# **Conjugated Block Copolymers via Functionalized Initiators and Click Chemistry**

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ABSTRACT: 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

INTRODUCTION Conjugated block copolymers (BCPs) are comprised of two or more  $\pi$ -conjugated polymer blocks and are promising for use in organic electronic applications.<sup>1-4</sup> 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, or microelectronics.<sup>5-7</sup> 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.<sup>8</sup> 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.<sup>7,9–11</sup>

Conjugated polymers are typically made by step-growth or condensation polymerization reactions, which provide little control over the final polymer molecular weight and polydisis 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  $\pi$ - $\pi$  stacking direction of polymer crystallites. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 154–163

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persity. 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.<sup>12-14</sup> Click chemistry can provide an efficient method to couple conjugated macroreagents 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.<sup>13-16</sup> This method enables the preparation of well-defined macroreagents 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

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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 (<sup>1</sup>H NMR), size-exclusion chromatography (SEC), and matrixassisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). <sup>1</sup>H 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.

#### **EXPERIMENTAL**

#### Instrumentation

## Nuclear Magnetic Resonance Spectroscopy

Solution <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy was performed on a 500-MHz Varian Inova NMR. Chloroform-*d* (CDCl<sub>3</sub>, Cambridge Isotope Laboratories) was used as the solvent with TMS (0.05%) as an internal standard. Data were processed using SpinWorks 3.1.8.1.<sup>17</sup>

#### Size-Exclusion Chromatography

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 (UV-vis) detector, a Wyatt Technology HELEOS II multiangle 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  $min^{-1}$  at 40 °C. Weight average molecular weights ( $M_w$ ) 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).

## Matrix-Assisted Laser Desorption/Ionization-Time of Flight Mass Spectrometry

Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) spectra were collected using a Bruker Daltonics Autoflex II mass spectrometer, which is equipped with an N<sub>2</sub> laser ( $\lambda = 337$  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<sup>-1</sup>) and the analyte (10 mg mL<sup>-1</sup>) were prepared in THF and then mixed in a 10:2 ratio. A volume of 1  $\mu$ L was



applied to the target via the dried droplet method.<sup>18</sup> Mass spectra were collected in reflection mode, and the instrument was externally calibrated with polystyrene standards.

## **Differential Scanning Calorimetry**

Thermograms were recorded on a TA Instruments differential scanning calorimetry (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<sup>-1</sup>, cooled to 40 °C at 5 °C min<sup>-1</sup>, then equilibrated for 10 min before heating to 250 °C at 5 °C min<sup>-1</sup>. Second heating cycles are reported. Plots are baseline subtracted for easier viewing.

## Grazing Incidence Small-/Wide-Angle X-ray Scattering

Grazing incidence wide-angle X-ray scattering (GIWAXS) and grazing incidence small angle X-ray scattering (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  $2-3 \times 10^{-6}$  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.<sup>19</sup> Plots are normalized and plotted on a logarithmic scale.

#### Transmission Electron Microscopy

TEM images were acquired on a JEOL JEM-1400LaB6 TEM operating at an accelerating voltage of 120 keV. All the TEM images, which were collected using a Gatan 2K CCD camera. Samples were prepared by casting solutions of 3 mg ml<sup>-1</sup> polymer solution at 1500 rpm for 30 s onto poly(3,4-ethyle-nedioxythiophene) 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 min before measurements.

