

Controlling micro-phase separation in semi-crystalline/amorphous conjugated block copolymers

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Experimental Methods

General Considerations

All reagents were used as received, unless otherwise stated. 2,5-Dibromine-3-hexylthiophene, and 3-bromothiophene were purchased from JK Chemicals, tert-butylmagnesium chloride in THF (1M), methylmagnesium chloride in THF(3M), [1,3-bis-(diphenylphosphino)propane]dichloronickel (Ni(dppp)Cl₂), dibromohexane, HPLC hexane, and HPLC tetrahydrofuran were purchased from Sigma-Aldrich, *i*-propylmagnesium chloride in THF (2M) was purchased from Acros Organics, and *n*-butyllithium in hexane (2.2M) and *n*-bromosuccinimide were purchased from Alfa Aesar. All other reagents were purchased from Beijing Chemicals. HPLC grade tetrahydrofuran and hexane were dried over sodium metallic.

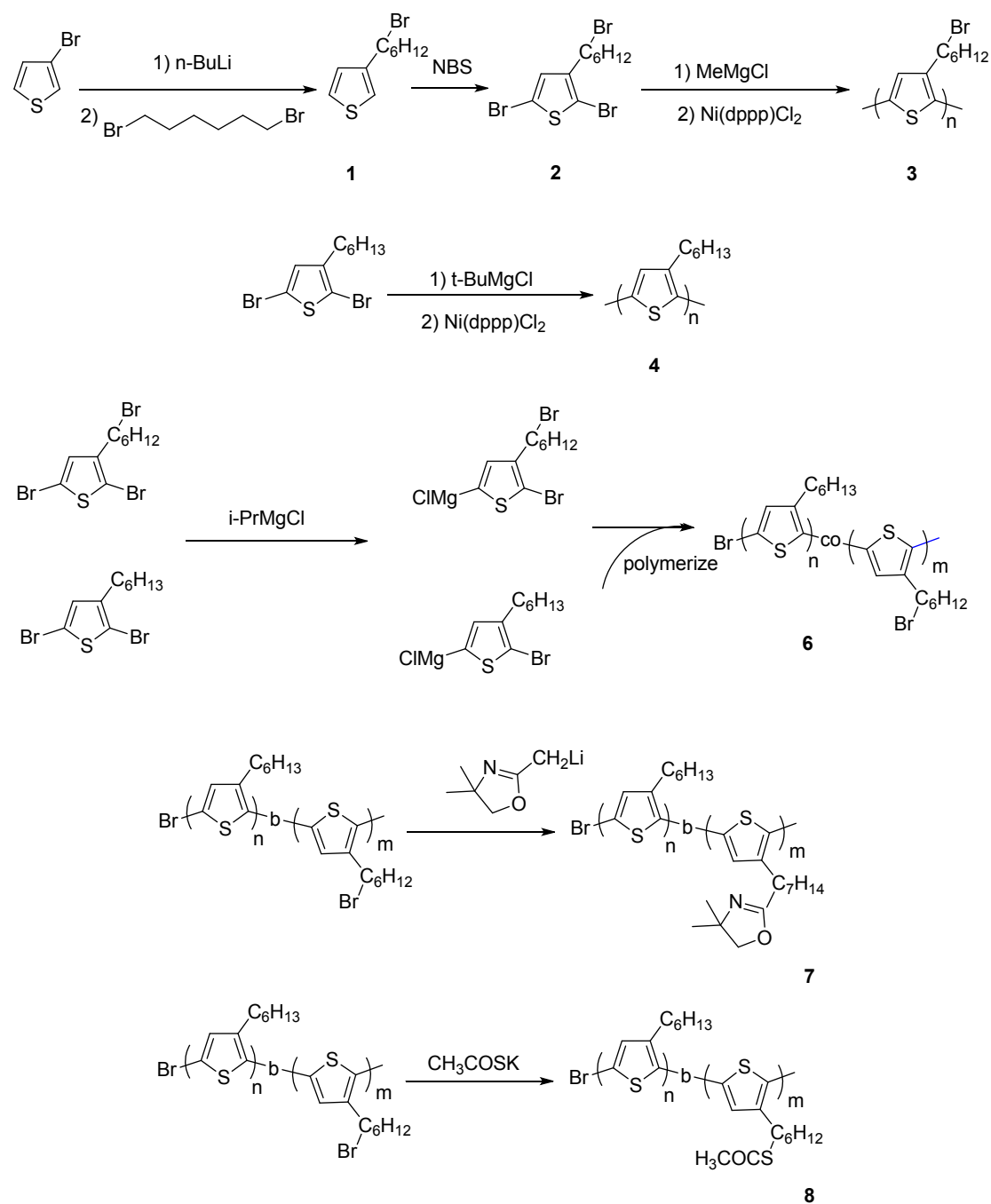
Instrumentation

Absorption spectra were recorded using a Hitachi U-3010 spectrophotometer. Solution measurements were made in chloroform at ~ 0.02 mg/mL. ¹H-NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz). Polymer molecular weights were determined using a Varian PL-GPC 50 (THF, 40 °C) with narrow weight distribution polystyrene standards. AFM images were obtained with a Veeco Multimode microscope. STEM imaging was carried out at 200 kV using a FEI Tecnai G2 F20 U-TWIN instrument. Wide-angle X-ray scattering spectra were recorded on a Panalytical X'Pert-pro MPD X-ray power diffract meter by using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). DSC measurements were taken using a PerkinElmer Diamond DSC differential scanning calorimeter at a heating rate of 10K min⁻¹ under N₂ flow.

X-ray Diffraction Analysis. Polymer samples were drop-casted from chloroform solutions (10 mg/ml) onto quartz substrates. These samples were then annealed at 120 °C for 30 min.

