# Electronic Supplementary Information

# Impact of $\pi$ -Conjugated Gradient Sequence Copolymer on Polymer Blend Morphology

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#### I. Materials

Flash chromatography was performed on SiliCycle silica gel (40-63  $\mu$ m) and thin layer chromatography was performed on Merck TLC plates pre-coated with silica gel 60 F254. iPrMgCl (2 M in THF) was purchased in 100 mL quantities from Aldrich. Ni(cod)<sub>2</sub>, dppe, 1,6-dibromohexane, 3-bromothiophene and 2-bromotoluene were purchased from Strem. N-Bromosuccinimide (NBS) was purchased from Aldrich, recrystallized from boiling water and dried over P<sub>2</sub>O<sub>5</sub>. All reagent grade materials and solvents were purchased from Aldrich, Acros, EMD, or Fisher and used without further purification unless otherwise noted. THF was dried and deoxygenated using an Innovative Technology (IT) solvent purification system composed of activated alumina, copper catalyst, and molecular sieves. All glassware was oven-dried at 150 °C for at least 1 h before use.

### II. General Experimental

<u>NMR Spectroscopy</u>: <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR spectra for all compounds were acquired in CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub> as noted on a Varian MR400 or a Varian Inova 400 Spectrometer operating at 400, 162 and 100 MHz, respectively. For <sup>1</sup>H and <sup>13</sup>C NMR spectra the chemical shift data are reported in units of  $\delta$  (ppm) relative to tetramethylsilane (TMS) and referenced to residual solvent. <sup>31</sup>P NMR spectra are referenced to external H<sub>3</sub>PO<sub>4</sub>. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), triplet (t) and broad resonance (br). All NMR spectra were recorded at rt.

<u>Mass Spectrometry</u>: HRMS data were obtained on a Micromass AutoSpec Ultima Magnetic Sector mass spectrometer.

<u>*Gel-Permeation Chromatography:*</u> Polymer molecular weights were determined by comparison with polystyrene standards (Varian, EasiCal PS-2 MW 580-377,400) on a Waters 1515 HPLC instrument equipped with Waters Styragel® (7.8 x 300 mm) THF HR 0.5, THF HR 1, and THF HR 4 type columns in sequence and analyzed with Waters 2487 dual absorbance detector (254 nm). Samples were dissolved in THF (with mild heating) and passed through a 0.2 µm PTFE filter prior to analysis.

<u>MALDI-TOF-MS</u>: Spectra were recorded using Waters Tofspec-2E in reflectron mode at a unit mass resolution of 5000. The matrix dithranol was prepared at a concentration of 0.1 M in CHCl<sub>3</sub>. A polymer solution in CHCl<sub>3</sub> (10  $\mu$ L, 10<sup>-4</sup> M) was mixed with the matrix solution (10  $\mu$ L) and 1  $\mu$ L of this mixture was spotted on the target plate and then air-dried. The spectra were calibrated to a mixture of standard peptides.

<u>*UV-vis Spectroscopy:*</u> UV-vis spectra were acquired using a Perkin Elmer Lambda 850 UV-vis Spectrometer. Solution samples were prepared at 10 mg/mL polymer in CHCl<sub>3</sub> and diluted by a factor of  $10^3$ . Glass slides were cleaned with detergent in water, rinsed with water and acetone, and dried under N<sub>2</sub>. Thin films were spin cast from 10 mg/mL polymer solution onto glass slides at 1000 rpm for 30 s. Thermal annealing was done in a vacuum oven (0.01 torr, 150 °C, 1 h).

<u>Gas Chromatography</u>: Gas chromatography was carried out using a Shimadzu GC 2010 containing a Shimadzu SHRX5 (crossbound 5% diphenyl – 95% dimethyl polysiloxane; 15 m, 0.25 mm ID, 0.25 µm) column.

<u>Differential Scanning Calorimetry</u>: DSC was performed on a TA Instruments DSC Q2000. Samples (~5 mg) were sealed in aluminum pans (Tzero Hermetic) and sealed using a TA Instruments crimper. For non-isothermal scans, samples were equilibrated above their melting temp, cooled to 0 °C at a rate of 5 °C/min, and then heated at a rate of 10 °C/min through the melt.

<u>Atomic Force Microscopy</u>: Polymer solutions (10 mg/mL) in CHCl<sub>3</sub> were passed through a 0.4 µm PTFE filter and spin-coated onto glass slides (1000 rpm, 1 min). The samples were annealed in a vacuum oven (0.01 torr, 150 °C, 1 h) and cooled to rt under vacuum. The obtained films were analyzed by tapping

mode phase contrast AFM using a Bruker Dimension Icon. A silicon tipped cantilever with a spring constant of ~ 40 N/m and a resonance frequency of ~ 310 kHz (Bruker model TESP) was used.

<u>X-ray Diffraction</u>: Polymer solutions (10 mg/mL) in CHCl<sub>3</sub> were drop-cast onto glass slides and dried under vacuum for 1 h. The films were cut into small pieces using a razor blade and the obtained solids were annealed in a vacuum oven (0.01 torr, 150 °C, 1 h). Samples were analyzed using a Bruker AXS in the 2-theta geometry. Samples were scanned at a rate of 1 sec/step from  $2\theta = 4$  to  $30^{\circ}$  with a step size of 0.04°.

