. The other factors investigated, such as side chain length on the PFTBT unit and casting from room temperature or refluxing solvent do not have a dramatic effect on the final orientation. However, individual polymer samples cast from either room temperature or refluxing solvent typically have a different split in isotropic vs oriented crystals. We speculate that this may be a film thickness effect, since thicker films would be expected to have more isotropic distributions since interfacial effects are lessened. While we try to maintain similar thicknesses in all samples by control of concentration, there will be some variation particularly when
casting from refluxing solvent. Other factors such as sample purity and molecular weight were also investigated but no clear trends were found.

Figure 6.5: Summary of GIWAXS results of \textit{in situ} measurements for P3HT9-\textit{b}-PF8HTBT, P3HT-\textit{b}-PF8TBT, and P3HT-\textit{b}-PF1EHTBT. Temperatures for each plot are inset and temperature ramp is indicated on the left next to the structure of each compound. Images proceed in sequence from left to right.
To gain additional insight into the processes for these materials, several polymers were selected for *in situ* measurements to observe the structure of the polymer films evolve during the annealing process. While previous measurements show that the samples have significant differences in orientation if annealed above or below their melting temperature, the exact mechanism for allowing the reorientation of the P3HT crystals was unclear. For this study, samples were subjected to heating cycles reaching 165°C or 220°C (maximum temperature obtainable using beamline equipment) and GIWAXS images were taken roughly every 5 °C with the sample periodically moved slightly during measurements to avoid excessive beam damage. Due to the time required to collect data, all samples could not be studied in this manner, so a sampling of different polymers was selected: P3HT9-\(b\)-PF8TBT, P3HT2-\(b\)-PF8HTBT3, and P3HT7-\(b\)-PF1EHTBT1. These were selected to represent a range of the different side chains for the PFTBT block ranging from eight to one carbon on the fluorene and ethyl-hexyl, hexyl, and hydrogen for side-chains on the thiophene rings. The resulting videos (Chp6_P3HT2bPF8HTBT3_220C.mpg, Chp6_P3HT2bPF8HTBT3_165C.mpg, Chp6_P3HT9bPF8TBT_165C.mpg, and Chp6_P3HT7bPF1EHTBT1_165C.mpg) are included in Supporting Information with key transitions shown in Figure 6.5. Differential Scanning Calorimetry (DSC) data for these polymers (Figure S6.8) and linecuts of the images used in the video files (Figure S6.9, Figure S6.10, Figure S6.11, & Figure S6.12) are also included in Supporting Information. The P3HT9-\(b\)-PF8TBT was included as it is the same class of block copolymer that produced the superior 3% device previously reported, although best performance for this particular block
copolymers is lower (around 1%). The first series in Figure 6.5A (Chp6_P3HT2bPF8HTBT3_220C.mpg) for P3HT-\textit{b}-PF8HTBT heats the sample to the melting point of P3HT-\textit{b}-PF8HTBT (220°C) and then cooled. As can be seen the alkyl stacking peak is initially diffuse, becomes sharper and better defined at elevated temperatures until melting at around 220°C. Upon cooling the alkyl stacking peak appears again around 155 °C in the out-of-plane direction (orthogonal to the original direction). However, more remarkable is the presence of a lamellar stacking peak at \( q_z = 0.186 \text{ Å}^{-1} \) (lamellar order is shown in Figure 6.6B). This peak is present at the lower temperature, but is nearly obscured by the beam stop and the second order peak overlaps with P3HT so its presence is only obvious at the higher temperatures where side chains are fluid like and P3HT crystals are absent. As the film cools, the order is disrupted and the peak disappears. The origin of this peak likely arises from a lamellar PFTBT crystal structure. Using the same polymer in the series shown in Figure 6.5B (Chp6_P3HT2bPF8HTBT3_165C.mpg) heating only to 165°C, we see some different behavior. In this case, the in-plane alkyl stacking is preserved throughout the heating cycle. An interesting subtle feature is observed around 160°C, where the single broad peak splits into two sharper peaks at 0.167 Å\(^{-1}\) and 0.188 Å\(^{-1}\); however these peaks are ephemeral and quickly coalesce back into the single broad peak. Figure 6.5C (Chp6_P3HT9bPF8TBT_165C.mpg) shows the same experiment for P3HT-\textit{b}-PF8TBT where similar observations can be made. One key difference is that the PF8TBT peak location is shifted slightly to \( q_z = 0.16 \text{ Å}^{-1} \). This is significant since it shows the peak location to be dependent on the alkyl side-chain length with larger structures corresponding to longer side-chains. Figure 6.5D
(Chp6_P3HT7bPF1EHTBT1_165C.mpg) shows the results from P3HT-b-PF1EHTBT. Here the PFTBT stacking peak is not observable, although an almost imperceptible peak can be observed after cooling to 62 °C. More remarkable in this series is a feature at 161°C extending from 0.15-0.45 Å⁻¹ in qₓ and split in qᵧ by about 0.02 Å⁻¹. Close examination of data from P3HT-b-PF8HTBT in Figure 6.5A reveals a similar feature at temperatures near 180.5°C and 173.5°C. The origin of this feature is not clear, but may be attributable to the side chains on the TBT unit of the PFTBT block as they are not present in the P3HT-b-PF8TBT sample.

Figure 6.6: Summary of GIWAXS results of in situ measurements of P3HT-b-PF8HTBT films cooled from 165°C (A), in situ at 220°C (B) and cooled from 220°C (C) showing the change in orientation of P3HT after annealing above the melting point. Linecuts in qᵧ and qₓ are included adjacent to each GIWAXS image with peaks denoted by arrows.