Solution-Assembly of Fibrils. According to the previous literature, a stock solution of polymer was prepared by dissolving polymer (1 mg) in CHCl₃ (100 μ L) by vortexing. CHCl₃ (195 μ L) was added to the stock solution of polymer (18 μ L) and CH₂Cl₂ was added (1.365 mL) after which the vial was capped and vigorously shaken. The solutions were then placed in the dark for 1 day. For AFM imaging purposes, solutions were spin-coated onto mica substrates at 1500 rpm for 30 second.

Synthesis



Scheme S1. Synthetic routes used to prepare the 3-bromohexylthiophene monomer, 2,5-dibromo-3-bromohexylthiophene, poly-(3-hexylthiophene) (P3HT), poly-(3-bromohexylthiophene) (P3BrHT), statistical copolymer, 2, 5-poly(3-(2(4,4-dimethyl-oxazolin-2-yl)-heptyl)thiophene)-b-poly(3-bromohexylthiophene) and 2, 5-poly(3-hexylthiolacetate thiophene)-b-poly(3-bromohexylthiophene) block copolymers.

3-Bromohexylthiophene (1)

The monomer was synthesized according to the literature. To a 500 mL three-necked round-bottom flask equipped with stirring was added 3-bromothiophene (30 g, 0.18 mol), and 250 mL of hexanes was added via syringe. The flask was chilled down to -40 °C and the solution was stirred for 10 min. *n*-Butyllithium (81.8 mL, 0.18 mol) was added dropwise via syringe at this temperature. After the mixture was stirred for 10 min, 15 mL of THF was added dropwise via syringe. The solution was stirred for 1 h, the cooling bath was removed, and the solution was allowed to warm to -10 °C. Dibromohexane (110 mL, 0.72 mol) was added in one portion and the solution was warmed to room temperature. The solution was stirred for 6 h at room temperature, and then extracted with diethyl ether for three times and organic extracts were washed with water for three times. The organic layer was dried over anhydrous magnesium sulfate and the removal of solvent gave a crude product. The product was further purified by vacuum distillation. ¹H NMR (CDCl₃): δ 7.24 (d, 1H), 6.92 (d, 2H), 3.40 (t, 2H), 2.64 (t, 2H), 1.87 (m, 2H), 1.65 (m, 2H), 1.48 (m, 2H), 1.36 (m, 2H).