#### Transmission Electron Microscopy:

**Sample Preparation.** Glass slides were cleaned by thoroughly scrubbing the surface with a cotton swab soaked in aqueous detergent solution (Alconox), rinsed with deionized H<sub>2</sub>O and acetone, and dried in a stream of N<sub>2</sub>. Polymer solutions (10 mg/mL) in CHCl<sub>3</sub> were spin-cast (1000 rpm, 30 s) onto the freshly cleaned glass slides which were partially masked with electrical tape. After casting, the tape was peeled off and the thin films (< 100 nm thick) were then floated onto the surface of deionized water by slowly submerging the glass slide at a ~15 degree angle at the exposed interface. The floating film was then lifted onto a 200-mesh copper grid (Ted Pella Co.) for TEM analysis.



**Figure S1.** (A) TEM sample preparation procedure. (B) Optical micrograph of the polymer thin film on the grid with 20X magnification. Scale bar is 100 µm.

**TEM Analysis.** Using a JEOL 2010F Analytical Electron Microscope thin films were analyzed in the scanning mode (STEM) using high angle annular dark field (HAADF) detection and energy dispersive spectroscopy (EDS). An accelerating voltage of 200 kV at 95  $\mu$ A was used under a 10<sup>-7</sup> Pa vacuum pressure. After standard TEM alignment, the STEM probe was aligned using the Ronchigram method. STEM images were obtained using 10<sup>4</sup> X magnification, a probe size of 1 nm, scan rate of 2  $\mu$ s/line, and camera length of 12 cm. Then, a region of interest was defined to obtain EDS data using EDAX detector and Genesis software.

#### **III. Synthetic Procedures**



**2,5-dibromo-3-hexylthiophene (S1):** To a 100 mL oven-dried Schlenk flask, cooled to 0 °C under positive N<sub>2</sub> pressure, were added 3-hexylthiophene (5.00 g, 29.7 mmol, 1.00 equiv) and THF (50 mL). Freshly recrystallized NBS (10.8 g, 74.3 mmol, 2.50 equiv) was added in a single portion and the mixture was stirred for 2 h. The reaction was then warmed to rt and quenched using saturated aq NaHCO<sub>3</sub> (50 mL), diluted with Et<sub>2</sub>O (100 mL), washed with water (100 mL) and brine (100 mL), dried over MgSO<sub>4</sub>, treated with decolorizing carbon, filtered, and concentrated in vacuo to give an orange oil. This crude oil was purified by vacuum distillation (85 °C, 0.031 torr) to afford the title compound as a clear, colorless oil (6.53 g, 67%). HRMS (EI): Calcd. for C<sub>10</sub>H<sub>14</sub>Br<sub>2</sub>S [M<sup>+</sup>] 323.9183; found, 323.9176.



**3-(6-bromohexyl)thiophene (S2):** To a 200 mL oven-dried Schlenk flask, cooled to -78 °C under vacuum and refilled with N<sub>2</sub>, were added 3-bromothiophene (2.00 mL, 21.3 mmol, 1.00 equiv) and dry, degassed hexanes (50 mL). A solution of n-butyllithium in hexanes (1.6 M, 12.7 mL, 20.0 mmol, 0.95 equiv) was added dropwise over several minutes and the mixture was stirred for 10 min. THF (5 mL) was injected dropwise over several minutes and the mixture stirred an additional 1 h at -78 °C to produce a white precipitate and a transparent, colorless supernatant. The supernatant liquid was then removed via cannula transfer and replaced with hexanes/THF (10:1, 55 mL). 1,6-Dibromohexane (32.7 mL, 213 mmol, 10.0 equiv) was added and the slurry was then warmed to rt and stirred for another 2 h. The reaction was quenched using saturated aq NaHCO<sub>3</sub> (50 mL), diluted with Et<sub>2</sub>O (100 mL), washed with water (100 mL) and brine (100 mL), dried over MgSO<sub>4</sub>, treated with decolorizing carbon, filtered, and concentrated in vacuo to give a viscous orange oil. Excess 1,6-dibromohexane was removed by distillation (0.04 torr, 55 °C) and the remaining oil was purified by silica gel column chromatography (ethyl acetate/hexane gradient from 1/99 to 5/95 v/v) to obtain a clear, colorless oil (2.74 g, 55%). HRMS (EI): Calcd. for  $C_{10}H_{15}SBr$  [M<sup>+</sup>] 246.0078; found, 246.0073.



**2,5-dibromo-3-(6-bromohexyl)thiophene (S3):** To a 100 mL oven-dried Schlenk flask under positive  $N_2$  pressure, were added **S2** (2.50 g, 1.01 mmol, 1.00 equiv), THF (25 mL) and acetic acid (25 mL). Freshly recrystallized NBS (3.80 g, 2.12 mmol, 2.10 equiv) was added in one portion and the mixture was stirred

at rt for 2 h. The reaction was then quenched using saturated aq NaHCO<sub>3</sub> (50 mL), diluted with Et<sub>2</sub>O (100 mL), washed with water (100 mL) and brine (100 mL), dried over MgSO<sub>4</sub>, treated with decolorizing carbon, filtered, and concentrated in vacuo to give an orange oil. This crude oil was purified by silica gel column chromatography (ethyl acetate/hexane, 1/10 v/v) to obtain a clear, colorless oil (2.63 g, 64%). HRMS (EI): Calcd. for  $C_{10}H_{13}SBr_3$  [M<sup>+</sup>] 401.8288; found, 401.8302.