The key observations of this study are summarized in Figure 6.6 which shows the GIWAXS image with linecuts for P3HT-b-PF8HTBT cooled from 165°C, the in situ measurement at 220°C, and the film cooled from 220°C. As seen in Figure 6.6A, in general films cooled from below the melting point show a face-on
orientation indicated by out-of-plane π stacking and in-plane alkyl stacking. The peaks associated with alkyl and π stacking completely disappear when heated above the melting point (Figure 6.6B) and the usual in-plane π stacking and out-of-plane alkyl stacking associated with the edge-on P3HT orientation are observed upon cooling (Figure 6.6C). The peak at 0.186 Å⁻¹ seen in Figure 6.6B is a curious observation since it corresponds to a distance of 34 Å, which is somewhat large for a crystal lattice yet far too small for a self-assembled structure.³¹ The peak is also extraordinarily broad indicating a range of characteristic distances with considerable dispersion in qₓ and qₜ. It is also worth noting that a very weak peak at qₓ = 1.4 Å⁻¹ is observed in the in situ measurement. Interestingly, the observed structure suggests edge-on orientation which is in contrast to a previously studied blend system which shows a face-on orientation for PFTBT.²⁰ This suggests that not only is the P3HT crystal structure orthogonal to its typical orientation but so is the PFTBT block, although in general the homopolymer films in this work do not indicate a preferred stacking direction (Figure S6.5). A schematic of a potential lamellar crystal structure that generally fits with these observations is shown in Figure S6.13 with peak spacing and max/min spacing plotted for reference. This structure is anti-symmetric across the TBT unit and symmetric across the fluorene unit. This allows the side chains to have minimal steric crowding. While other configurations are possible, the proposed morphology is in rough agreement with the data.
Figure 6.7: Comparison of device efficiency as a function of annealing temperature with DSC data for P3HT9-\textit{b}-PFTBT. Average efficiency and standard deviations are plotted for three batches of devices (denoted with red squares, yellow triangles, and green circles) cast from similar conditions (8mg ml\textsuperscript{-1} chloroform, 1500 rpm, ITO/PEDOT:PSS/Polymer/Al) and annealed after aluminum deposition for 10 minutes at the specified temperature. Standard deviation for the data point at 245°C is on the order of symbol size. Inset GIWAXS images at 200°C and 250°C showing change in P3HT crystal orientation.

In order to study the effect of crystal orientation on performance we use P3HT9-\textit{b}-PF8TBT with the same architecture as in the previous report (no side chains on thiophene rings of PFTBT), though this particular block copolymer has maximum performance of only about 1% (Table S6.3). Figure 6.7 shows a plot of average performance as a function of annealing temperature. The conditions for these devices were suboptimal, but were chosen so as to obtain very repeatable performance data. As can be readily seen, the effect of annealing above the melting transition, which results in a significant change in the P3HT crystal orientation, has minimal effect on the performance, close to the variation of performance from
device to device. Never the less, an effect on performance on the order of about 5-10% may be ascertained from the data.

Figure 6.8: Schematic of evolution of block copolymer film after casting. (A) shows as cast film with P3HT face-on. Upon heating above the melting point (B) the P3HT crystals melt and a lamellar structure (PFTBT) can be observed. After cooling (C), the P3HT crystals reform with an edge on orientation and disrupt the structure of PFTBT.

The physical picture for why the P3HT crystallites have a face-on orientation is still somewhat speculative, but with the available data we can draw a sequence that explains the observations (Figure 6.8). Prior work on X-ray reflectivity of PF8TBT/P3HT homopolymer blend films revealed that the PFTBT homopolymer preferred to segregate to the substrate interface, which may reduce or eliminate the preference of P3HT alkyl stacking normal to the surface. Additionally, although phase separation may be weak and somewhat disordered, we expect our block copolymer is separating into vertically oriented nanodomains that may be helpful in
producing films that have a face-on configuration.\textsuperscript{30} \textit{In situ} measurements have revealed a lamellar structure assignable to PFTBT in the block copolymer that has large domain spacing associated with it. This may lead to some geometric constraint that favors a face-on orientation of P3HT to accommodate the large lattice of the PFTBT block (as depicted in Figure 6.8A). Whatever the cause of the initial face-on orientation of P3HT, this configuration is clearly robust until the block copolymer film is heated above its melting point (Figure 6.8B). Here, P3HT in the melt is able to order itself relative to the substrate and as the film is cooled, the normal P3HT alkyl stacking pattern is observed (Figure 6.8C). It is noted that this comes at the cost of the ordering of the PFTBT polymer and elimination of the corresponding peaks in GIWAXS. Given that the sequence we outline here only depends weakly on the covalent linkage between the polymer blocks, we investigated the polymer blend under similar processing conditions and indeed some face-on orientation is observed for the a 1:1 blend of P3HT:PFTBT (Figure S6.14). Interestingly, for this case we see a split between face-on and edge-on P3HT crystallites which differ from the observed dominate face-on vs edge-on behavior observed for the block copolymers. Even though we would expect that the blend would phase separate, we still expect that some regions of the film would be similar to the block copolymer case. So for regions which are predominantly P3HT, we would expect the usually face-on orientation and for regions that are more mixed (and similar to the block copolymer morphology), we see some edge-on orientation, which is in line with the observations. An interesting follow on study would be to study the effect of blending block copolymers with homopolymer in order to see if the split between isotropic,
edge-on, and face-on could be directly tuned; however this is beyond the scope of this report.

6.3. Conclusion

Here we have performed a study on a series of P3HT-\(b\)-PFTBT polymers where we have systematically varied the side chains on the PFTBT block from methyl, hexyl, and octyl on the fluorene unit and hexyl and ethyl-hexyl on the thiophene rings to achieve a better understanding of the relationship between molecular characteristics, morphology, and photovoltaic performance. We found that the addition of side-chains to the PFTBT block results in lower photovoltaic power conversion efficiencies by at least an order of magnitude relative to block copolymers without side-chains on the PFTBT block. The block copolymers with added side-chains were found to contain relatively small domains (<10 nm) which may contribute to charge recombination and result in the poor photovoltaic performance. Small and poorly defined domains were found by GISAXS which we expect to have a negative impact on performance. Additionally, as other reports have noted, the addition of side chains may result in unfavorable changes in packing that can impact performance. Future work will focus on utilization of side chains that increase the degree of phase separation which may result in a more favorable morphology. The face-on orientation of P3HT, which is somewhat unique to this block copolymer system, was found to be essentially independent of side-chains on the PFTBT block but dependent on the annealing temperature. Annealing above the melting point of P3HT in the block copolymer was found to result in the edge-on
orientation typically observed neat P3HT films whereas the face-on orientation was observed for annealing temperatures below the melting point. *In situ* measurement reveal that the orientation is fixed in the as cast film and only after P3HT crystals melt and recrystallize do they change orientation to the typically observed edge-on orientation. Annealing temperature and P3HT crystallite orientation was found to have a small impact on the photovoltaic performance of these all-conjugated block copolymers.