2,5-Dibromo-3-bromohexylthiophene (2)

3-Bromohexylthiophene (27.39 g, 0.11 mol) was dissolved in THF and acetic acid (135 mL: 135 mL/v:v) in a 500 mL one necked flask equipped for stirring. *n*-Bromosuccinimide (39.16 g, 0.22 mol) was added to the solution in one portion, and the solution was stirred for 6 h. Then the solution was extracted with diethyl ether for three times, and the organic extracts were washed with water for three times and sodium bicarbonate (aq.) twice. The organic layer was dried over anhydrous magnesium sulfate and the removal of solvent gave a crude product. Purification was performed using petroleum ethers as an eluent on a silica gel chromatographic. The 2,5-dibromo-3-bromohexylthiophene was recovered as a colorless oil. ¹H NMR (CDCl₃): δ 6.78 (s, 1H), 3.40 (t, 2H), 2.52 (t, 2H), 1.87 (m, 2H), 1.25-1.55 (m, 6H).

Poly(3-bromohexylthiophene) (P3BrHT) (3)

Melmagnesium chloride (0.14 mL, 3.0 M in THF, 0.40 mmol) was added dropwise to a solution of 2,5-dibromo-3-bromohexylthiophene (162.436 mg, 0.40 mmol) in dry THF (3.2 mL) under a argon atmosphere. The mixture was refluxed for 2 h, then transferred to a flask containing Ni(dppp)Cl₂ (1.04 mg, 0.002 mmol). The solution was refluxed overnight, and the reaction was quenched with methanol. The red solution was precipitated into methanol and purified by Soxhlet extraction using methanol, hexane, and chloroform. The chloroform fraction was concentrated to afford the polymer as a deep red solid (40.2mg, 41%, RR = 98%). ¹H NMR (CDCl₃): δ 6.98 (1H), 3.40 (2H), 2.80 (2H), 1.88 (2H), 1.73 (2H), 1.25-1.51 (4H). $M_n=21.7$ kg/mol, $M_w=35.3$ kg/mol, PDI = 1.63.

Poly-(3-hexylthiophene) (P3HT) (4)

t-Butylmagnesium chloride (0.40 mL, 1.0 M in THF, 0.40 mmol) was added dropwise to a solution of 2,5-dibromo-3-hexylthiophene (130 mg, 0.40 mmol) in dry THF

(2.34 mL) under a argon atmosphere. The mixture was refluxed for 2 h, then transferred to a flask containing Ni(dppp)Cl₂ (1.04 mg, 0.002 mmol). The solution was refluxed overnight, and the reaction was quenched with methanol. The deep red solution was precipitated into methanol and purified by Soxhlet extraction using methanol, hexane, and chloroform. The chloroform fraction was concentrated to afford the polymer as a purple solid (34.6 mg, 52%, RR = 93%). ¹H NMR (CDCl₃): δ 6.98 (1H), 2.80 (2H), 1.71 (2H), 1.26-1.56 (6H), 0.90-0.94 (3H). $M_n=20.6$ kg/mol, $M_w=27.4$ kg/mol, PDI = 1.33.

Poly-(3-bromohexylthiophene-*block*-3-hexylthiophene) (5)

The feed molar ratio of 3-hexylthiophene and 3-bromohexylthiophene was changed from 30:70, 50:50 to 70:30. The molecular weights were controlled by fixing the ratio of the amount of Ni catalyst to the total monomer amount at 1:200, 1:400 and 1:200. The typical synthesis procedure of P3HT-*b*-P3BrHT block copolymers (feed molar ratio of 50:50) was as follows: *t*-butylmagnesium chloride (0.40 mL, 1.0 M in THF, 0.40 mmol) was added dropwise to a solution of 2,5-dibromo-3-hexylthiophene (130 mg, 0.40 mmol) in dry THF (2.34 mL) under a argon atmosphere. This mixture was allowed to reflux for 2 h, then the solution was transferred to a argon filled flask containing Ni(dppp)Cl₂ (2.17 mg, 0.002 mmol) (Solution A). In a separate flask methylmagnesium chloride (0.14 mL, 3.0 M in THF, 0.40 mmol) was added to 2,5-dibromo-3-bromohexylthiophene (162 mg, 0.40 mmol) in dry THF (3.2 mL) and the solution was refluxed for 2 h (Solution B). Solution A was refluxed for 0.5 h at which time solution B was added dropwise. The combined mixture was refluxed overnight, then quenched with methanol and precipitated into methanol. The precipitated solid was purified by Soxhlet extraction using methanol, hexane, and chloroform. The chloroform fraction was concentrated to afford the polymer as a deep purple solid (68.9 mg, 41.9 %, RR=93%). ¹H NMR (CDCl₃): δ 6.98 (2H), 3.40 (2H), 2.80(4H), 1.90 (4H), 1.71-1.26 (12H), 0.90-0.93 (3H). $M_n=17.8$ kg/mol, $M_w=26.5$ kg/mol, PDI = 1.49.