#### **Synthesis**

#### Materials

Anhydrous tetrahydrofuran (THF), anhydrous toluene, dichloromethane, chloroform, tetrahydrofuran, hexanes, acetone, methanol, 1,3-bis(diphenylphosphino)propane]dichloronickel(II) (Ni [dppp]Cl<sub>2</sub>), isopropylmagnesium chloride (<sup>i</sup>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-*tert*-butylphosphine) palladium(0) (Pd[t-Bu<sub>3</sub>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. 2,5dibromo-3-hexylthiophene, 2,5dibromo-3-dodecylthiophene, and 7'-bromo-9',9'-dioctyl-fluoren-2'-yl-4,4,5,5,-tetramethyl-[1,3,2]dioxaborolane (2) were synthesized as previously described.<sup>20–24</sup>

## 2-(4-Bromophenyl)ethyl 4-Methylbenzenesulfonate (1)

4-Bromophenyl ethanol (1.96 g 9.75 mmol) was dissolved in dichloromethane (8 mL) at 0  $^{\circ}$ C. Tosyl chloride (2.34 g, 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 h 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.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 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<sub>2</sub>), 2.95–2.88 (t, 2H, CH<sub>2</sub>), 2.47–2.43 (s, 3H, Ar—CH<sub>3</sub>),

## 2-(4-Bromophenyl)ethyl 4-Methylbenzenesulfonate Bis(tri-tert-butylphosphine)palladium(0)

Similar to previously reported synthesis, (1) (0.25 g 0.87 mmol) and bis(tri-*tert*-butylphosphine)palladium(0) (82 mg, 0.16 mmol) were dissolved in 3 mL of anhydrous toluene in an inert atmosphere and heated to 70 °C for 3 h.<sup>16</sup> Material was used without further purification.

#### Tosyl-Functionalized Poly(9,9-dioctylfluorene)

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.<sup>16</sup> The monomer solution was purged with N<sub>2</sub> for 30 min 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

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.0–7.5 (m, 81H, Ar—*H*), 2.31– 1.91 (m, 52H, Ar—C—C*H*<sub>2</sub>—), 1.39–0.97 (m, 276H, —C*H*<sub>2</sub>—), 0.97–0.50 (m, 135H, —C*H*<sub>2</sub>—), 4.34–4.21 (t, 2H, Ar—CH<sub>2</sub>—C*H*<sub>2</sub>—OTs), 3.11–2.96 (t, 2H, Ar—C*H*<sub>2</sub>—CH<sub>2</sub>—OTs), 3.11–2.96 (t, 3H, —SO<sub>2</sub>—Ph—C*H*<sub>3</sub>)

## PF2

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.0–7.5 (m, 188H, Ar—*H*), 2.31–1.91 (m, 128H, Ar—C—CH<sub>2</sub>—), 1.39–0.97 (m, 661H, —CH<sub>2</sub>—), 0.97–0.50 (m, 317H, —CH<sub>2</sub>—), 4.34–4.21 (t, 2H, Ar—CH<sub>2</sub>—CH<sub>2</sub>—OTs), 3.11–2.96 (t, 2H, Ar—CH<sub>2</sub>—CH<sub>2</sub>—OTs), 3.11–2.96 (t, 3H, —SO<sub>2</sub>—Ph—CH<sub>3</sub>)

## Azide-Functionalized Poly(9,9-dioctylfluorene)

Azide-functionalized poly(9,9-dioctylfluorene) (PF-azide) was prepared by dissolving PF—tosylate (0.32 g, 0.64 mmol) in 5 mL of anhydrous THF followed by addition of azidotrime-thylsilane (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

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 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<sub>3</sub>), 3.01–2.91 (t, 2H, Ar— $CH_2$ — $CH_2$ —N<sub>3</sub>)

#### PF2

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.0–7.5 (m, 185H, Ar—*H*), 2.31–1.91 (m, 131H, Ar—C—CH<sub>2</sub>—), 1.39–0.97 (m, 698H, —CH<sub>2</sub>—), 0.97–0.50 (m, 330H, —CH<sub>2</sub>—), 3.63–3.55 (t, 2H, Ar—CH<sub>2</sub>—CH<sub>2</sub>—N<sub>3</sub>), 3.01–2.91 (t, 2H, Ar—CH<sub>2</sub>—CH<sub>2</sub>—N<sub>3</sub>)

## Alkyne-Functionalized Poly(3-alkylthiophene)

Alkyne-functionalized poly(3-alkylthiophene) (P3AT-alkyne) was prepared using a general procedure described elsewhere.<sup>25</sup>