**(o-tolyl)bis(triphenylphosphino)nickel bromide (S4):**  $Ni(cod)_2$  (517 mg, 1.88 mmol, 1.00 equiv) and PPh<sub>3</sub> (986 mg, 3.76 mmol, 2.00 equiv) were dissolved in toluene (10 mL) in an oven-dried 25 mL round-bottom flask equipped with a stir bar, under N<sub>2</sub>. 2-Bromotoluene (354 mg, 2.07 mmol, 1.10 equiv) was added in a single portion and the mixture was stirred at rt for 1 h. Hexanes (20 mL) were added and the resulting precipitate was collected by filtration. The solids were purified by recrystallization from THF/hexanes at -35 °C to afford the title compound as an orange powder (345 mg, 24%).



(o-tolyl)(1,2-bis(diphenylphosphino)ethane)nickel bromide (3): In a 25 mL oven-dried round-bottom flask equipped with a stir bar, under N<sub>2</sub>, **S4** (340 mg, 0.45 mmol, 1.00 equiv) was dissolved in THF (5 mL). Then, dppe (198 mg, 0.50 mmol, 1.10 equiv) was added and the mixture was stirred at rt for 1 h. The volume of THF was reduced to ~1 mL under reduced pressure and hexanes (10 mL) were added. The resultant precipitate was isolated by filtration, washed with hexanes (10 mL) and Et<sub>2</sub>O (10 mL), and recrystallized from THF/hexanes (20 mL) at -35 °C to afford the title compound as a fine yellow powder (215 mg, 76%). HRMS (EI): Calcd. for  $C_{33}H_{31}BrNiP_2$  [M<sup>+</sup>] 626.0438, found, 626.0428.



**1**: In an N<sub>2</sub> environment, **S1** (195 mg, 0.597 mmol, 1.00 equiv) was dissolved in THF (5 mL) in a 25 mL Schlenk tube equipped with a stir-bar. A 2 M solution of *i*-PrMgCl in THF (270  $\mu$ L, 0.537 mmol, 0.90 equiv) was added and the reaction stirred at rt for 30 min. An aliquot of the solution (0.1 mL) was quenched with 6 M aq HCl (0.1 mL), extracted with CHCl<sub>3</sub> (2 x 1 mL) and analyzed by GC, showing a mixture of regioisomers in the ratio of 79:21. Note that only the 2-bromo isomer (1) undergoes polymerization in the presence of catalyst **3**, giving highly regioregular materials.<sup>1</sup>



**2:** In an N<sub>2</sub> environment, **S3** (242 mg, 0.597 mmol, 1.00 equiv) was dissolved in THF (5 mL) in a 25 mL Schlenk tube equipped with a stir-bar. A 2 M solution of *i*-PrMgCl in THF (270  $\mu$ L, 0.429 mmol, 0.90 equiv) was added and the reaction stirred at rt for 30 min. An aliquot of the solution (0.1 mL) was quenched with 6 M aq HCl (0.1 mL), extracted with CHCl<sub>3</sub> (2 x 1 mL) and analyzed by GC, showing a mixture of regioisomers in the ratio of 80:20. Note that only the 2-bromo isomer (**2**) undergoes polymerization in the presence of catalyst **3**, giving highly regioregular materials.<sup>1</sup>



**poly(3-hexylthiophene) (P3HT)**: To a 50 mL oven-dried Schlenk flask, a solution of **1** in THF (5 mL, 0.43 mmol) was injected via syringe and diluted with THF (25 mL). A stock solution of **3** in THF (0.86 mL, 4.3 µmol) was then injected and the mixture was stirred at rt for 1 h. Hence, the monomer:catalyst ratio was initially 100:1, and the expected value of  $M_n$  is therefore 16.6 kDa. The polymerization was quenched with 5 M aq HCl (5 mL), extracted with CHCl<sub>3</sub> (3 x 5 mL) and dried in vacuo. The resultant purple solid was dissolved in a minimum amount of CHCl<sub>3</sub> (~2 mL) upon heating and precipitated into MeOH (20 mL). The precipitate was collected on Whatman filter paper and purified by Soxhlet extraction using MeOH, acetone, hexanes, dichloromethane, and CHCl<sub>3</sub> respectively. The CHCl3 fraction was dried in vacuo to afford the polymer as a purple solid (76 mg, 85%). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C):  $M_n$  = 32.4 kDa, D = 1.12.