Poly-(3-bromo-hexylthiophene-*stat*-3-hexylthiophene) (6)

i-Propylmagnesium chloride (0.27 mL, 2.0 M in THF, 0.54 mmol) was added dropwise to a solution of 2,5-dibromo-3-bromohexylthiophene (110 mg, 0.27 mmol) and 2,5-dibromo-3-hexylthiophene (87 mg, 0.27 mmol) in dry THF (7 mL) under a argon atmosphere. The mixture was refluxed for 1.5 h then transferred to argon filled flask containing Ni(dppp)Cl₂ (1.44 mg, 0.00265 mmol). This mixture was refluxed overnight then quenched with methanol. The resulting deep red solution was precipitated into methanol and purified by Soxhlet extraction using methanol, hexane, and chloroform. The chloroform fraction was concentrated to afford the polymer as a deep purple solid (54.5 mg, 46.3%, RR = 96%). ¹H NMR (CDCl₃): δ 6.98 (2H), 3.40 (2H), 2.81 (4H), 1.89 (4H), 1.72-1.24 (12H), 0.92 (3H). $M_n=34.3$ kg/mol, $M_w=47.9$ kg/mol, PDI = 1.4.

2, 5-Poly(3-(2(4,4-dimethyloxazolin -2-yl)-heptyl)thiophene)-*b*-poly

(3-bromohexylthiophene) (7)

n-BuLi (0.64 mL, 1.4 mmol) was added dropwise via syringe to the solution of freshly dried 2,4,4-trimethyloxazoline (16.95 mg, 1.5 mmol) dissolved in dried THF (3 mL) which was cooled to -70 °C, and the solution was stirred for 2h. In a separate flask, poly-(3-bromohexylthiophene-block-3-hexylthiophene) (63.2 mg, 0.15 mmol) ($M_n = 17.8$ kg/mol, $M_w = 26.5$ kg/mol, PDI = 1.49) was dissolved in dry THF (5 mL). The polymer solution was transferred to oxazoline lithium salt solution via cannula within 30 s. The cooling bath was removed, and the mixture was stirred for 1 h and quenched with hexane. The solid polymer was purified by Soxhlet extraction using hexane. Thus, 63.3 mg of polymer was obtained with 93% yield. $^1\text{H NMR}$ (CDCl_3): δ 6.98 (2H), 3.88(2H), 2.80 (4H), 2.24(2H), 1.70-1.25 (24H), 0.91 (3H). $M_n = 17.7$ kg/mol, $M_w = 28.4$ kg/mol, PDI = 1.6.

2, 5-Poly(3-hexylthiolacetate thiophene)-b-poly(3-bromohexylthiophene) (8)

Potassium thiolacetate (83.22 mg, 0.73 mmol) was added in one portion to a solution of poly-(3-bromohexylthiophene-block-3-hexylthiophene) (60 mg, 0.146 mmol) ($M_n = 17.8$ kg/mol, $M_w = 26.5$ kg/mol, PDI = 1.49) in dry THF (10 mL) under a argon atmosphere. This mixture was refluxed overnight then quenched with methanol. The resulting orange solution was precipitated into methanol and purified by Soxhlet extraction using methanol. The chloroform fraction was concentrated to afford the polymer as a deep purple solid (55 mg, 93%, RR = 95%). $^1\text{H NMR}$ (CDCl_3): δ 6.98 (2H), 2.88 (2H), 2.81 (4H), 2.31(2H), 1.71-1.26 (16H), 0.92 (3H). $M_n = 17.6$ kg/mol, $M_w = 30.5$ kg/mol, PDI = 1.7.