## P3HT1

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.13–6.64 (s, 88H, Ar—*H*), 3.09–2.37 (t, 176H, Ar—CH<sub>2</sub>—), 2.08–1.09 (m, 845H, -CH<sub>2</sub>—), 1.09–0.60 (m, 265H, -CH<sub>3</sub>), 4.52–4.41 (t, 2H, Ar— CH<sub>2</sub>—CH<sub>2</sub>—0—CO—), 4.27–4.18 (t, 2 H, Ar—CH<sub>2</sub>—CH<sub>2</sub> -O—CO—)

## P3HT2

<sup>1</sup>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— $CH_2$ —  $CH_2$ —0—CO—), 4.27–4.18 (t, 2H, Ar— $CH_2$ —O—CO—)

## P3DDT1

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.13–6.64 (s, 109H, Ar—*H*), 3.09–2.37 (t, 230H, Ar—CH<sub>2</sub>—), 2.08–1.09 (m, 2332H, -CH<sub>2</sub>—), 1.09–0.60 (m, 352H, -CH<sub>3</sub>), 4.52–4.41 (t, 2H, Ar— CH<sub>2</sub>—CH<sub>2</sub>—0—CO—), 4.27–4.18 (t, 2H, Ar—CH<sub>2</sub>—CH<sub>2</sub>— 0—CO—)

## P3DDT2

<sup>1</sup>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— $CH_2$ —C  $H_2$ —O—CO—), 4.27–4.18 (t, 2H, Ar— $CH_2$ —O—CO—)

## Poly(3-alkylthiophene)-b-poly(9,9-dioctylfluorene)

Poly(3-alkylthiophene)-*b*-poly(9,9-dioctylfluorene) (P3AT-*b*-PF) was synthesized using a procedure described elsewhere.<sup>16</sup> In a typical reaction, PF-azide (4) (106 mg, 9.6 mmol), P3AT-alkyne (5) (128 mg, 8.53 mmol), and copper(I) bromide (8.8 mg, 61.5 mmol) were added to a dry 50-mL round bottom flask and purged with nitrogen. Anhydrous THF (9 mL) 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 <sup>1</sup>H NMR spectra for BCPs synthesized are included in the Supporting Information Figures S10–S15.

#### P3HT1-b-PF1

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.10–7.41 (m, 67H, Ar—*H*), 7.15–6.88 (s, 92H, Ar—*H*), 3.01–2.35 (t, 199H, Ar—*CH*<sub>2</sub>—), 2.35–1.88 (m, 46H, —*CH*<sub>2</sub>—), 1.88–1.01 (m, 1032H, —*CH*<sub>2</sub>—), 1.01–0.50 (m, 397H, —*CH*<sub>3</sub>), 4.49–4.39 (t, 2.00H, Ar—*CH*<sub>2</sub>—*CH*<sub>2</sub>—0—*CO*—), 4.24–4.12 (t, 1.98H, Ar—*CH*<sub>2</sub>—*CH*<sub>2</sub>—*CH*<sub>2</sub>— -0—*CO*—), 4.65–4.55 (t, 2.05H, Ar—*CH*<sub>2</sub>—*CH*<sub>2</sub>—N<sub>3</sub>C<sub>2</sub>H—), 3.34–3.17 (t, 2.51H, Ar—*CH*<sub>2</sub>—*CH*<sub>2</sub>— N<sub>3</sub>C<sub>2</sub>H—)

#### P3HT1-b-PF2

<sup>1</sup>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*<sub>2</sub>—), 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— $CH_2$ — $CH_2$ —0—CO—), 4.24–4.12 (t, 1.92H, Ar— $CH_2$ —  $CH_2$ —0—CO—), 4.65–4.55 (t, 1.86H, Ar— $CH_2$ — $CH_2$ — $N_3C_2$ H—), 3.34–3.17 (t, 2.72H, Ar— $CH_2$ — $CH_2$ — $N_3C_2$ H—)

