

Supporting Information for:

**Impact of Copolymer Sequence on Solid-state Properties for Random, Gradient and Block Copolymers containing Thiophene and Selenophene**

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## I. Materials

Flash chromatography was performed on SiliCycle silica gel (40-63  $\mu\text{m}$ ) and thin layer chromatography was performed on Merck TLC plates pre-coated with silica gel 60 F254.  $i\text{PrMgCl}$  (2 M in THF) was purchased in 100 mL quantities from Aldrich.  $\text{Ni}(\text{cod})_2$ , dppe and 2-bromotoluene were purchased from Strem. N-bromosuccinimide (NBS) was purchased from Aldrich, recrystallized from boiling water and dried over  $\text{P}_2\text{O}_5$ . Zinc dust was purified by washing with dilute HCl, water, ethanol, and diethylether. 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 120  $^\circ\text{C}$  for at least 1 h before use.

## II. General Experimental

**NMR Spectroscopy:**  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR spectra for all compounds were acquired in  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$  as noted on a Varian MR400 or a Varian Inova 400 Spectrometer operating at 400, 162 and 100 MHz, respectively. For  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra the chemical shift data are reported in units of  $\delta$  (ppm) relative to tetramethylsilane (TMS) and referenced to residual solvent.  $^{31}\text{P}$  NMR spectra are referenced to external  $\text{H}_3\text{PO}_4$ . 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.

**Mass Spectrometry:** HRMS data were obtained on a Micromass AutoSpec Ultima Magnetic Sector mass spectrometer.

**Gel-Permeation Chromatography:** 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  $\mu\text{m}$  PTFE filter prior to analysis.

**MALDI-TOF-MS:** 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 10 mg/mL in a solution of 50/50 (v/v)  $\text{CH}_3\text{CN}/\text{EtOH}$ . The instrument was mass calibrated with a mixture of peptides in the matrix. The polymer sample was dissolved in  $\text{CHCl}_3$  to obtain a  $\sim 1$  mg/mL solution. A 3  $\mu\text{L}$  aliquot of the polymer solution was mixed with 3  $\mu\text{L}$  of the matrix solution. 1  $\mu\text{L}$  of this mixture was placed on the target plate and then air-dried.

**UV-vis Spectroscopy:** UV-vis spectra were acquired using a Perkin Elmer Lambda 850 UV-vis Spectrometer. Solution samples were prepared at  $1 \times 10^{-4}$  M in  $\text{CHCl}_3$ . Thin-films were spin-cast on glass slides from 2 mg/mL solutions in chlorobenzene.

**Gas Chromatography:** Gas chromatography was carried out using a Shimadzu GC 2010 containing a Shimadzu SHR5 (crossbound 5% diphenyl – 95% dimethyl polysiloxane; 15 m, 0.25 mm ID, 0.25  $\mu\text{m}$  df) column.

**Differential Scanning Calorimetry:** DSC was performed on a TA Instruments DSC Q2000. Samples were placed in aluminum hermetic pans and sealed using a TA Instruments crimper. For non-isothermal scans, samples (2-5 mg) were equilibrated at 280  $^\circ\text{C}$ , cooled to 0  $^\circ\text{C}$ , and re-heated to 280  $^\circ\text{C}$  with a heating rate of 10  $^\circ\text{C}/\text{min}$ . For a detailed description of the non-isothermal recrystallization process, see page S37.

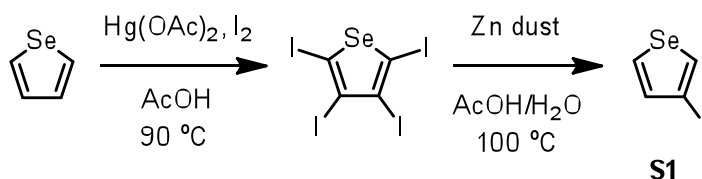
**Atomic Force Microscopy:** Polymer solutions (5 mg/mL) in chlorobenzene were passed through a 0.4  $\mu\text{m}$  PTFE filter and spin-coated onto glass slides (500 rpm, 1 min). The samples were isothermally recrystallized from the melt in a vacuum oven (0.04 torr, 220  $^\circ\text{C}$ , 1 h) and 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  $\sim 40$  N/m and a resonance frequency of  $\sim 310$  kHz (Bruker model TESP) was used.



Small Angle X-ray Scattering: Polymer samples (~ 5 mg) were isothermally recrystallized in a vacuum oven from the melt (0.04 torr, 220 °C, 1 h) and cooled to rt under vacuum. The obtained pellets were secured with scotch tape to the sample holder in a Bruker Nanostar. Spot focus sealed Cu K $\alpha$  radiation X-ray tube with a peak power of 1.5 kW was used with a pinhole collimator. Data were collected using a Hi Star area detector and intensities as a function of the scattering vector  $q$  were obtained by integration over angles  $\varphi = 0-360^\circ$  and  $2\theta = 0.1-3.0^\circ$ .