Figures

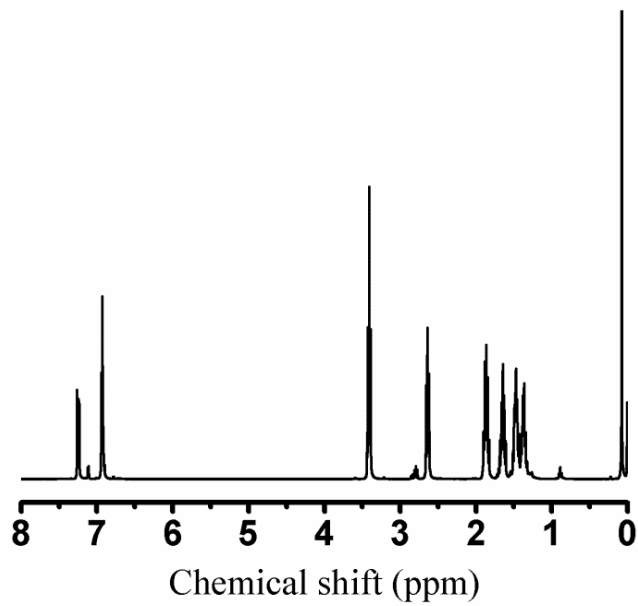


Fig. S1 ¹H-NMR spectrum of 3-bromohexylthiophene.

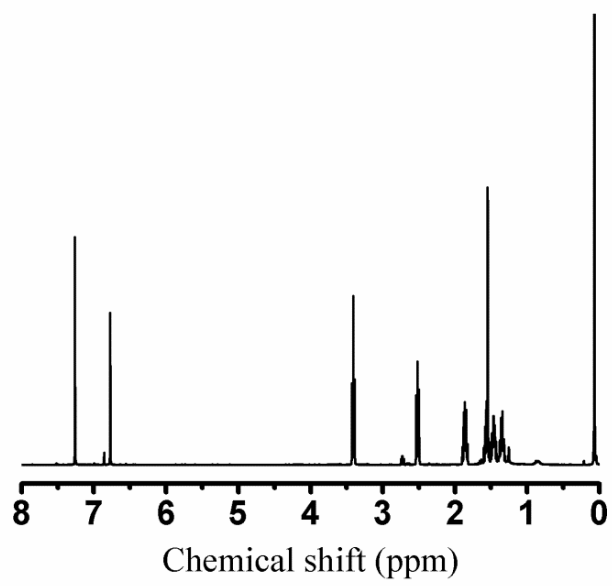


Fig. S2 ¹H-NMR spectrum of 2,5-dibromo-3-bromohexylthiophene.

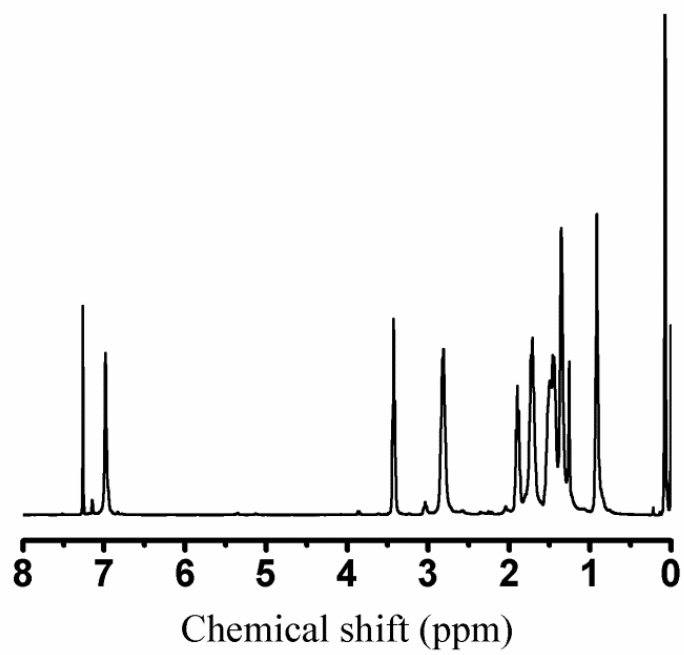


Fig. S3 ¹H-NMR spectrum of P3HT(5)-s-P3BrHT(5).