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**6.4. References**


(15) Wang, J.; Ueda, M.; Higashihara, T. Synthesis and Morphology of All-Conjugated Donor-acceptor Block Copolymers Based on poly(3-Hexylthiophene)


6.5. Supporting Information

6.5.1. Instrumentation

6.5.1.1. Nuclear Magnetic Resonance Spectroscopy (NMR)

Figure S6.1: $^1$H NMR Spectra for block copolymers.
Solution $^1$H NMR spectroscopy was performed on a 500 MHz Varian Inova NMR. Chloroform-d (CDCl$_3$, Cambridge Isotope Laboratories) was used as the solvent with TMS (0.05%) as an internal standard. Data was processed using SpinWorks 3.1.8.1 and example plots are shown in Figure S1. For block copolymers, the % P3HT was determined by integration of the respective aromatic regions of each polymer block.

**6.5.1.2. Size-Exclusion Chromatography (SEC)**

Polymer molecular weights and polydispersities (PDIs) were obtained by 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, a Wyatt Technology HELEOS II multi-angle laser light scattering (MALLS) detector ($\lambda$=658 nm), and a Wyatt Technology Optilab reX RI detector. This system enables SEC with simultaneous refractive index (SEC-RI), UV/VIS (SEC-UV/VIS), and MALLS (SEC-MALLS) detection. THF was used as the mobile phase at a flow rate of 1 mL/min at 40 °C. Weight average molecular weights ($M_w$) and polydispersity index (PDI) were determined using SEC-RI calibrated with a set of monodisperse polystyrene standards (Astra Software Version 5.3.4). Additional characterization was performed using UV/visible detection and is described in detail in a subsequent section.
6.5.1.3. Differential Scanning Calorimetry (DSC)

Thermograms were recorded on a TA Instruments DSC Q20-2255 equipped with a refrigerated cooling system against an empty sealed pan as reference. In a typical run, the sample was heated to 250 °C at 5 °C/min before being cooled to 0 °C at 5 °C/min for three total cycles. Second heating cycles are reported.

6.5.1.4. Grazing Incidence Small/Wide Angle X-ray Scattering (GISAXS/GIWAXS)

For characterization of domain size and crystal orientation, both homopolymer and block copolymer samples were prepared for GISAXS/GIWAXS measurements by casting 12 mg polymer per ml chloroform solutions stirred at room temperature or heated to refluxing conditions (90°C) onto silicon substrates. These samples were then annealed at either 230°C for 15 minutes (generally above the melting point of P3HT) or 165°C (generally below the melting point of P3HT) for 20 minutes.

GIWAXS and GISAXS measurements were carried out at the X9 undulator beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. An X-ray energy of 14.0 keV was selected using a silicon monochromator, and images were collected using two area detectors: a Pilatus 300k (Dectris) for small-angle measurements and a Photonic Sciences fiber-coupled CCD for wide-angle data. Sample measurement was carried out under vacuum which is in the range of 2-3 × 10⁻⁶ bar. GIWAXS images presented herein are median filtered
and processed using the GIXSGUI package for Matlab (Mathworks), data are corrected for X-ray polarization, detector sensitivity and geometrical solid-angle.\textsuperscript{2} Plots are normalized and plotted on a logarithmic scale. Data was collected with incident angles of 0.07°, 0.10°, and 0.15° and, except where noted, data at 0.10° is presented herein. Chi distributions were extracted using custom python code and the pyXS software package (http://www.bnl.gov/ps/x9/software/pyXS.asp) as previously described.\textsuperscript{3}

GIWAXS videos were obtained from measurements obtained at Sector 8 of the Advanced Photon Source, Argonne National Laboratory.\textsuperscript{4} Beamline 8-ID-E operates at an energy of 7.35 keV and images were collected from a Pilatus 1MF camera (Dectris). Using the GIXSGUI package for Matlab (Mathworks), data are corrected for X-ray polarization, detector sensitivity and geometrical solid-angle.\textsuperscript{2} For GIWAXS, the beam size is 200 µm (h) × 20 µm (v), and the sample detector distance is 204 mm. Incidence angle was fixed at 0.2°. Sample measurement and thermal annealing were carried out under vacuum, with the sample stage interfaced with a Lakeshore 340 unit. The maximum obtainable temperature with this experimental setup is 220°C.