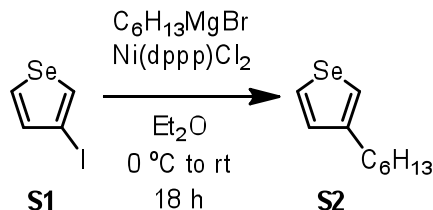
### III. Synthetic Procedures

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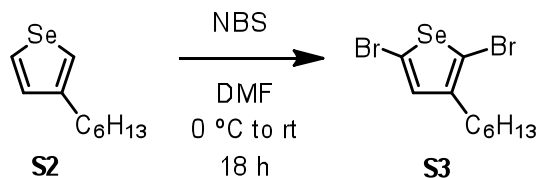
**3-iodoselenophene (S1):** The title compound was prepared by slight modification of a literature procedure.<sup>1</sup> To a 1 L two-neck round-bottom flask equipped with a stir bar and septa under positive  $\text{N}_2$  pressure was added selenophene (5.00 g, 38.2 mmol, 1.00 equiv), acetic acid (200 mL), and mercury acetate (60.8 g, 191 mmol, 5.00 equiv). The flask was heated to  $90\text{ }^\circ\text{C}$  and crushed iodine (48.4 g, 191 mmol, 5.00 equiv) was added in several portions over 15 min. After stirring for 1 h, the mixture was cooled to rt, water (300 mL) was added, and the flask was cooled to  $-4\text{ }^\circ\text{C}$  and stored for 18 h. The solids were collected by filtration. This material was then stirred with a potassium iodide solution (500 mL, 0.5 M) for 3 h, filtered, washed with water (500 mL), and dried in vacuo overnight. Without further purification, the intermediate tetraiodoselenophene (20.7 g, 32.6 mmol, 1.00 equiv) was transferred under positive  $\text{N}_2$  pressure to a 100 mL oven-dried Schlenk flask equipped with a stir bar and reflux condenser. Acetic acid/water mixture (80 mL, 4:1 v/v) and freshly purified zinc dust (6.39 g, 97.8 mmol, 3.00 equiv) were added and the flask heated to  $100\text{ }^\circ\text{C}$  for 2 h. After cooling to ambient temperature, the reaction mixture was diluted with  $\text{Et}_2\text{O}$  (100 mL) and neutralized by washing with saturated aq  $\text{NaHCO}_3$  (3 x 100 mL). The organic layer was washed with water and brine (100 mL each), dried over  $\text{MgSO}_4$  and decolorizing carbon, and concentrated under reduced pressure to afford a yellow oil. This crude oil was purified by distillation ( $35\text{ }^\circ\text{C}$ , 0.04 torr) to yield the title compound as a clear, colorless oil (4.36 g, 52%). A fraction of 3,4-diiodoselenophene was isolated by distillation and re-subjected to the same reaction conditions with 1 equiv of zinc, and purified by the same procedure described above to yield an additional crop of the title compound (total yield: 5.26 g, 63%). HRMS (EI): Calcd. for  $\text{C}_4\text{H}_3\text{ISe}$  [ $\text{M}^+$ ] 257.8445, found, 257.8447.

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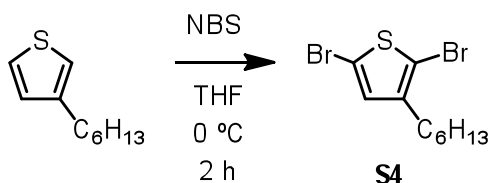


**3-hexylselenophene (S2):** To a 100 mL oven-dried Schlenk flask, cooled to rt under positive  $\text{N}_2$  pressure, were added 3-iodoselenophene (**S1**) (10.0 g, 38.9 mmol, 1.00 equiv),  $\text{Ni}(\text{dppe})\text{Cl}_2$  (0.211 g, 0.0389 mmol, 0.010 equiv) and diethylether (40 mL). The flask was cooled to  $0\text{ }^\circ\text{C}$  and a 2 M solution of  $\text{C}_6\text{H}_{13}\text{MgBr}$  in  $\text{Et}_2\text{O}$  (23.5 mL, 46.7 mmol, 1.20 equiv) was added dropwise over 5 min. The flask was warmed to rt overnight, quenched with aq  $\text{HCl}$  (2% v/v, 5 mL), diluted with 50 mL  $\text{Et}_2\text{O}$ , and washed with water and brine (50 mL). The organics were dried over  $\text{MgSO}_4$ , treated with decolorizing carbon, and concentrated in vacuo to give a yellow oil. This crude oil was purified by vacuum distillation ( $62\text{ }^\circ\text{C}$ , 0.036 torr) to afford the title compound as a clear, colorless oil (3.63 g, 43%). HRMS (EI): Calcd. for  $\text{C}_{10}\text{H}_{15}\text{Se}$  [ $\text{M}^+$ ] 216.0417, found, 216.0417.