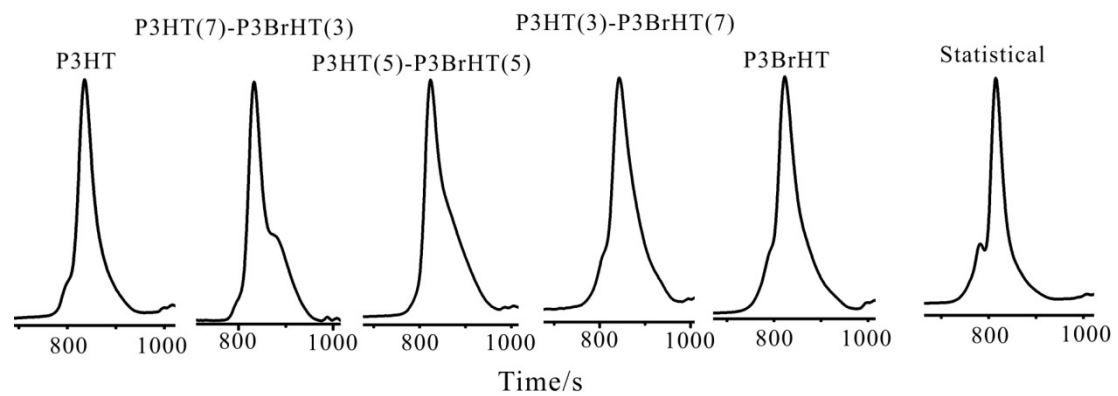


Fig. S4 GPC profiles of different polymers.

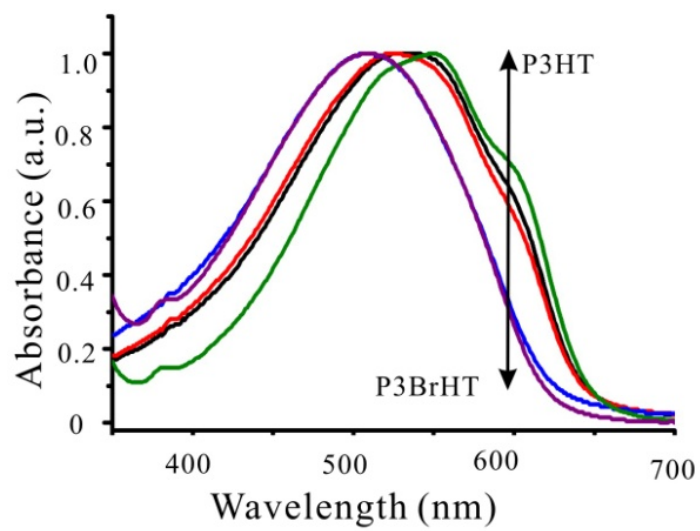


Fig. S5 The absorption spectra of pristine polymer films.

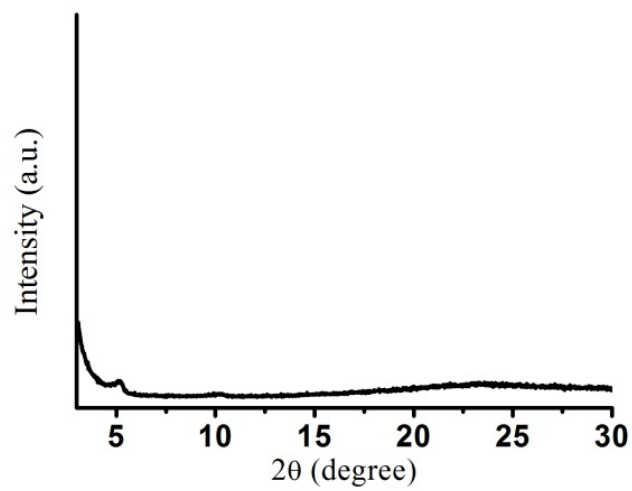


Fig. S6 The XRD spectrum of P3HT(5)-s-P3BrHT(5) film.