**poly(3-(6-bromohexyl)thiophene) (P3BrHT)**: To an oven-dried Schlenk flask, a solution of **2** in THF (5 mL, 0.429 mmol) was injected via syringe. A stock solution of **3** in THF (5 mM, 0.86 mL, 4.29 µmol) was then injected and the mixture was stirred at rt for 1 h. Hence, the monomer:catalyst ratio was initially 100:1, and the theoretical value of  $M_n$  is therefore 24.5 kDa. The polymerization was quenched with 5 M aq HCl (5 mL), extracted with CHCl<sub>3</sub> (3 x 5 mL) and dried in vacuo. The resultant red/magenta solid was dissolved in a minimum amount of CHCl<sub>3</sub> (~2 mL) upon heating and precipitated into MeOH (20 mL). The precipitate was collected on Whatman filter paper and purified by Soxhlet extraction using MeOH, acetone, hexanes, and CHCl<sub>3</sub>. The CHCl<sub>3</sub> fraction was dried in vacuo to afford the polymer as a red/magenta solid (96 mg, 91%). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C):  $M_n = 33.1$  kDa, D = 1.09.



**poly(3-hexylthiophene-***co***-3-(6-bromohexyl)thiophene)** (random): Under a N<sub>2</sub> atmosphere, solutions of **1** (15 mL, 0.01 M) and **2** (15 mL, 0.01 M) were combined in an oven-dried 50 mL Schlenk flask and cooled to 0 °C. A stock solution of **3** in THF (5.0 mM, 0.60 mL, 3.0 µmol) was transferred to the flask via syringe. Hence, the total monomer to catalyst ratio was 100:1, giving a theoretical  $M_n$  value of 20.6 kDa. Aliquots were drawn periodically and analyzed by <sup>1</sup>H NMR spectroscopy and GPC to give the cumulative mole fraction of **2** in the copolymer and the normalized chain length (see Figure 3 in the main text). After 2 h, the polymerization was quenched with 5 M aq HCI (5 mL) and extracted with CHCl<sub>3</sub> (3 x 5 mL) and dried in vacuo. The resultant purple solid was dissolved in a minimum amount of CHCl<sub>3</sub> (~2 mL) upon heating and precipitated into MeOH (20 mL). The precipitate was collected on Whatman filter paper and purified by Soxhlet extraction using MeOH, acetone, hexanes, dichloromethane, and chlorobenzene. The chlorobenzene fraction was dried in vacuo to afford the polymer as a purple solid (52 mg, 84%). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C):  $M_n = 34.7$  kDa, D = 1.15.



**poly(3-hexylthiophene**-*block*-**3**-(**6**-bromohexyl)thiophene) (block): Under a N<sub>2</sub> atmosphere, a stock solution of **1** (10 mL, 0.01 M) was transferred to an oven-dried 50 mL Schlenk flask and cooled to 0 °C. A stock solution of **3** in THF (5.0 mM, 0.40 mL, 2.0 µmol) was transferred to the flask via syringe. After stirring for 2 h, nearly complete conversion of **1** was confirmed by gas chromatography (>98%). GPC of the macro-initiator block indicated  $M_n$  = 14.5 kDa, D = 1.09 (theoretical  $M_n$  for the first block is 8.3 kDa). Subsequently, the stock solution of **2** (10 mL, 0.01 M) was injected. Aliquots were drawn periodically and analyzed by <sup>1</sup>H NMR spectroscopy and GPC to give the cumulative mole fraction of **2** in the copolymer and the normalized chain length, respectively. After an additional 2 h at 0 °C, the polymerization was quenched with 5 M aq HCl (5 mL) and extracted with CHCl<sub>3</sub> (3 x 5 mL) and dried in vacuo. The resultant purple solid was dissolved in a minimum amount of CHCl<sub>3</sub> upon heating and precipitated into MeOH. The precipitate was collected on Whatman filter paper and purified by Soxhlet extraction using MeOH, acetone, hexanes, CH<sub>2</sub>Cl<sub>2</sub>, and CHCl<sub>3</sub>. The CHCl<sub>3</sub> fraction was dried in vacuo to afford the polymer as a purple solid (182 mg, 81%). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C):  $M_n$  = 34.4 kDa, D = 1.19.



**poly(3-hexylthiophene**-*grad*-**3-(6-bromohexyl)thiophene)** (gradient): Under a N<sub>2</sub> atmosphere, a solution of **1** (15 mL, 0.01 M) was transferred to an oven-dried 25 mL Schlenk flask and cooled to 0 °C. A solution of **2** (3 mL, 0.05 M) was loaded into a 5 mL plastic syringe and attached to a syringe pump apparatus. With constant stirring, a stock solution of **3** in THF (5.0 mM, 0.60 mL, 3.0 µmol) was transferred to the flask via syringe, and the syringe pump was activated to deliver **2** at a rate of 0.05 mL/min. Hence, the total monomer to catalyst ratio was 100:1 after complete syringe pump addition and the theoretical value of  $M_n$  is therefore 20.6 kDa. Aliquots were drawn periodically and analyzed by <sup>1</sup>H NMR spectroscopy and GPC to give the cumulative mole fraction of **2** in the copolymer and the normalized chain length, respectively. After 2 h at 0 °C, the polymerization was quenched with 5 M aq HCl (5 mL) and extracted with CHCl<sub>3</sub> (3 x 5 mL) and dried in vacuo. The resultant purple solid was dissolved in a minimum amount of CHCl<sub>3</sub> (~1 mL) upon heating and precipitated into MeOH (20 mL). The precipitate was collected on Whatman filter paper and purified by Soxhlet extraction using MeOH, acetone, hexanes, CH<sub>2</sub>Cl<sub>2</sub>, and CHCl<sub>3</sub>. The CHCl<sub>3</sub> fraction was dried in vacuo to afford the polymer as a purple solid (43 mg, 70%). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C):  $M_n = 29.1$  kDa, D = 1.14.