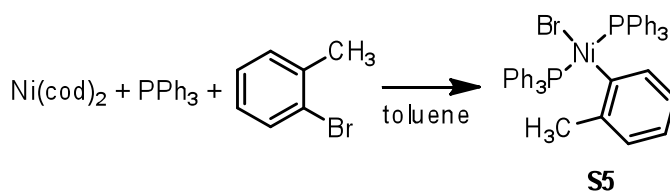
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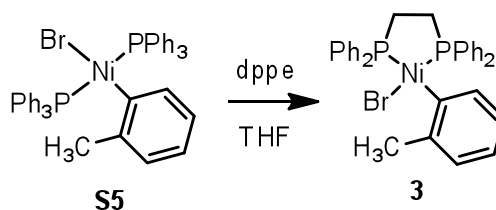
**2,5-dibromo-3-hexylselenophene (S3):** To a 100 mL oven-dried Schlenk flask cooled to rt under positive  $\text{N}_2$  pressure, were added 3-hexylselenophene (**S2**) (3.60 g, 16.7 mmol, 1.00 equiv) and anhydrous DMF (50 mL). The flask was cooled to 0 °C in an ice bath, protected from light, and a solution of N-bromosuccinimide (NBS) (6.25 g, 35.1 mmol, 2.50 equiv) in DMF (40 mL) was then added dropwise. The flask warmed to room temperature overnight with constant stirring, and the mixture was then washed with 10% aq  $\text{NaHSO}_3$  (100 mL), water (100 mL), and brine (100 mL). The organic layer was dried over  $\text{MgSO}_4$ , treated with decolorizing carbon, and concentrated in vacuo to give a brownish-orange oil. This crude oil was purified by silica gel column chromatography (in hexanes) to afford the title compound as a clear, colorless oil (3.91 g, 63%). HRMS (EI): Calcd. for  $\text{C}_{10}\text{H}_{13}\text{SeBr}_2$  [ $\text{M}^+$ ] 371.8627, found, 371.8636.



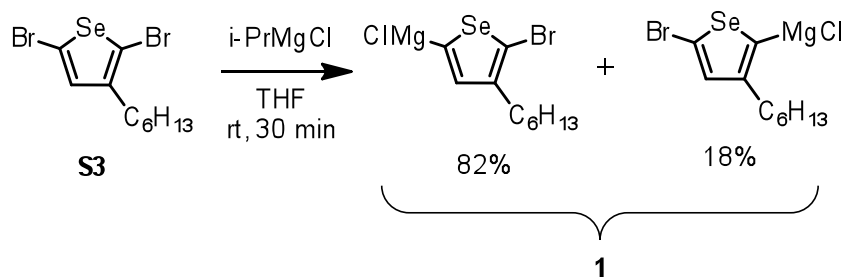
**2,5-dibromo-3-hexylthiophene (S4):** To a 100 mL oven-dried Schlenk flask, cooled to 0 °C under positive  $\text{N}_2$  pressure, were added 3-hexylthiophene (5.00 g, 0.030 mmol, 1.00 equiv) and THF (50 mL). Freshly recrystallized NBS (10.8 g, 0.061 mmol, 2.05 equiv) was added in a single portion and the mixture was stirred for 2 h. The reaction was then warmed to rt and quenched using saturated aq  $\text{NaHCO}_3$  (50 mL), diluted with  $\text{Et}_2\text{O}$  (100 mL), washed with water (100 mL) and brine (100 mL), dried over  $\text{MgSO}_4$ , treated with decolorizing carbon, 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  $\text{C}_{10}\text{H}_{14}\text{Br}_2\text{S}$  [ $\text{M}^+$ ] 323.9183; found, 323.9176.



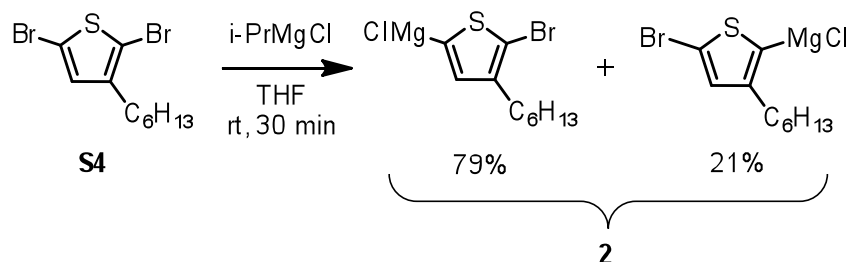
**(o-tolyl)bis(triphenylphosphino)nickel bromide (S5):**  $\text{Ni}(\text{cod})_2$  (517 mg, 1.88 mmol, 1.00 equiv) and  $\text{PPh}_3$  (986 mg, 3.76 mmol, 2.00 equiv) were dissolved in toluene (10 mL) in an oven-dried 25 mL round bottom flask equipped with a stir bar, under a nitrogen atmosphere. 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%).



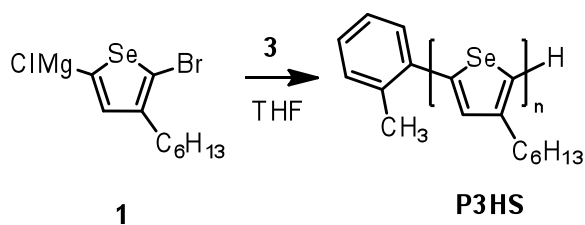
**(o-tolyl)(1,2-bis(diphenylphosphino)ethane)nickel bromide (3):** In a 25 mL oven-dried round-bottom flask equipped with a stir bar, under a nitrogen atmosphere, **S5** (340 mg, 0.45 mmol, 1.00 equiv) was dissolved in THF (5 mL). Then, dppe (198 mg, 0.50 mmol, 1.10 equiv) was added and the mixture was stirred at rt for 1 h. The volume of THF was reduced to ~ 1mL under reduced pressure and hexanes (10 mL) were added. The resultant precipitate was isolated by filtration, washed with hexanes (10 mL) and diethylether (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<sub>33</sub>H<sub>31</sub>BrNiP<sub>2</sub> [M<sup>+</sup>] 626.0438, found, 626.0428.