6.5.2. Materials

Anhydrous tetrahydrofuran (THF), 1,3-bis(diphenylphosphino)propane]dichloronickel(II) (Ni[dppp]Cl\textsubscript{2}), isopropylmagnesium chloride (\textsuperscript{t}PrMgCl) with LiF 1.3M in THF, 3-hexylthiophene, 3-bromothiophene, 2-ethylhexyl bromide, magnesium, 9,9-dioctylfluorene-2,7-
diboronic acid bis(1,3-propanediol) ester, 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, 9,9-dimethyl-2,7-dibromofluorene, and tetrakis(triphenylphosphine) palladium(0) (Pd[PPh$_3$]$_4$) were obtained from Aldrich and used as received. 2,5-Dibromo-3-hexylthiophene, 9,9-dimethylfluorene-2,7-diboronic acid bis(pinacol ester), 4,7-bis(5-bromo-4-hexylthiophene-2-yl)benzo[c][1,2,5]thiadiazole, and 4,7-bis(5-bromo-4-(2′-ethyl)hexylthiophene-2-yl)benzo[c][1,2,5]thiadiazole were synthesized in a manner similar to literature procedures. Block copolymers of poly(3-hexylthiophene) and poly((9,9-dialkylfluorene)-2,7-diyl-alt-[4,7-bis(alkylthiophen-5-yl)-2,1,3-benzothiadiazole]-2′,2″-diyl) were made by a sequential Gringard Methathesis (GRIM) / Suzuki polycondensation approach reported previously. Characteristics of homopolymers and block copolymers are summarized in Tables S1 and S2.
<table>
<thead>
<tr>
<th>Name</th>
<th>$M_W$(PS) (kDa)$^a$</th>
<th>$M_N$(PS) (kDa)$^a$</th>
<th>PDI$^a$</th>
<th>$\frac{dn}{dc}$</th>
<th>$M_W$(LS) (kDa)$^b$</th>
<th>$M_N$(LS) (kDa)$^b$</th>
<th>PDI$^b$</th>
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Table S6.1: Table of homopolymer samples. $^a$Mass average ($M_W$), number average ($M_N$) molecular weights, and polydispersity (PDI) relative to polystyrene (PS) standards. $^b$Mass average ($M_W$), number average ($M_N$) molecular weights and polydispersity (PDI) calculated from multi-angle laser light scattering (LS, MALLS). PFTBT polymers absorb at the wavelength of the laser used for MALLS measurements which interferes with the measurement so only polystyrene-relative molecular weights are reported. Characteristics of P3HT8 and P3HT10 were reported previously and are included here for reference. MALLS not available for P3HT8, P3HT9, and P3HT10.
<table>
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<tr>
<th>Name</th>
<th>%P3HT (NMR)a</th>
<th>$M_W(PS)$ (kDa)b</th>
<th>$M_N(PS)$ (kDa)b</th>
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<th>Mass Fraction Analysisc</th>
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<td>32.5</td>
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Table S6.2: Table of block copolymer samples. aP3HT content determined by integration of P3HT and PFTBT aromatic regions from $^1$H NMR. bMass average ($M_W$), number average ($M_N$) molecular weights, and polydispersity (PDI) relative to polystyrene (PS) standards. cSample composition from fitting routine detailed in the section on “Determination of block copolymer purity” in terms of P3HT homopolymer (P3HT), PFTBT homopolymer (PFTBT), diblock copolymer P3HT-$b$-PFTBT (DBCP), and triblock copolymer P3HT-$b$-PFTBT-$b$-P3HT (TBCP). Characteristics of P3HT8bPF8TBT and P3HT10bPF8TBT were reported previously and are included here for reference.8,10
### 6.5.3. Organic Photovoltaic Devices

<table>
<thead>
<tr>
<th>Material</th>
<th>Efficiency (%)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>Fill Factor (%)</th>
<th>Anneal</th>
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<tr>
<td>P3HT1bPF8HTBT1</td>
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<td>0.172</td>
<td>0.006</td>
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<tr>
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<td>160°C 15 min</td>
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</tr>
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<td>0.49</td>
<td>25</td>
<td>165°C 20 min</td>
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**Table S6.3:** Table of maximal performance for selected block copolymer devices made during the course of this work. Most materials listed here have been extensively optimized due to low initial performance. Performance for P3HT8bPF8TBT previously reported in Nano Letters.\(^8\) Photovoltaic performance of P3HT10bPF8TBT was not previously reported but synthesis was reported in Polymer Chemistry.\(^10\)

Solar cells were fabricated using a conventional layup of ITO/PEDOT:PSS/Active Layer/Al. ITO substrates were washed with acetone before
being cleaned in an oxygen plasma for 3 minutes. PEDOT:PSS (Aldrich) was spin cast onto the substrate at 5000 rpm for 40 seconds before being dried at 120°C for 10 min in air and then being transferred to an Argon glovebox. Various solution concentrations were used in this work, typically between 5-10mg/ml in anhydrous chloroform (Aldrich). In one typical procedure, the solution was stirred overnight at 100°C and allowed to return to room temperature before casting at 1500 rpm for 30 seconds. After casting, samples were typically annealed for 10 min at 100°C before thermal deposition of 100 nm of aluminum at 10⁻⁶ torr. Samples were then annealed at various temperatures typically for durations of 10 min (though for some samples longer durations were used). Resulting devices are summarized in Table S3.

### 6.5.4. Determination of Block Copolymer Purity

In order to determine the amount of block copolymer (diblock and triblock) as well as homopolymer (P3HT and PFTBT) in our samples, we first determine the amount of each polymer constituent at each elution time. This was accomplished assuming linearity of absorbance with concentration in accordance with the Beer-Lambert law and independence of the absorbance of each polymer block. The direct conjugation between the polymers is, in theory, a concern for the independence of the absorbance of each polymer block. However, this is not a practical limitation for our material system as the fluorene unit effectively isolates the rest of the PFTBT block from the P3HT block as demonstrated in previous studies with single F8TBT/TBTF8 units attached.⁹ Therefore, any influence of the absorbance properties from the linker are not substantially different than those of chain ends
and are assumed to rapidly dissipate for reasonably large polymers. A practical consideration for our experimental setup found that for strongly absorbed wavelengths (i.e. 450 nm for P3HT) occasionally some minor deviations from linearity could be observed in the homopolymer traces due to the effect of transmitted light being small relative to incident light leading to signal saturation in the detector. Each homopolymer was injected into the SEC system at known concentration and the signal over the elution times where the polymer was present were summed and divided by the product of the concentration and injected volume of each sample to give the total absorbance of each polymer at a particular wavelength (i.e. $A_{500\,nm}^{P3HT}$) as in Equation 1.