**oligo(3-hexylthiophene)**: In a glovebox, a solution of **1** was diluted in THF to give a monomer stock solution (3 mL, 0.01 M) in a 20 mL scintillation vial. A solution of nickel catalyst **3** in THF (0.60 mL, 5.0 mM, 3.0 µmol) was transferred to the vial and the mixture was stirred at rt for 1 h. The monomer:catalyst ratio was 10:1, giving a theoretical  $M_n$  of 1.66 kDa. The oligomerization reaction was quenched with 5 M aq HCl (5 mL), extracted with CHCl<sub>3</sub> (3 x 5 mL) and dried in vacuo to obtain the crude product as a red solid (3.5 mg, 73%). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C):  $M_n = 2.1$  kDa, D = 1.15. A solution of the oligomer in CHCl<sub>3</sub> was concentrated under reduced pressure, and analyzed by MALDI-TOF-MS without any further purification.



oligo(3-(6-bromohexyl)thiophene): In a glovebox, a solution of 1 was diluted in THF to give a monomer stock solution (3 mL, 0.01 M) in a 20 mL scintillation vial. A solution of nickel catalyst 3 in THF (0.60 mL,

5.0 mM, 3.0 µmol) was transferred to the vial and the mixture was stirred at rt for 1 h. The monomer:catalyst ratio was 10:1, giving a theoretical  $M_n$  of 2.45 kDa. The oligomerization reaction was quenched with 5 M aq HCl (5 mL), extracted with CHCl<sub>3</sub> (3 x 5 mL) and dried in vacuo to obtain the crude product as a red solid (5.4 mg, 71%). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C):  $M_n$  = 2.3 kDa, D = 1.15. A solution of the oligomer in CHCl<sub>3</sub> was concentrated under reduced pressure, and analyzed by MALDI-TOF-MS without any further purification.



**oligo(3-hexylthiophene**-*co*-**3-(6-bromohexyl)thiophene**): In a glovebox, a solution of **1** in THF (3 mL, 0.01 M) was mixed with a solution of **2** in THF (3 mL, 0.01M) in a 20 mL scintillation vial. A solution of nickel catalyst **3** in THF (1.2 mL, 5.0 mM, 6.0 µmol) was transferred to the vial and the mixture was stirred at rt for 1 h. The monomer:catalyst ratio was 10:1, giving a theoretical  $M_n$  of 2.06 kDa. The oligomerization reaction was quenched with 5 M aq HCl (5 mL), extracted with CHCl<sub>3</sub> (3 x 5 mL) and dried in vacuo to obtain the crude product as a red solid (6.4 mg, 63%). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C):  $M_n = 2.7$  kDa, D = 1.16. A solution of the oligomer in CHCl<sub>3</sub> was concentrated under reduced pressure, and analyzed by MALDI-TOF-MS without any further purification.





**Figure S2.** NMR spectra for **S1**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.76 (s, 1H), 2.49 (t, *J* = 7.6 Hz, 2H), 1.52 (m, 2H), 1.28 (br m, 6H), 0.87 (t, *J* = 7.2 Hz, 3H). The symbol \* denotes residual water in the CDCl<sub>3</sub>. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.98, 130.94, 110.26, 107.89, 31.54, 29.53, 29.46, 28.76, 22.55, 14.06.



**Figure S3.** NMR spectra for **S2**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 (m, 1H), 6.92 (m, 2H), 3.39 (t, *J* = 6.8 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.84 (m, 2H), 1.62 (m, 2H), 1.45 (m, 2H), 1.34 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.98, 128.22, 125.19, 119.92, 33.99, 32.72, 30.33, 30.12, 28.39, 27.97.



**Figure S4.** NMR spectra for **S3**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.76 (s, 1H), 3.39 (t, *J* = 7.2 Hz, 2H), 2.50 (t, *J* = 7.6 Hz, 2H), 1.84 (m, 2H), 1.55 (m, 2H), 1.45 (m, 2H), 1.34 (m, 2H). The symbol \* denotes residual water in the CDCl<sub>3</sub>. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.59, 130.86, 110.43, 108.06, 33.85, 32.62, 29.33, 29.27, 29.13, 29.86.



**Figure S5.** NMR spectra for **S4.** <sup>1</sup>H NMR (400 MHz,  $CD_2CI_2$ )  $\delta$  7.50-7.20 (bm, 30H), 7.15 (m, 1H), 6.27 (m, 2H), 5.91 (m, 1H), 2.06 (br, 3H). The symbol \* denotes residual water in the  $CD_2CI_2$ . <sup>31</sup>P NMR (162 MHz,  $CD_2CI_2$ )  $\delta$  21.9 (s).