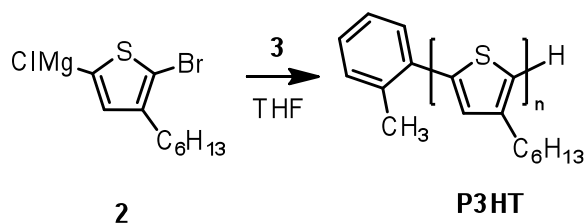
**1:** In a nitrogen environment, **S3** (83.6 mg, 0.224 mmol, 1.00 equiv) was dissolved in THF (2.2 mL) in a 25 mL Schlenk tube equipped with a stir-bar. A 2 M solution of *i*-PrMgCl in THF (101 μL, 0.202 mmol, 0.90 equiv) was added and the reaction stirred at rt for 30 min. An aliquot of the solution (0.1 mL) was quenched with 6 M aq HCl (0.1 mL), extracted with CHCl<sub>3</sub> (2 x 1mL) and analyzed by GC, showing a mixture of regioisomers in the ratio of 82:18, on average.



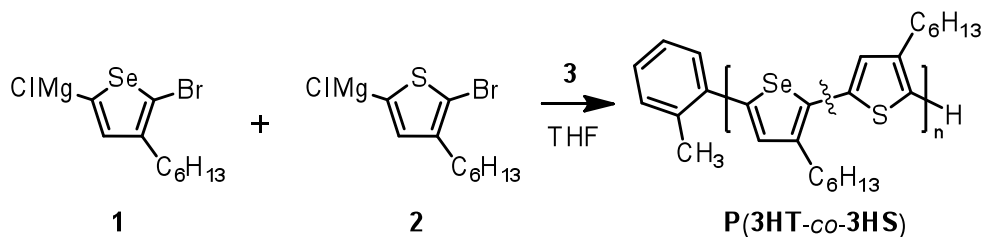
**2:** In a nitrogen environment, **S4** (109 mg, 0.333 mmol, 1.00 equiv) was dissolved in THF (1.5 mL) in a 25 mL Schlenk tube equipped with a stir-bar. A 2 M solution of *i*-PrMgCl in THF (158 μL, 0.317 mmol, 0.90 equiv) was added and the reaction stirred at rt for 30 min. An aliquot of the solution (0.1 mL) was quenched with 6 M aq HCl (0.1 mL), extracted with CHCl<sub>3</sub> (2 x 1mL) and analyzed by GC, showing a mixture of regioisomers in the ratio of 79:21, on average.



**poly(3-hexylselenophene) (P3HS):** In an oven-dried Schlenk flask, a solution of **1** in THF was diluted with THF to give a monomer stock solution (15.5 mL, 0.01 M, 0.155 mmol). A stock solution of the nickel catalyst **3** in THF (5 mM, 0.26 mL, 1.29  $\mu$ mol) was transferred to the flask via syringe and the mixture was stirred at rt for 1 h under nitrogen. The polymerization was quenched with 5 M aq HCl (5 mL), extracted with  $\text{CHCl}_3$  (3 x 5 mL) and dried in vacuo. The resultant blue solid was dissolved in a minimum amount of  $\text{CHCl}_3$  (~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, dichloromethane, and chlorobenzene. The chlorobenzene fraction was dried in vacuo to afford the polymer as a blue solid (26 mg, 78%). Gel permeation chromatography relative to polystyrene standards (THF, 40  $^{\circ}\text{C}$ ):  $M_n$  = 30.7 kDa, PDI = 1.19.

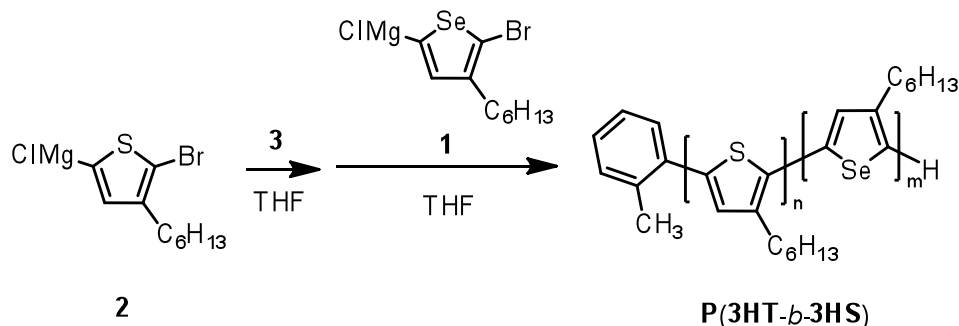


**poly(3-hexylthiophene) (P3HT):** To an oven-dried Schlenk flask, a solution of **2** in THF (3.32 mL, 0.05 M, 0.166 mmol) was injected via syringe. A stock solution of the nickel catalyst **3** in THF (5 mM, 0.28 mL, 1.38  $\mu$ mol) was then injected and the mixture was stirred at rt for 1 h. The polymerization was quenched with 5 M aq HCl (5 mL), extracted with  $\text{CHCl}_3$  (3 x 5 mL) and dried in vacuo. The resultant blue solid was dissolved in a minimum amount of  $\text{CHCl}_3$  (~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, dichloromethane, and  $\text{CHCl}_3$ . The chloroform fraction was dried in vacuo to afford the polymer as a blue solid (8.5 mg, 30%). Gel permeation chromatography relative to polystyrene standards (THF, 40  $^{\circ}\text{C}$ ):  $M_n$  = 28.4 kDa, PDI = 1.10.