#### P3HT2-b-PF2

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.10–7.41 (m, 97H, Ar—*H*), 7.15–6.88 (s, 42H, Ar—*H*), 3.01–2.35 (t, 102H, Ar—*CH*<sub>2</sub>—), 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<sub>2</sub>—CH<sub>2</sub>—0—CO—), 4.24–4.12 (t, 1.90H, Ar—CH<sub>2</sub>—CH<sub>2</sub>— 0—CO—), 4.65–4.55 (t, 1.93H, Ar—CH<sub>2</sub>—CH<sub>2</sub>—N<sub>3</sub>C<sub>2</sub>H—), 3.34–3.17 (t, 1.83H, Ar—CH<sub>2</sub>—CH<sub>2</sub>— N<sub>3</sub>C<sub>2</sub>H—)

#### P3DDT1-b-PF1

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.10–7.41 (m, 49H, Ar—*H*), 7.15–6.88 (s, 69H, Ar—*H*), 3.01–2.35 (t, 149H, Ar—*CH*<sub>2</sub>—), 2.35–1.88 (m, 37H, —*CH*<sub>2</sub>—), 1.88–1.01 (m, 1642H, —*CH*<sub>2</sub>—), 1.01–0.50 (m, 296H, —*CH*<sub>3</sub>), 4.49–4.39 (t, 2.00H, Ar— *CH*<sub>2</sub>—*CH*<sub>2</sub>—0—CO—), 4.24–4.12 (t, 2.08H, Ar—*CH*<sub>2</sub>—*CH*<sub>2</sub>— 0—CO—), 4.65–4.55 (t, 1.86H, Ar—*CH*<sub>2</sub>—*CH*<sub>2</sub>—N<sub>3</sub>C<sub>2</sub>H—), 3.34–3.17 (t, 1.48H, Ar—*CH*<sub>2</sub>—*CH*<sub>2</sub>— N<sub>3</sub>C<sub>2</sub>H—)

#### P3DDT1-b-PF2

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.10–7.41 (m, 89H, Ar—*H*), 7.15–6.88 (s, 108H, Ar—*H*), 3.01–2.35 (t, 228H, Ar—*CH*<sub>2</sub>—), 2.35–1.88 (m, 58H, —*CH*<sub>2</sub>—), 1.88–1.01 (m, 2600H, —*CH*<sub>2</sub>—), 1.01–0.50 (m, 476H, —*CH*<sub>3</sub>), 4.49–4.39 (t, 2.00H, Ar—*CH*<sub>2</sub>—*CH*<sub>2</sub>—0—*CO*—), 4.24–4.12 (t, 2.03H, Ar—*CH*<sub>2</sub>— CH<sub>2</sub>—0—*CO*—), 4.65–4.55 (t, 1.30H, Ar—*CH*<sub>2</sub>—*CH*<sub>2</sub>—*N*<sub>3</sub>*C*<sub>2</sub>H—), 3.34–3.17 (t, 1.94H, Ar—*CH*<sub>2</sub>—*CH*<sub>2</sub>— *N*<sub>3</sub>*C*<sub>2</sub>H—)

#### P3DDT2-b-PF2

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.10–7.41 (m, 83H, Ar—*H*), 7.15–6.88 (s, 39H, Ar—*H*), 3.01–2.35 (t, 90H, Ar—*CH*<sub>2</sub>—), 2.35–1.88 (m, 61H, –*CH*<sub>2</sub>—), 1.88–1.01 (m, 1359H, –*CH*<sub>2</sub>—),



#### **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.15,25 Functionalized polyfluorenes can be synthesized through catalyst-transfer Suzuki-Miyaura polymerization initiated by a functionalized Pd catalyst.<sup>13,16</sup> 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.<sup>25</sup>

Our overall synthetic approach to prepare conjugated BCPs is shown in Scheme 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.<sup>25</sup> 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 alkynefunctionalized polythiophenes were found to have good stability, solubility, and reactivity in click reactions with azidefunctionalized poly(ethylene glycol).<sup>25</sup> This procedure was applied to the synthesis of both P3HT-alkyne and P3DDTalkyne (Table 1). <sup>1</sup>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 [Fig. 1(A)].