**Figure S6**. NMR spectra for **3**. <sup>1</sup>H NMR (400 MHz,  $CD_2Cl_2$ )  $\delta$  8.15 (m, 4H), 7.70 (m, 2H), 7.55-7.46 (m, 9H), 7.30 (t, 1H), 7.21 (t, 1H), 7.06 (m, 2H), 6.69 (m, 2H), 6.57 (m, 2H), 6.39 (m, 1H), 2.5-2.2 (m, 3H), 2.18 (s, 3H), 1.7-1.5 (m, 1H). The symbol \* denotes residual water in the  $CD_2Cl_2$ . <sup>31</sup>P NMR (162 MHz,  $CD_2Cl_2$ )  $\delta$  55.01 (d, *J* = 18.5 Hz), 37.25 (d, *J* = 18.3 Hz).



**Figure S7.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for (A) **P3HT**  $\delta$  6.98 (s, 1H), 2.81 (br, 2H), 1.71 (br, 2H), 1.44-1.36 (br, 6H), 0.92 (br, 3H) and (B) **P3BrHT**  $\delta$  6.98 (s, 1H), 3.42 (t, 2H), 2.81 (t, 2H), 1.90 (q, 2H), 1.71 (m, 2H), 1.48 (br, 4H).



**Figure S8.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra for the (A) **random copolymer**  $\delta$  6.98 (s, 2H), 3.42 (t, 2H), 2.80 (br, 4H), 1.88 (q, 2H), 1.70 (br, 4H), 1.44-1.33 (m, 10H), 0.90 (t, 3H), (B) **gradient copolymer**  $\delta$  6.98 (s, 2H), 3.42 (t, 2H), 2.80 (br, 4H), 1.88 (q, 2H), 1.70 (br, 4H), 1.44-1.33 (m, 10H), 0.90 (t, 3H), and (C) **block copolymer**  $\delta$  6.98 (s, 2H), 3.42 (t, 2H), 2.80 (br, 4H), 1.88 (q, 2H), 1.70 (br, 4H), 1.88 (q, 2H), 1.70 (br, 4H), 1.44-1.33 (m, 10H), 0.90 (t, 3H), and (C) **block copolymer**  $\delta$  6.98 (s, 2H), 3.42 (t, 2H), 2.80 (br, 4H), 1.88 (q, 2H), 1.70 (br, 4H), 1.44-1.33 (m, 10H), 0.90 (t, 3H).

#### V. *M*<sub>n</sub> and **Đ** versus Conversion

0

0

20

40

60

conversion (%)

80

#### General procedure for obtaining plots of $M_n$ and D versus conversion:

To an oven-dried 50 mL Schlenk flask equipped with a stir bar and a septum, THF (10 mL) was added and cooled to 0 °C under nitrogen. Then, monomers **1** and **2** (30 mL, 0.01 M) and a  $C_{24}H_{50}$  solution (0.5 mL, 0.1 M in THF) were added by syringe and the solution was stirred for 1 min. An aliquot (0.2 mL) was withdrawn and quenched with aq. HCl (1 mL, 5 M) and the organics extracted with CHCl<sub>3</sub> (3 × 1 mL). GC analysis afforded the initial ratio of monomer to internal standard peak areas. Then, the catalyst solution (0.5 mL, 5 mM) was added to the reaction. Aliquots (~0.2 mL) were taken from the reaction periodically via syringe and quenched with aq. HCl (1 mL, 5 M). Each aliquot was then extracted with CHCl<sub>3</sub> (2 mL) and the solvent removed in vacuo. The solids were then dissolved in THF (1 mL), divided and analyzed by GC and GPC. Conversion of each monomer was calculated from the decrease in peak areas relative to the internal standard ( $C_{24}H_{50}$ ) peak.



Table S1. Data plotted in Fig. S9.

conv. %	<i>M</i> <sub>n</sub> (kDa)	Ð
10.3	1.8	1.12
15.4	5.6	1.09
21.8	6.7	1.08
35.6	9.1	1.09
49.1	12.0	1.11
66.6	15.3	1.16
78.5	16.4	1.17
88.2	18.9	1.15

**Figure S9.** Plot of  $M_n$  (•) and D ( $\bigcirc$ ) versus conversion for the homopolymerization of **1** with catalyst **3**, at 0 °C in THF. Conditions: [**1**]<sub>0</sub> = 0.01 M, [**1**]<sub>0</sub>/[**3**]<sub>0</sub> = 100 (theoretical  $M_n$  = 16.6 kDa at 100% conversion)

1.0

100



**Figure S10.** Plot of  $M_n$  (•) and D ( $\bigcirc$ ) versus conversion for the homopolymerization of **2** with catalyst **3**, at 0 °C in THF. Conditions: [**2**]<sub>0</sub> = 0.01 M, [**2**]<sub>0</sub>/[**3**]<sub>0</sub> = 100 (theoretical  $M_n$  = 24.5 kDa at 100% conversion).

#### VI. MALDI-TOF-MS Data



**Figure S11.** MALDI-TOF mass spectrum of oligo(3HT). The main peaks ( $\bullet$ ) correspond to the expected series m/z = 92+n\*166, which agrees with tolyl and H end groups. The minor peaks ( $\bullet$ ) are 43 mass units larger than the main peaks, suggesting tolyl/isopropyl terminated chains which may result from chain termination by residual isopropylmagnesium chloride leftover from the Grignard metathesis step.