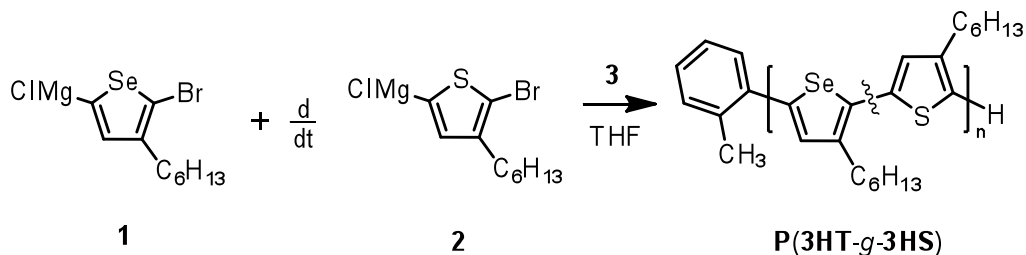


**poly(3-hexylselenophene-co-3-hexylthiophene) (P(3HT-co-3HS)):** Under a nitrogen atmosphere, solutions of **1** (3.50 mL, 0.145 M) and **2** (3.32 mL, 0.153 M) were combined in an oven-dried 100 mL Schlenk flask and diluted with THF to give an initial monomer concentration of 0.02 M. A stock solution of the nickel catalyst **3** in THF (5 mM, 2.0 mL, 10.1  $\mu$ mol) was transferred to the flask via syringe. After stirring at rt for 30 min, the polymerization was quenched with 5 M aq HCl (5 mL) and extracted with  $\text{CHCl}_3$  (3 x 5 mL) and dried in vacuo. The resultant blue solid was dissolved in a minimum amount of  $\text{CHCl}_3$  (~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, dichloromethane,

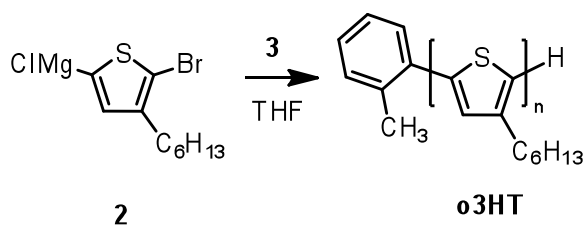
and chlorobenzene. The chlorobenzene fraction was dried in vacuo to afford the polymer as a blue solid (170 mg, 88%). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C):  $M_n$  = 32.6 kDa, PDI = 1.11.



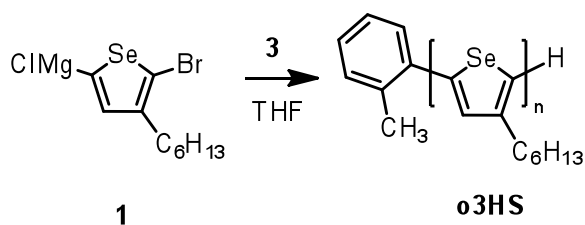
**poly(3-hexylselenophene-*block*-3-hexylthiophene) (P(3HT-*b*-3HS)):** Under a nitrogen atmosphere, a stock solution of **2** (3.90 mL, 0.153 M) was transferred to an oven-dried 100 mL round bottom flask and diluted with THF to give an initial monomer concentration of 0.01 M. A stock solution of the nickel catalyst **3** in THF (5 mM, 2.34 mL, 11.7  $\mu$ mol) was transferred to the flask via syringe. After stirring at rt for 1 h, nearly complete conversion of **2** was confirmed by gas chromatography (>98%). GPC of the macro-initiator block indicated  $M_n$  = 12.5 kDa, PDI = 1.09. Subsequently, the stock solution of **1** (3.55 mL, 0.162 M) was injected. After an additional 1 h at rt, the polymerization was quenched with 5 M aq HCl (5 mL) and extracted with  $\text{CHCl}_3$  (3 x 5 mL) and dried in vacuo. The resultant blue solid was dissolved in a minimum amount of  $\text{CHCl}_3$  upon heating and precipitated into MeOH. The precipitate was collected on Whatman filter paper and purified by Soxhlet extraction using MeOH, acetone, hexanes,  $\text{CH}_2\text{Cl}_2$ , and chlorobenzene. The chlorobenzene fraction was dried in vacuo to afford the polymer as a blue solid (182 mg, 81%). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C):  $M_n$  = 28.7 kDa, PDI = 1.15.