$$A_{500\,nm}^{P3HT} = \frac{\sum S_{500\,nm}}{c \times v}$$

Since the signal from the detector is in arbitrary units and not calibrated to give unit-less absorbance measurements, there is an additional constant that should be included to obtain unit-less absorbance per unit mass; however as it will cancel out when we invert the matrix to obtain the mass of each polymer in the block copolymer, we neglect it here. The mass at each polymer as a function of the elution time for the block copolymer may then be readily obtained by measuring the signal at two wavelengths and inverting the absorbance matrix obtained from the homopolymer measurements as in Equation 2. Typically the absorbance at 500 nm and 550 nm was used for this study; however in a of couple cases, saturation issues at 500 nm from the P3HT homopolymer (P3HT6 in Table S1) or poor signal quality in the homopolymer trace (P3HT8bPF8TBT in Table S2) necessitated the use of a
different wavelength (300nm) for this analysis. In order to obviate any small error in the calculated mass at each elution time, the total mass fraction for each sample was fixed to within 10% of the $^1$H NMR calculated value (Table S1).

\[
\begin{align*}
M_{3HT} & = A_{500 \text{ nm}} \begin{bmatrix} A_{500 \text{ nm}} & A_{550 \text{ nm}} \\ A_{550 \text{ nm}} & A_{550 \text{ nm}} \end{bmatrix}^{-1} [S_{500}]
\end{align*}
\]

Having obtained the mass of each polymer for each elution time, we need to solve for the mass fractions of each component. This is accomplished by using the constrained minimization function from the optimization toolbox in Matlab (fmincon). The primary concern here is obtaining a unique solution to the optimization problem. Generically, it is possible that several of the parameters we are investigating could trade off against each other in a manner that would lean to a non-unique solution; however, as will be discussed, this turns out not to be a major concern due to the near independence of the parameters investigated. The first equation we must solve for is the characteristic equation for the SEC column as given by Equation 3.

\[
MW(t) = e^{a_0 + a_1 \cdot t + a_2 \cdot t^2 + a_3 \cdot t^3} = A \cdot e^{b_1 \cdot t + b_2 \cdot t^2 + b_3 \cdot t^3}
\]

While perhaps not immediately obvious by cursory inspection of Equation 3, the prefactor A will not be unique in any optimization without an additional constraint added to the system. This is because while the relative size of the various constituents in the separation can be found in the course of optimization, the molecular weight is not an intrinsic property that can be solved for in these equations. We solve this numerical issue by adding a constraint that the P3HT
homopolymer’s mass average molecular weight as determined by using Equation 3 is the same as that determined by light scattering (MALLS) measurements of the same homopolymer. Thus the parameter $a_0$ is solved analytically during the optimization using Equation 4 which can be readily obtained by using Equation 3 and the definition of mass average molecular weight and solving for $a_0$ (where P3HT(t) is the homopolymer SEC trace as a function of elution time t, $M_W$ is the known P3HT mass average molecular weight, and $a_1$ and $a_2$ are coefficients from Equation 3).

\[
\text{Equation 4: } a_0 = \ln\left(\frac{M_W \sum P3HT(t)}{\sum P3HT(t) \cdot e^{a_1 t + a_2 t^2}}\right)
\]

This choice is somewhat arbitrary and in principle any other fixed value could be used to obtain similar final results. However, this allows us to obtain values for the molecular weights that are in some sense based on the light scattering determined molecular weight of P3HT (although this data is not reported or used in any of the following analysis). Initial values for $a_1$ and $a_2$ are based on the polystyrene calibration curve as an initial guess at how the polymers elute through the column. While there can be substantial deviations between polystyrene based molecular weights and the true molecular weight, this is a reasonable starting point. After optimization, we can plot the resulting molecular weight versus elution time (Figure S6.2, polystyrene curve plotted for reference). A potential improvement would be to allow the optimization to optimize between different experiments while sharing the same column parameters; however this is a significantly more
complicated optimization routine to code and would require additional computational time.

![Graph of SEC calibration curves with polystyrene calibration curve included for reference.](image)

**Figure S6.2:** Plot of fit SEC calibration curves with polystyrene calibration curve (black) included for reference.

With the molecular weight curve defined, we now discuss the other key variables in the optimization. The P3HT homopolymer curve we directly obtain from its SEC trace. We then use the Schulz-Zimm distribution with the $M_n$ and PDI as adjustable parameters to define a PFTBT block attached to the P3HT homopolymer. We then mathematically sum the masses of these two polymer distributions factoring the mass fractions at each molecular weight and keeping...
track of the mass fractions of each polymer in order to obtain a molecular weight and mass fraction distribution for the resulting block copolymer. The same procedure is done for triblock copolymers, with two P3HT polymers added to the distribution. The $M_n$ and PDI of the PFTBT polymer incorporated into the diblock and triblock copolymer are allowed to be different. Finally, the Schulz-Zimm distribution is used to define a PFTBT homopolymer distribution. In addition, the mass fractions of the P3HT and PFTBT homopolymers and diblock and triblock copolymers are optimization variables. While there are a lot of variables (10 material variables, 2 column parameters, $a_1$ & $a_2$, and the mass fractions of each block in the sample which we constrain to be within 10% of the $^1$H NMR determined value) to put into a fitting equation, fortunately, most of these are naturally independent. The diblock copolymer is by definition larger than the P3HT homopolymer as additional mass has been added to it, and the triblock is generally larger than the diblock. Similarly, for these materials the residual PFTBT homopolymer is usually the about the same size as the P3HT homopolymer or slightly smaller depending on the sample. These factors allow for a well posed problem that can be readily solved by minimizing the squared difference between a synthetic SEC trace for the PFTBT mass curve and P3HT mass curves with the derived data discussed earlier. The results of this optimization for P3HT7-b-PF1EHTBT1 are shown in Figure S6.3.
As can be readily seen in Figure S6.3, the fit to the data for both the P3HT and PFTBT mass curves is extraordinarily good. Slight undulations present in the PFTBT data around 1000-3000 g/mol are likely due to discrete sizes of the PF1EHTBT oligomer. These undulations are not captured in the fit since the Schulz-Zimm distribution is a continuous distribution. The peak positions for the block copolymers and homopolymers are significantly different, adding validity to the optimization approach. Additionally, we can see that the triblock copolymer contributes more to the P3HT signal than PFTBT signal relative to what is seen in the diblock copolymer as we would expect since there are two P3HT blocks for this
case. The polystyrene molecular weights, polydispersity, \( dn/dc \), and MALLS of the homopolymers used in this work are summarized in Table S6.1. The results for the amount of each homopolymer and block copolymer in the sample obtained using the described method are shown in Table S6.2 along with the sample's %P3HT determined by \(^1\)H NMR integration of the aromatic regions of each polymer and the sample's mass average (\( M_W \)), number average (\( M_N \)) molecular weights, and polydispersity (PDI) relative to polystyrene standards.
Figure S6.4: Plot of GISAXS data showing extracted q values (d-spacing is 2 $\cdot$ $\pi/q$).
Figure S6.5: Plot of GIWAX (first two rows) and GISAXS (second two rows) for all homopolymer materials. Linecuts in $q_y$ are included as an inset for GISAXS data. Films cast from room temperature chloroform and annealed at 165°C. Other casting/annealing conditions yielded similar results.
Figure S6.6: Example chi distribution analysis showing predominantly edge-on, face-on, and isotropic distributions.