**Figure S12.** MALDI-TOF mass spectrum of oligo(3BrHT). The main peaks ( $\bullet$ ) correspond to the expected series m/z = 92+n\*245, which agrees with tolyl and H end groups. The two minor sets of peaks are 80 ( $\bullet$ ) and 160 ( $\bullet$ ) mass units less than the main peaks. The ratio of minor to major peaks increases with increasing laser power, suggesting that some amount of bromine atoms are fragmented from the side chains during the ionization process.<sup>2</sup> For example, the major peak at m/z = 2542 represents the tolyl/H terminated 10-mer and the two minor peaks at m/z = 2382 and 2462 are missing 1 and 2 bromine atoms, respectively.



**Figure S13.** MALDI-TOF mass spectra of oligo(3HT-co-3BrHT). See Figure S14 on the following page for comprehensive peak assignments.



Fig. S14. Peak assignments for the MALDI spectra of oligo(3HT-co-3BrHT)

#### VII. Batch Copolymerizations Procedure and Data

#### General procedure for conducting batch copolymerizations:

To an oven-dried 50 mL Schlenk flask filled with N<sub>2</sub>, THF (20 mL) and monomers **1** (2.5 mL, 0.1 M) and **2** (2.5 mL, 0.1 M) were injected and the flask was cooled to 0 °C. As an internal standard,  $C_{24}H_{50}$  solution (0.5 mL, 0.2 M in THF) was injected, stirred for 1 min, and an aliquot (~ 0.2 mL) was drawn and quenched with 5 M aq. HCl (~ 1 mL), extracted with CHCl<sub>3</sub> (2 mL) and dried in vacuo. GC analysis afforded the initial ratio of monomer to internal standard peak areas. Then, catalyst **3** (1 mL, 5 mM) was injected and aliquots (~0.1 mL) were periodically drawn and quenched with 5 M aq HCl (~1 mL), extracted with CHCl<sub>3</sub> (2 mL) and dried in Vacuo. A portion of each aliquot was dissolved in THF (~1 mL) and passed through a 0.2 µm PTFE filter for GC and GPC analysis. The remaining portions of each aliquot were then precipitated from MeOH (10 mL), dried under vacuum and taken up in CDCl<sub>3</sub> for <sup>1</sup>H NMR analysis.



**Figure S15.** (A) Plot of monomer conversion versus time for the copolymerization of **1** (•) and **2** ( $\circ$ ) with catalyst **3** at rt in THF. (B) Plot of  $M_n$  (•) and D ( $\circ$ ) versus conversion for the copolymerization of **1** and **2** with catalyst **3** at rt in THF. Conditions: [**1**]<sub>0</sub>/[**2**]<sub>0</sub> = 1, [**1**+**2**]<sub>0</sub> = 0.01 M, [**1**+**2**]<sub>0</sub>/[**3**]<sub>0</sub> = 100 (theoretical  $M_n$  = 20.8 kDa at 100% conversion).

#### VIII. Semi-batch Copolymerization Procedures and Data

#### Procedure for Conducting Semi-batch Copolymerizations:

To an oven-dried 50 mL Schlenk flask filled with N<sub>2</sub>, THF (10 mL) and monomer **1** (15 mL, 0.01 M) were injected and the flask was cooled to 0 °C. Then monomer **2** (3 mL, 0.05 M) was taken up into a syringe, the needle was inserted through the septum and the syringe barrel was loaded in a syringe pump. Catalyst **3** (0.6 mL, 5 mM) was injected into the flask and the syringe pump was simultaneously activated to deliver 0.05 mL/min of **2**. Aliquots (~0.2 mL) were drawn and quenched with 5 M aq HCI (~1 mL), extracted with CHCl<sub>3</sub> (2 mL) and dried in vacuo. A portion of each aliquot was dissolved in THF (~1 mL) and passed through a 0.2 µm PTFE filter for GPC analysis. The remaining portions of each aliquot were then precipitated from MeOH (10 mL), dried under vacuum and taken up in CDCl<sub>3</sub> for <sup>1</sup>H NMR analysis to determine the cumulative mole fraction of **2** in the copolymer.





**Figure S16.** (A) Representative <sup>1</sup>H NMR spectra for the aliquots drawn during the semi-batch polymerization procedure and (B) GPC chromatograms for each of the aliquots.

## IX. UV/Vis Spectra





**Figure S17.** UV-vis absorbance spectra of the homopolymers (A) **P3HT** and (B) **P3BrHT** in solution (----), as cast thin films (----) and annealed thin films (----).



**Figure S18.** UV-vis absorbance spectra of the (A) **random**, (B) **gradient** and (C) **block** copolymers in solution (---), as cast thin films (---) and annealed thin films (---).

# X. Differential Scanning Calorimetry (DSC)

Samples (~5 mg) were hermetically sealed in aluminum pans for DSC analysis. For each polymer, a preliminary heating scan was done to determine the  $T_m$  value. Then, new samples were prepared and DSC scans were performed using the following non-isothermal recrystallization protocol:

- 1. Premelting. Equilibrate temperature to T =  $(T_m + 20)$  °C for 5 min.
- 2. Cooling Scan. Ramp temperature to 0 °C at -5 °C/min
- 3. Heating Scan. Ramp temperature to T =  $(T_m + 20)$  °C at 10 °C/min



Figure S19. DSC thermograms for (A) the P3HT and (B) the P3BrHT homopolymers.