Azide-functionalized poly(9,9-dioctylfluorene) (PF-azide) is prepared through the use of an externally added, functionalized palladium catalyst. The palladium catalyst  $Pd(t-Bu_3P)_2$ is reacted with (**1**) using a method similar to those described by Yokozawa et al.<sup>14</sup> The resulting Pd complex initiates the polymerization of (**2**) resulting in tosylatefunctionalized 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 <sup>1</sup>H NMR





SCHEME 1 Synthetic scheme for the preparation of P3AT-alkyne, PF-azide, and P3AT-b-PF block copolymers.

analysis indicates quantitative transformation of PF-tosylate to PF-azide [Fig. 1(B)].

The degree of functionality can be analyzed using a combination of <sup>1</sup>H NMR, SEC-MALLS, and MALDI-TOF. As shown in Figure 1, NMR peaks corresponding to the expected functional groups are present for hydroxyl and alkyne functionalized polythiophenes and tosylate and azide-functionalized PFs. <sup>1</sup>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 <sup>1</sup>H NMR molecular weight estimates to SEC-MALLS estimates, the degree of

**TABLE 1** Characteristics of Conjugated Polymer Macroreagents

Sample	<i>M</i> <sub>n</sub> MALLS (kg mol <sup>-1</sup> )	PDI, SEC-RI	DP, SECª	DP, <sup>1</sup> H NMR <sup>b</sup>	Functionality MALDI (%) <sup>c</sup>
P3HT1	11.9	1.23	72	88	62±6
P3HT2	7.3	1.20	44	41	71±2
P3DDT1	17.1	1.25	68	109	80±5
P3DDT2	9.2	1.20	37	43	91±3
PF1	4.9	1.49	13	13	96±1
PF2	6.2	1.75	16	31	42±0

 $^{\rm a}$  DP calculated from MALLS  $M_{\rm n}$  divided by repeat unit molecular weight.

<sup>b</sup> DP calculated from the relative integrated intensities of aromatic hydrogens to polymer functional group hydrogens.

<sup>c</sup> 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.

functionality can be estimated. The molecular weight estimates by <sup>1</sup>H NMR and SEC are in good agreement for all macroreagents except for P3DDT1 and PF2 (Table 1). For these samples, the higher DP estimates from <sup>1</sup>H NMR analysis reflects incomplete functionalization, roughly 62 and 52% on a molar basis for P3DDT1 and PF2, respectively. Table 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 mass spectrometry (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 to 90%. The percent functionality is calculated based on the monoisotopic peak of each major distribution for a particular mer. As detail in Supporting Information (Tables S1 and S2), at least three mer distributions are chosen and an average and standard deviation is calculated. The result of this calculation are generally lower than that predicted by <sup>1</sup>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.<sup>26</sup> 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 lowermolecular weight fraction of the polymer samples. Consistent with the measurements by <sup>1</sup>H NMR and SEC-MALLS, MALDI-TOF measurements show a higher degree of functionality for P3DDT2 and P3HT2 compared with P3DDT1 and P3HT1.



FIGURE 1 <sup>1</sup>H NMR of (A) PF-tosylate and PF-azide, (B) P3AT-OH and P3AT-alkyne, and (C) final P3AT-*b*-PF product.

As can be seen in Table 1 and Figure 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 <sup>1</sup>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. <sup>1</sup>H NMR and SEC-MALLS indicate poor functionality, and MALDI-TOF indicates a significant amount of OH functionalized product as an impurity (see Tables S1 and S2 in Supporting Information). Our previous work has shown poor functionality for PF with molecular weighs greater than 7 kg mol $^{-1.16}$  Thus, for the reaction conditions detailed herein, we obtain PF with a high degree of functionality and molecular weight controlled by catalyst to monomer ratio only for polymer chains with an average molecular weight of 5 kg mol $^{-1}$ .