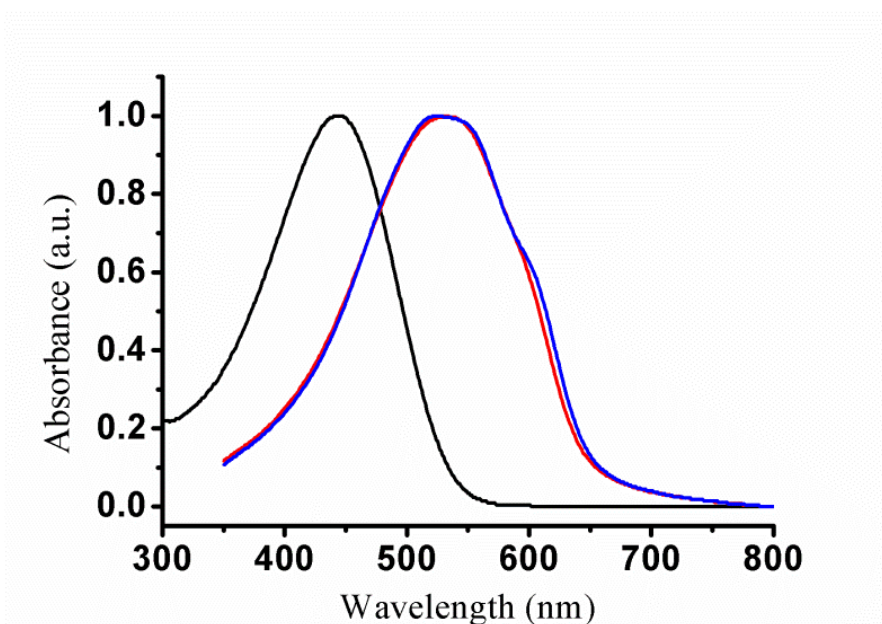


Fig. S7 The absorption spectra of statistical copolymer (P3HT(5)-s-P3BrHT(5)) solution (black line) , pristine film (red line) and annealed film (blue line).

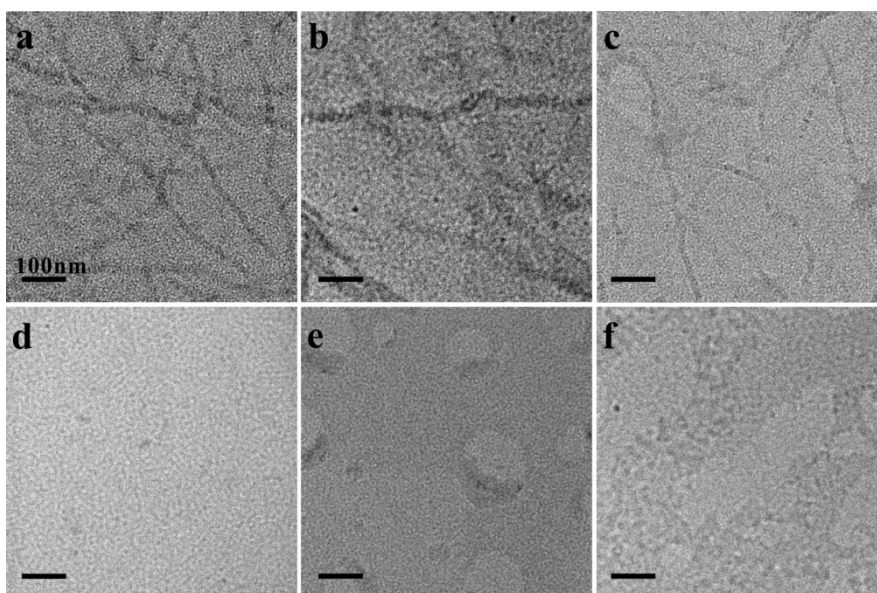


Fig. S8 Representative TEM images of fibrils of P3HT (a), P3HT(7)-b-P3BrHT(3) (b), P3HT(5)-b-P3BrHT(5) (c), P3HT(3)-b-P3BrHT(7) (d), P3BrHT (e), and P3HT(5)-s-P3BrHT(5) (f).