Figure S20. DSC thermograms of the (A) random, (B) gradient, and (C) block copolymers.

#### XI. Powder X-ray Diffraction Data

Polymer solutions in  $CHCl_3$  (10 mg/mL) were drop cast onto glass slides and annealed in a vacuum oven (0.01 torr, 150 °C, 1 h). The films were than scraped from the substrate and finely chopped into a powder using a razor blade. The powders were analyzed by XRD and the data is plotted in the semilog scale after subtraction of the background (glass slide alone).



Figure S21. Powder XRD data for the homopolymers and the each of the copolymers.



**Figure S22.** Cartoon of the **P3HT** crystallites with interchain and interlamellar d-spacings based on the crystallographic reflections in shown Figure S21.

# XII. Atomic Force Microscopy (AFM) Images



**Figure S24.** Atomic Force Microscopy (AFM) images (A,C) height and (B,D) phase data of the homopolymers (A, B) **P3HT** and (C, D) **P3BrHT** as-cast thin films. All of the images are  $1 \times 1 \mu m$  scan area. The scale bar is 100 nm. The RMS roughness values are 1.03 nm for P3HT (A) and 0.527 nm for P3BrHT (C).



**Figure S25.** Atomic Force Microscopy (AFM) images (A,C,E) height and (B,D,F) phase data of the (A, B) **random**,(C, D) **gradient**, and (E,F) **block** copolymer annealed (0.01 torr, 150 °C, 1 hr) thin films,  $1 \times 1 \mu m$  scan area. The scale bar is 100 nm. The RMS roughness values are 0.714 nm for the random (A), 0.546 nm for the gradient (C), and 0.693 for the block copolymer (E).

#### Measurement of polymer film thickness

Polymer solution in CHCl<sub>3</sub> (2 mg/mL) spin cast on glass slide (1000 rpm, 1 min), thermally annealed (0.01 torr, 150 °C, 1 h). The obtained film was scratched with the tip of a syringe needle down the center of the sample and subsequently analyzed by tapping mode AFM. The height data is shown below.



Figure S26. AFM images and z-y height profile for the scratched thin film.

#### XII. Polymer Blend Sample Preparation

Polymer blends were prepared using a 1:1 volume ratio, based on the Connolly Solvent Excluded Molecular Volume of the repeating units calculated in ChemBio3D Ultra (CambridgeSoft). The values thus used for molecular volume were 166.3 and 186.7 Å<sup>3</sup> for the 3HT and 3BrHT repeating units, respectively. Hence, a 1:1 volume ratio blend corresponds to a 1.12:1.00 mole ratio of 3HT:3BrHT. In a typical case, P3HT (18 mg, 0.110 mmol, 1.12 equiv) and P3BrHT (24 mg, 0.098 mmol, 1.00 equiv) were dissolved in CHCl<sub>3</sub> (4.2 mL).



**Figure S27.** Ball-and-stick model for the repeating unit structure in (A) P3HT and (B) P3BrHT with the Connolly molecular surface superimposed.

#### XIII. Transmission Electron Microscopy (TEM) Images

Domain sizes were measured at randomly chosen areas on the sample on at least two independently prepared samples. In the case of domains with oval shape, both the long and short dimension were measured and used in the calculation of average domain size (as shown with white arrows below in panel A).





**Figure S28.** (A) STEM/HAADF images of the polymer blend with gradient copolymer additive at the indicated weight percentages. (B) Histograms of domain sizes measured from multiple areas on at least two independently prepared samples.

Thin films were annealed in a vacuum oven (0.01 torr, 150 °C, 1 h) and subsequently analyzed by STEM (HAADF) to elucidate the effects of thermal annealing on the blend morphology, with and without copolymer additives. It appears that the domain sizes remain the same before and after annealing, likely due to the fact that the melting temp of the P3HT domains is significantly higher than 150 °C. Attempts to anneal at higher temperatures, however, led to cross-linking of the P3BrHT domains. Interestingly, though, the P3BrHT domains become highly crystalline as a result of thermal annealing, with bright nano-wires clearly visible in the TEM images.



**Figure S29.** STEM/HAADF images of P3HT/P3BrHT blend with and without 10% gradient copolymer additive, after annealing a vaccum oven at 150 °C for 1 hour. The left-hand panels are at 10 kX magnification, whereas the right-hand panels are at 40 kX.



**Figure S30.** STEM/HAADF images of P3HT/P3BrHT blend with 10% random or block copolymer additive, after annealing a vacuum oven at 150 °C for 1 hour. The left-hand panels are at 10 kX magnification, whereas the right-hand panels are at 40 kX.

#### **XIV. REFERENCES**

- 1. R. S. Loewe, P. C. Ewbank, J. S. Liu, L. Zhai and R. D. McCullough, *Macromolecules*, 2001, **34**, 4324-4333.
- 2. J. S. Liu, R. S. Loewe and R. D. McCullough, *Macromolecules*, 1999, **32**, 5777-5785.