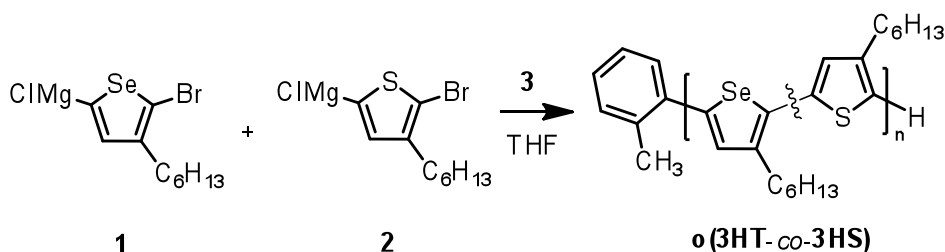
**poly(3-hexylselenophene-*gradient*-3-hexylthiophene) (p(3HT-*g*-3HS)):** Under a nitrogen atmosphere, a solution of **2** (15 mL, 0.01 M) was transferred to an oven-dried 25 mL Schlenk flask. A solution of **1** (3 mL, 0.05 M) was loaded into a 5 mL plastic syringe and attached to a syringe pump apparatus. With constant stirring, a stock solution of the nickel catalyst **3** in THF (5 mM, 0.5 mL, 3.0  $\mu$ mol) was transferred to the flask via syringe, and the syringe pump was activated to deliver **1** at a rate of 0.24 mL/min. After 1 h at rt, the polymerization was quenched with 5 M aq HCl (5 mL) and extracted with  $\text{CHCl}_3$  (3 x 5 mL) and dried in vacuo. The resultant blue solid was dissolved in a minimum amount of  $\text{CHCl}_3$  (~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, dichloromethane, and chlorobenzene. The chlorobenzene fraction was dried in vacuo to afford the polymer as a blue solid (54 mg, 84%). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C):  $M_n$  = 31.9 kDa, PDI = 1.13.



**oligo(3-hexylthiophene):** In a 20 mL scintillation vial, a solution of **2** was diluted in THF to give a monomer stock solution (5.60 mL, 0.040 M). A solution of the nickel catalyst **3** in THF (1.78 mL, 0.0126 M) was transferred to the flask and the mixture was stirred at rt for 1 h. 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 (11.6 mg, 88%). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C):  $M_n$  = 2.2 kDa, PDI = 1.23. A solution of the oligomer in CHCl<sub>3</sub> was passed over alumina (acidic, basic, and neutral), concentrated under reduced pressure, and analyzed by MALDI-TOF-MS without further purification.