Analysis of chi distributions has been discussed extensively in prior work, so a detailed explanation of the analysis is not reported here. The analysis proceeds by performing a series of radial linecuts at various values of chi and extracting the maximal value over the baseline. Angular distributions at $q = 0.38 \, \text{Å}^{-1}$ were taken between approximately 1.6-81° accounting for the intersection of the Ewald sphere, excluding data near the Yolanda streak, and extrapolating in an isotropic manner to 0° and 90°. Data was also multiplied by a factor of $\sin(\text{chi})$ to account for the mass at each angle of the distribution. The effect of extrapolation near 0° is negligible as the span of the extrapolation is small; however the extrapolation near 90° has the effect of systematically underestimating the face-on orientation. Other extrapolation...
methods were attempted including Gaussian distributions and orientation distributions; however while these generally provided good fits, for some data sets this results in erroneously large values in the extrapolated region, usually due to some sporadic fluctuations in the source data. Since these could not be easily excluded without unduly biasing the fits, the systematic bias inherent in isotropic extrapolation was deemed preferable and is used here. Nevertheless, it is good to bear in mind for the following analysis that the reported percentages for face-on orientation are a lower bound on this orientation, though the trends between the edge-on/face-on/isotropic orientations are certainly valid. To determine the relative amounts of P3HT crystallites in the three orientations, the isotropic portion was first determined by selecting the smallest isotropic curve, and intersection point, that intersects the data at angles greater than 5°. For predominantly edge-on orientations, this would typically be near 80° while for nearly isotropic or face-on distributions the intersection would typically be between 10-45°. The face-on distribution would be considered to be the intensity at angles between the intersection point and 90° after subtracting the intensity of the isotropic distribution. The edge-on distribution would be the intensity at all angles between 0° and the intersection point after subtracting the intensity of the isotropic distribution. Figure S6 shows this analysis for three primarily edge-on, face-on, and isotropic distributions. As is readily obvious from this plot, the edge-on distributions are relatively narrow whereas face-on distributions are considerably broader.
Figure S6.7: Plot of fraction of edge-on, face-on, and isotropic components of the distribution as a function of the difference between the annealing temperature and the melting point (as determined using the second DSC heating cycle).

Figure S6.7 shows the thermally annealed cases from the main text plotted as a function of the difference between the annealing temperatures (165°C and 230°C) and the melting point of each polymer sample as determined from the second heating cycle from DSC. From this data we can see strong reductions in face-on orientations for temperatures above the melting point and an increase in edge-on orientations. Isotropic orientations have no strong dependence on this parameter.

DSC heating and cooling curves for the materials tested are shown in Figure S6.8. Figure S6.9, Figure S6.10, Figure S6.11, and Figure S6.12 displays the linecuts of GIWAXS data from in situ measurements corresponding to GIWAXS videos. See main text for discussion of the data.
Figure S6.8: Heating and cooling DSC cycles for P3HT9-\textit{b}-PF8TBT, P3HT2-\textit{b}-PF8HTBT3, and P3HT7-\textit{b}-PF1EHTBT1 used for \textit{in situ} measurements
Figure S6.9: Line cuts corresponding to $q_z$ axis for all source GIWAXS images included in Chp6_P3HT2bPF8HTBT3_220C.mpg. Temperature in degrees Celcius included adjacent to each linecut.
Figure S6.10: Line cuts corresponding to $q_z$ axis for all source GIWAXS images included in Chp6_P3HT2bPF8HTBT3_165C.mpg. Temperature in degrees Celcius included adjacent to each linecut.
Figure S6.11: Line cuts corresponding to $q_z$ axis for all source GIWAXS images included in Chp6_P3HT9bPF8TBT_165C.mpg. Temperature in degrees Celcius included adjacent to each linecut.
Figure S6.12: Line cuts corresponding to $q_z$ axis for all source GIWAXS images included in Chp6_P3HT7bPF8EHTBT1_165C.mpg. Temperature in degrees Celcius included adjacent to each linecut.
Figure S6.13: Schematic of alternating PF8HTBT structure giving rise to lamellar domain spacing in agreement with GIWAXS data.

Figure S6.14: Plot of 1:1 P3HT:PF8TBT blend annealed at 165°C for 15 minutes. A) Shows GIWAXS image at incidence angle of 0.07° and B) shows chi linecut along P3HT alkyl stacking peak (q=0.38 Å⁻¹).
6.5.5. References

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This chapter is dedicated to a series of works that are currently in progress that will be completed soon. The current status of each is detailed and results for each are presented. The first is a recent work on neutron scattering and reflectivity on the dP3HT/PF system in both the block copolymer and blend. This work shows interesting aspects of self-assembly that were not accessible from X-ray scattering data. Following this is an in situ annealing study of a series of P3HT-$b$-PFTBT materials in which the influence of PFTBT on the morphology is detailed. This is followed by an in depth discussion of the crystallization of a large series of P3HT-$b$-PFTBT block copolymers. These materials were also tested in devices, but regrettably all those materials tested produced poor performing devices. Finally, the results of work done on P3DDT-$b$-PFTBT used in devices are described where some trends in performance were found.
7.1. Comparison of All-Conjugated Block Copolymers and Blends by Neutron Scattering and Reflectivity

This project is currently in progress. Excellent results were obtained by neutron scattering and reflectivity which was collected in January 2014 and form the core of this study. Supplementary X-ray scattering data was obtained at the Advance Photon Source at Argonne National Laboratory in April 2014. Additionally, Dr. Dan Olds of Los Alamos National Laboratory will be contributing a more sophisticated analysis of the data included herein which will provide additional insight into the system.