P3AT-*b*-PF BCPs are synthesized using a copper-catalyzed click reaction between PF-azide and P3AT-alkyne, and the

resulting products are summarized in Table 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 <sup>1</sup>H NMR (Fig. 1 and Supporting Information Figs. S9-S14) and SEC analysis (Fig. 3 and Supporting Information Fig. S1). As shown in Figure 3 and Supporting Information Figure S1, 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





FIGURE 2 MALDI-TOF analysis of PF1-tosylate.

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<sup>-1</sup>, 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 ratio and the crystallization behavior of the constituent polymer blocks. Previous work has found that P3HT crystallization typically dominates thin film morphology for BCPs with one P3HT block.<sup>27–29</sup> In P3HT-*b*-PF all-conjugated BCPs, we had determined that P3HT tends to dominate the crystallization at larger weight fractions of P3HT and likewise PF at low P3HT weight fraction, with co-crystallization being seen between about 30 and 50 wt % P3HT.<sup>16,30</sup> With the materials presented herein, we can compare P3HT and P3DDT all-conjugated BCPs. Since P3DDT has a crystallization tempera-

TABLE 2 Characteristics of Conjugated Block Copolymers

Sample	<i>M</i> <sub>n</sub> MALLS (kg mol <sup>-1</sup> )	PDI, SEC-RI	P3AT (wt %) <sup>a</sup>
P3HT1 <i>-b</i> -PF1	15.8	1.19	78
P3HT1- <i>b</i> -PF2	13.9	1.24	78
P3HT2- <i>b</i> -PF2	8.3	1.33	52
P3DDT1- <i>b</i> -PF1	25.1	1.27	84
P3DDT1- <i>b</i> -PF2	22.9	1.36	82
P3DDT2-b-PF2	11.9	1.31	65

<sup>a</sup> 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.



**FIGURE 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).

ture 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.

Polymer film samples were heated above 230 °C then slowly cooled to room temperature. As shown by GIWAXS images shown in Figure 4 and line cuts of GIWAXS data are also shown in Supporting Information Figure S2. 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 Fig. S2). 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 suggest 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-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



FIGURE 4 GIWAXS analysis of BCP films after thermal annealing at 230 °C.

detailed in Supporting Information (Fig. S3). As an example, the DSC for P3HT2-*b*-PF2 and its constituent polymers is shown in Figure 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 to 155 °C that may be attributable to PF. In general, BCPs show thermal transitions at temperature 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.

A variety of annealing conditions were investigated including solvent annealing in the presence of vapor chloroform for 5 days, as well as 24 h 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 Figures S4 and S5. As detailed in Figure 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  $\pi$ - $\pi$ 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.<sup>31</sup>

Assessment of GISAXS data in Supporting Information (Fig. S6) shows a weak peak for the P3HT-*b*-PF, but none for P3DDT-*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 7, a comparison of TEM and AFM images of P3HT1-*b*-PF1 reveals that this peak may be due to



**FIGURE 5** Differential scanning calorimetry curves from second heating cycle of PF2, P3HT2, and P3HT2-*b*-PF2.



**FIGURE 6** GIWAXS analysis for P3DDT2-*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 and 230 °C thermally annealed films, and films annealed in presence of chloroform vapor for five days at room temperature.

scattering of regularly sized P3HT crystallites embedded in an amorphous matrix. As detailed in Supporting Information (Fig. S7), 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 (Supporting Information Fig. S8). As shown in Supporting Information Figure S9, an AFM survey of other samples show similar results showing few if any difference 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.

#### 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,



FIGURE 7 Comparison of (A) AFM and (B) TEM images for P3HT1-b-PF1.

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  $\pi$ - $\pi$  stacking direction. For samples cast from refluxing chloroform, crystalline orientation exhibits nor 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.

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