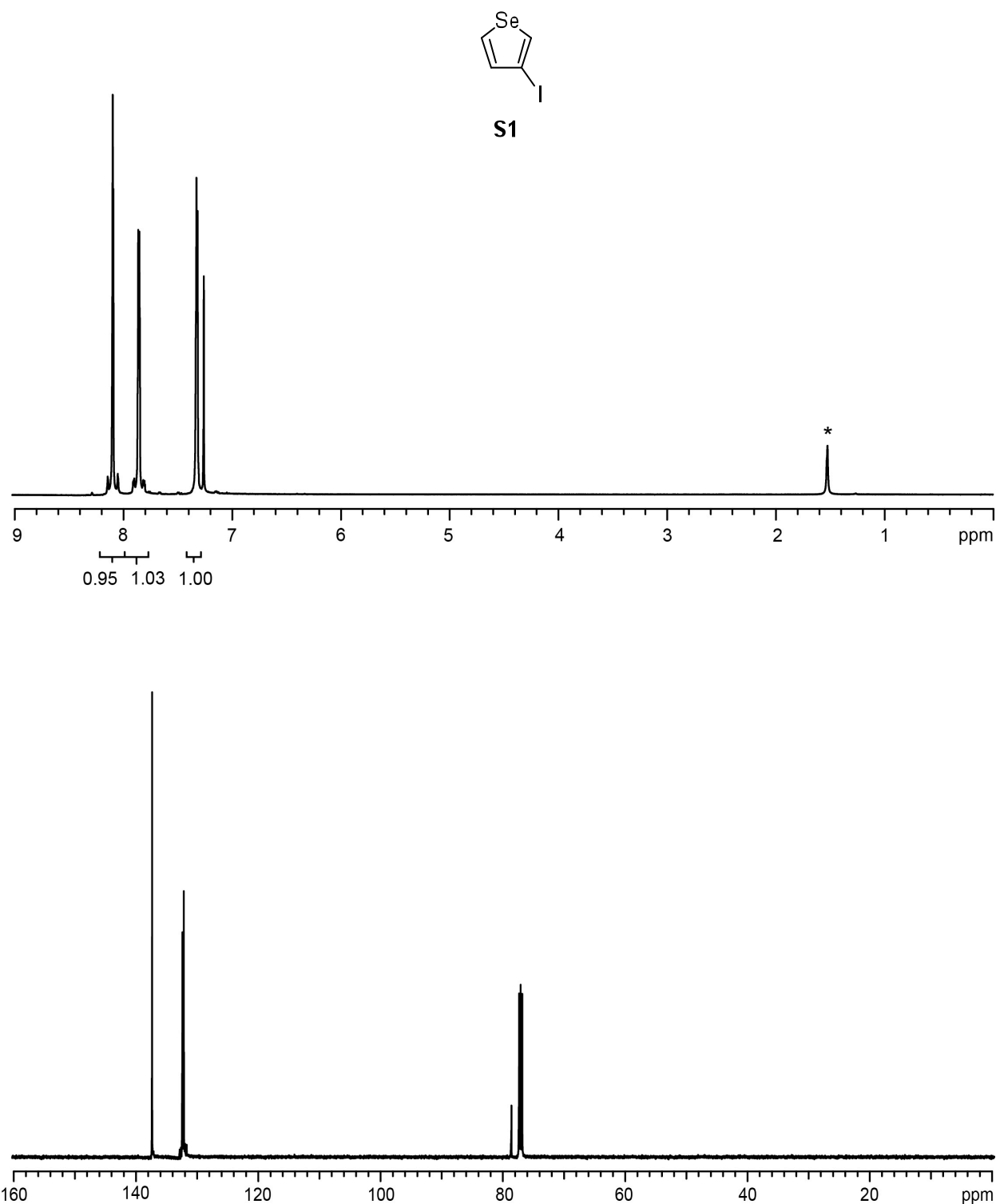


**oligo(3-hexylselenophene):** In a 20 mL scintillation vial, a solution of **1** was diluted in THF to give a monomer solution (6.14 mL, 0.040 M). A solution of the nickel catalyst **3** in THF (1.95 mL, 0.0126 M) was transferred to the vial and the mixture was stirred at rt for 1 h. The oligomerization reaction was quenched with 5 M HCl (5 mL), extracted with CHCl<sub>3</sub> (3 x 5 mL) and dried in vacuo to obtain the crude product as a purple solid (11.3 mg, 69%). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C):  $M_n$  = 2.7 kDa, PDI = 1.31. A solution of the oligomer in CHCl<sub>3</sub> was passed over alumina (acidic, basic, and neutral), concentrated under reduced pressure, and analyzed by MALDI-TOF-MS without further purification.



**oligo(3-hexylthiophene-co-3-hexylselenophene):** In a 20 mL scintillation vial, a solution of **1** was combined with a solution of **2**, diluted in THF to give the comonomer stock solution (2 mL, 0.09 M). A solution of the nickel catalyst **3** in THF (1.8 mL, 0.0050 M) was transferred to the vial and the mixture was stirred at rt for 1 h. The oligomerization reaction was quenched with 5M HCl (5 mL), extracted with CHCl<sub>3</sub> (3 x 5 mL) and dried in vacuo to obtain the crude product as a purple solid (8.5 mg, 30 %). Gel permeation chromatography relative to polystyrene standards (THF, 40 °C):  $M_n$  = 1.3 kDa, PDI = 1.24. A solution of the oligomer in CHCl<sub>3</sub> was passed over alumina (acidic, basic, and neutral), concentrated under reduced pressure, and analyzed by MALDI-TOF-MS without further purification.