7.1.1. Introduction

Conjugated polymers are promising materials for organic electronics such as organic photovoltaic devices.\textsuperscript{1,2} Recent advances have demonstrated all-polymer solar cells with power conversion efficiencies over 4%, competitive with polymer/fullerene blends.\textsuperscript{3-6} As demonstrated by our recent report of poly(3-hexylthiophene)\textsuperscript{block} poly((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2′,2″-diyl) (P3HT-\textsuperscript{b}-PFTBT), block copolymers of donor polymers and acceptor polymers have the potential to substantially improve the performance over the polymer blend by controlling phase separation.\textsuperscript{7} However, understanding of the morphology is complicated by the poor contrast between the blocks when using conventional X-ray scattering techniques showing only weak evidence of phase segregation.\textsuperscript{8,9} Resonant soft X-ray scattering (RSOXS) has been
used in some systems to enhance contrast in these types of films with limited contrast between the blocks; however use of this technique is limited.  

Here, we use neutron reflectivity (NR) and small angle neutron scattering (SANS) supplemented by grazing incidence small angle X-ray scattering (GISAXS) to probe the morphology of a deuterated poly(3-hexylthiophene) (dP3HT) and poly(9,9-dioctylfluorene) (PF8) system in both the blend and block copolymer and to explore the effect of thermal annealing on the morphology of the film as a function of time. Surface topology is also analyzed by electrostatic force microscopy (EFM).

7.1.2. Results and Discussion

Materials were synthesized using a sequential polymerization route described elsewhere where dP3HT was synthesized from a deuterated monomer using Grignard Metathesis polymerization which was then used as an end-capping reagent in a Suzuki reaction for the PF block. Figure S7.1 shows the size exclusion chromatography trace for the resulting reaction products showing good conversion to block copolymer with a trace amount of homopolymer. By using \(^1\)H NMR integration of the non-deuterated aromatic region, the polymer was determined to be approximately 60% dP3HT by weight.

For reference, pure films of dP3HT and PF were prepared in order to obtain scattering length densities for each which was determined to be 5.82 and 0.3 respectively (details in supporting information). The SLD profile for the block
copolymers film was determined at 3 different annealing durations (as cast, 15 min, and 150 min) with the SLD of each layer constrained to be within the SLD of the pure components. As can be seen in Figure 7.1, the initial profile shows a P3HT wetting layer at the air interface and a PF wetting layer at the silicon wafer interface. Although Fourier invariance suggests other morphologies are possible, this fits well with the data and is consistent with previous reports of P3HT wetting layers. As annealing proceeds, the wetting layers diffuse into the substrate and at 150 min the sample's depth profile appears homogeneous. For this case the average SLD of the polymer layer is 3.5 which would give a composition of 58% in good agreement with NMR results. The homogeneous profile suggests that the two polymers are well mixed in the layer with no preference for either interface. The profile as drawn would be consistent with horizontal phase separation, but as shown in Figure S7.2, a vertical phase separated structure with some roughness in the interface would provide nearly the same profile. By contrast, the data obtained from the blend was not able to be fit with a simple profile. Example fits that provide a good match to the data is shown in Figure 7.2. As with the block copolymer, the fit for the as cast film shows a wetting layer of P3HT; however the annealed films at 15 min and 150 min show profile fits that have large undulations. This would be consistent with bulk phase separation between the two polymers in the blend.
Figure 7.1: Neutron Reflectivity of dP3HT-\textit{b}-PF block copolymer films.

Figure 7.2: Preliminary fits of dP3HT/PF blends
A comparison of grazing incidence X-ray scattering of thin films and small angle neutron scattering of thick films is shown in Figure 7.3. The dP3HT/PF blend shows a broad feature in the as cast film between $q_y = 0.02-0.05\,\text{Å}^{-1}$ suggesting a broad range of domains ranging from 12-31 nm. However, upon annealing the profiles become featureless which suggests that the film no longer has small domains. By contrast, the block copolymer films show an initially featureless profile that produces a weak peak in intensity after 2.5 hr of annealing. The dominate feature size in the GISAXS measurement for the block copolymer is a prominent peak at $q_y = 0.025\,\text{Å}^{-1}$ corresponding to a domain size of 25nm. No secondary peak is present to suggest lamellar or other structures in the film; however since the peak is
broad (extending from \( qy = 0.02-0.04 \ \text{Å}^{-1} \) or 16-31 nm), it is likely that the block copolymer is too polydisperse to form an ordered nanostructure. The neutron scattering data is in agreement with the GISAXS data for the dominant feature; however additional information on the morphology can be extracted from the SANS data. In particular, significant changes in slope occur through the SANS data for both the block copolymer and blend which are provide information about the size of various scattering surfaces within the materials. This analysis is in progress and will be completed at a later date.

7.1.3. Conclusion

The use of neutron scattering analysis has proven to give better contrast X-ray scattering data and will provide valuable insights into the dynamics of these systems. GISAXS data provides verification of average domain size extracted from SANS data; however SANS data is able to provide us with information about the evolving structure of the polymer as a function of annealing time.
7.1.4. Supporting Information

Figure S7.1: SEC-RI trace of dP3HT-b-PF and starting dP3HT.

Figure S7.2: Plot of block copolymer film at 150 min fit with a multilayer having thickness period on the same order as expected for block copolymer domain size.
Figure S7.3: $^1$H NMR of dP3HT-$b$-PF.