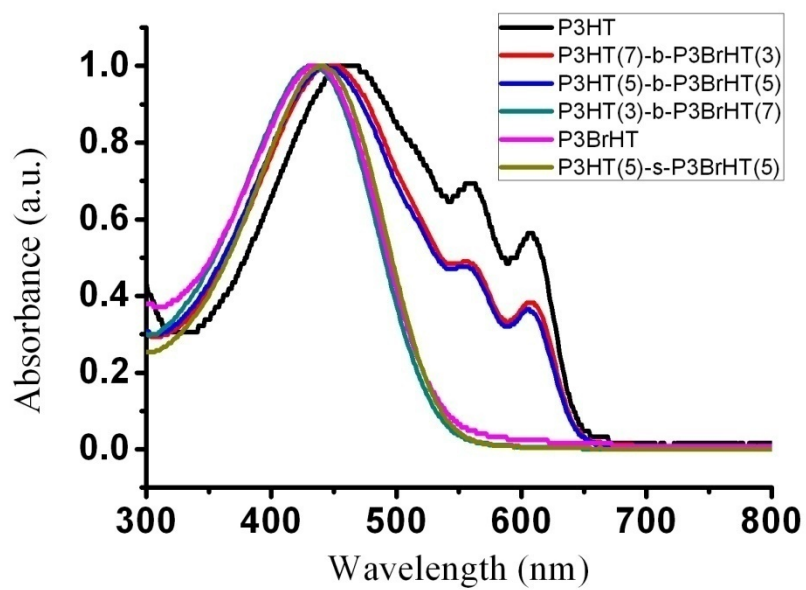


Fig. S9 Fibrils formed by addition of 7 parts CH_2Cl_2 to polymer in 1 part chloroform. The absorption spectra of different polymer solutions were shown above.

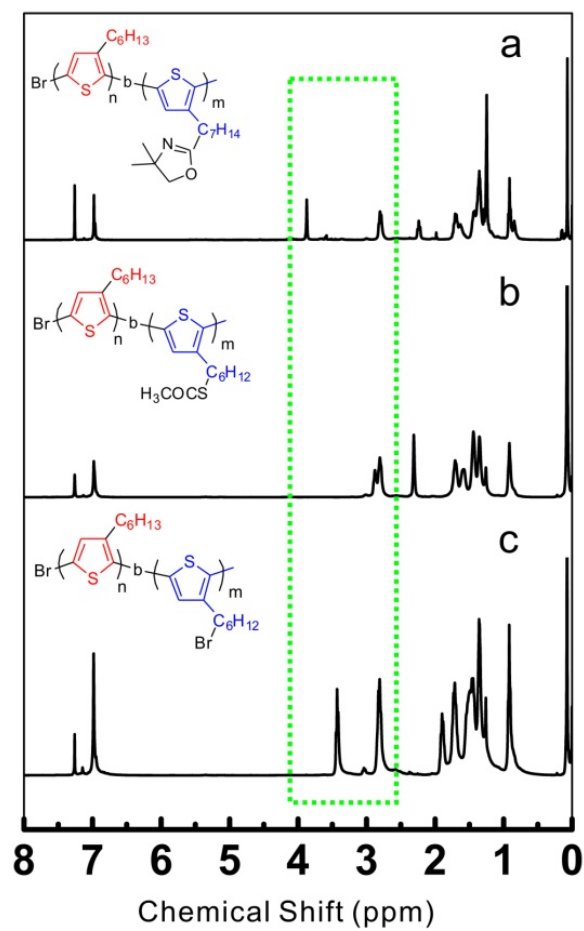


Fig. S10 $^1\text{H-NMR}$ spectra of 50:50 block copolymers (c) and polymers functionalized by thiolacetate (b) and 2,4,4-trimethyloxazoline (a).