### 7.2. P3DDT-$b$-PFTBT Organic Photovoltaic Devices

It's not clear whether this work will ever make it into a publication as the results are not as quantitative as would be desired. Nevertheless, this work has been presented at several conferences including the APS March meeting and the ACS Spring meeting in 2014. The work here uses P3DDT-$b$-PFTBT instead of P3HT-$b$-PFTBT as the active material in the block copolymer device. The goal was to obtain larger molecular weight block copolymers that could be obtained with the P3HT
system since the longer alkyl chain on the P3DDT might help solubilize the block copolymer. In practice, this was less effective than expected. This may imply that the solubility issues of the P3HT-\textit{b}-PFTBT block copolymers may have been due to some crosslinking in the TBT unit. This is bolstered by the fact that the addition of side chains to the TBT unit resulted in polymers that have good solubility. Nevertheless some interesting trends were obtained.

7.2.1. Introduction

Organic photovoltaics (OPVs) are a potential low cost solution to solar energy harvesting. Recently we reported on a 3% efficient device using poly(3-hexylthiophene) \textit{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) as the active component. Here we expand on this work by using poly(3-dodecylthiophene) (P3DDT) which has a lower crystallization temperature and increased solubility which may improve processability. Unfortunately, as P3DDT is somewhat less crystalline than P3HT, we also expect some deterioration in the overall performance due to decreased charge carrier mobility.
7.2.2. Results and Discussion

Figure 7.4: Select IV curves for best performing devices for three different P3DDT-b-PFTBT materials.

Several different P3DDT-b-PFTBT polymers were tested in the course of this work. Regretfully, most materials produced inferior performance. A sample of the best performing IV curves is shown in Figure 7.4. Most materials were synthesized from lower molecular weight P3DDT (< 10 kDa) which produced high quality block copolymers with reasonably good purity; however performance for these polymers was poor. Here we will focus on the highest performing block copolymer. Analysis of this polymer in Supporting Information Figure S7.4 revealed it to contain only 30% block copolymer with the majority of the impurities arising from P3DDT homopolymer. This result is surprising since it had been previously assumed that only very pure materials would result in high performing devices. Here it is assumed that the block copolymer acts to reduce the phase separation of the other components. Additionally, the addition of large amounts of homopolymer may be
favorable to performance if pure polymers produce domains that are too small since homopolymer would increase domain sizes.

7.2.3. Conclusion

P3DDT-\textit{b}-PFTBT devices have been produced which provide insight into the properties of block copolymers that may produce optimal devices. Larger block copolymers are found to increase performance. The presence of homopolymer impurities does not seem to produce significant detrimental effects on device performance for the case studied.
7.2.4. Supporting Information

Figure S7.4: UV/VIS analysis of 0.7% efficiency P3DDT-b-PFTBT polymer

<table>
<thead>
<tr>
<th></th>
<th>P3DDT</th>
<th>PF8TBT</th>
<th>BCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mw (kDa)</td>
<td>34.2</td>
<td>17.1</td>
<td>61.3</td>
</tr>
<tr>
<td>Mn (kDa)</td>
<td>26.7</td>
<td>11.0</td>
<td>50.6</td>
</tr>
<tr>
<td>PDI</td>
<td>1.28</td>
<td>1.55</td>
<td>1.21</td>
</tr>
</tbody>
</table>

Mass Percent P3DDT Homopolymer = 59
Mass Percent PF8TBT Homopolymer = 13
Mass Percent BCP = 28

Ratio of P3DDT mass/PF8TBT mass in mixture = 4.6
Ratio of P3DDT mass/PF8TBT mass in BCP = 5.0
DP Ratio of P3DDT/PF8TBT in mixture = 12.6
7.3. References


Chapter 8

Conclusion

Here we have presented several studies on the crystallization behavior of P3AT-\textit{b}-PF block copolymers. P3HT-\textit{b}-PF is found to have both PF and P3HT crystals when block ratios are nearly balanced. P3DDT-\textit{b}-PF shows a significantly broader range for crystallization for both blocks. We have also performed systematic studies on these materials under a variety of annealing conditions and quenching conditions and found that a single block copolymer may show various morphologies under specific conditions. In particular, we have found that a longer duration annealing favors the assembly of P3DDT crystals and slower quenching rates favors the formation of PF crystals. Both morphologies are displayed for long annealing followed by slow quenching and both are suppressed for short annealing followed by rapid quenching. Taken together, these suggest that optimal block copolymer devices where each block is crystalline may require multiple annealing temperatures and balanced block ratios in order to achieve an optimal morphology.
Since evidence of self-assembly was difficult to obtain from conventional x-ray scattering, we performed a study using small angle neutron scattering and reflectivity to more fully assess the self-assembly aspects of the system. We find that relative to the polymer blend, the block copolymer constrains the domain size distribution. Additionally, while a dramatic change in the domain size is observed in the first 15 minutes, the system shows continued evolution after 2.5 hrs.

Following the record breaking report of a block copolymer device with 3% efficiency, we performed additional studies on the P3AT-\textit{b}-PFTBT system. While the work performed herein was not able to meet or exceed the performance obtained previously, we gained additional insight into the dynamics of these systems. In particular, in situ X-ray measurements demonstrated that while previously thought to be amorphous, the PFTBT polymer does in fact have a defined lamellar crystal structure with a d-spacing roughly twice that of P3HT. This crystal structure is largely obscured at low temperature, but becomes apparent at temperatures higher than 100°C. Additional studies were performed on a large set of related P3HT-\textit{b}-PFTBT polymers in order to determine what factors were important for performance and crystal structure. Unfortunately, device performance for these materials was substantially below that of the record breaking polymer. Additional studies on P3DDT-\textit{b}-PFTBT devices found some surprising results in terms of important factors. Highest performing materials did not have the highest purity, but did have a significant fraction of a very high molecular weight material. Significantly, each polymer tested was very robust to processing conditions. This strongly suggests that performance is tied intimately to the molecular weight of the block
copolymer and the morphology is strongly tied to the properties of the material rather than processing conditions. Taken together, these results provide valuable insights into the synthesis of future materials for block copolymer devices.