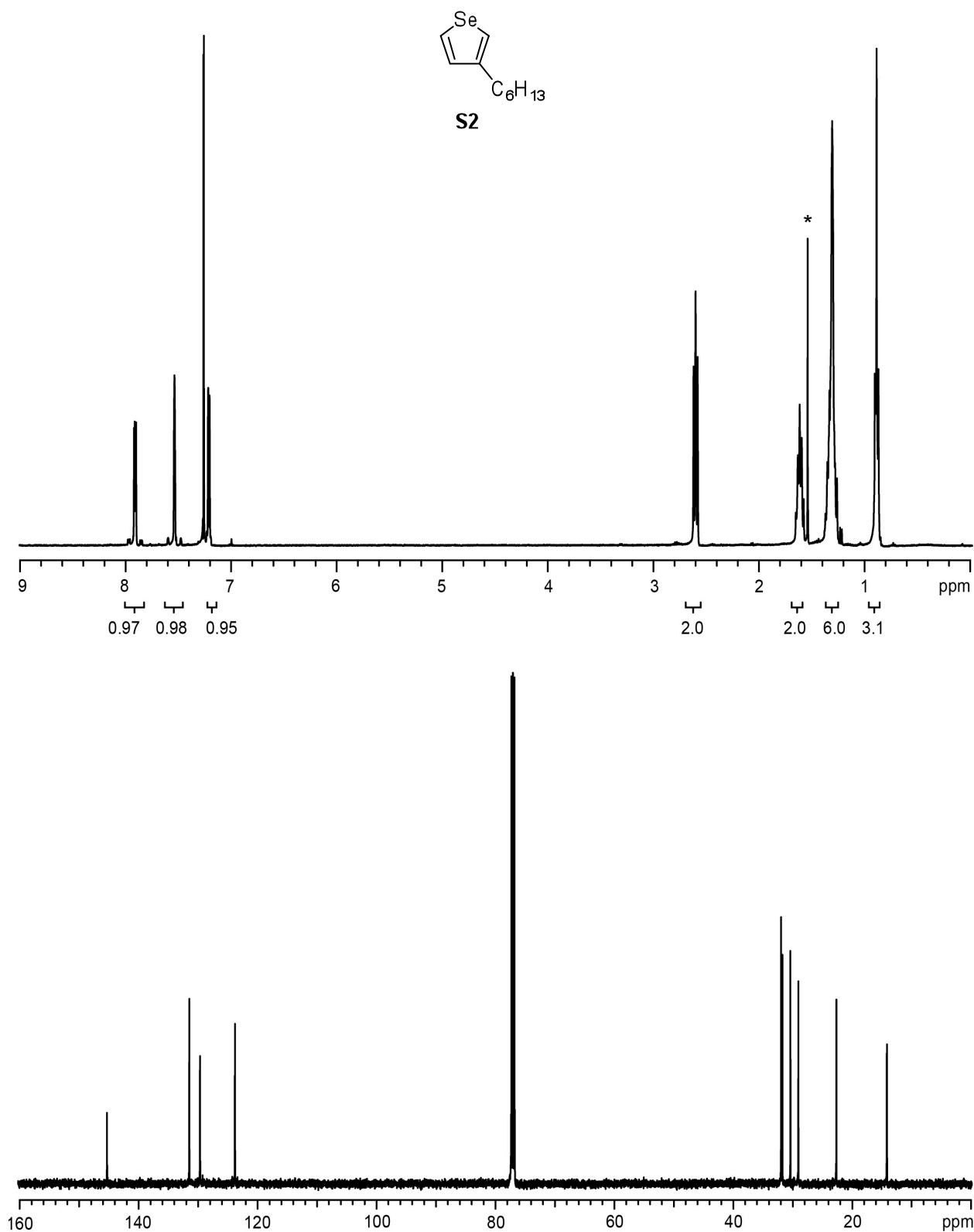
#### IV. NMR Spectra



**Figure S1.** <sup>1</sup>H and <sup>13</sup>C NMR spectra for **S1**.

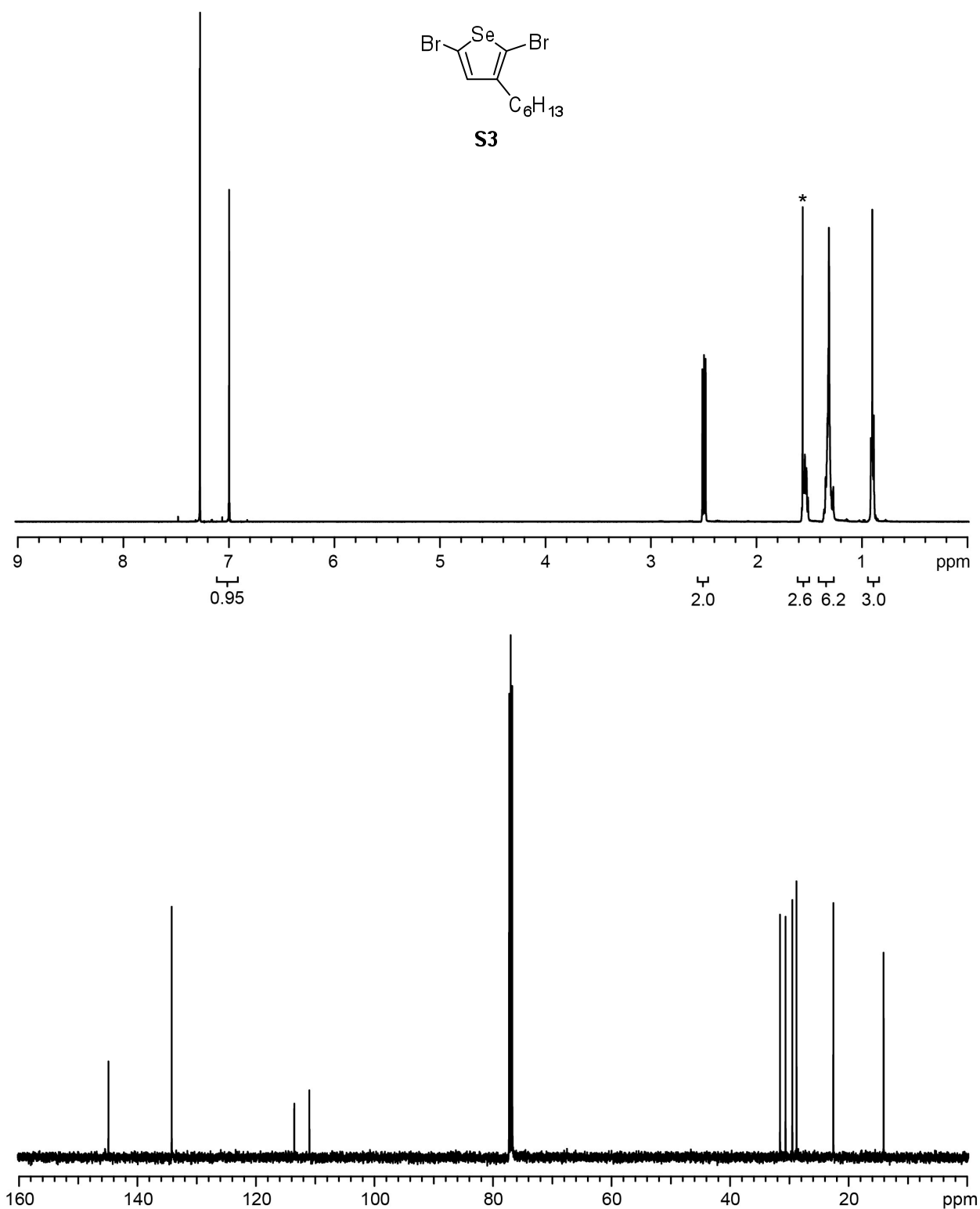
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.84 (dd, *J* = 5.6, 2.8 Hz, 1H), 7.31 (dd, *J* = 5.6, 1.2 Hz, 1H). The satellite peaks on the signals at 8.2-7.8 ppm arise from H-Se coupling. The symbol \*denotes residual water in the CDCl<sub>3</sub>. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.36, 132.40, 132.17, 78.59.



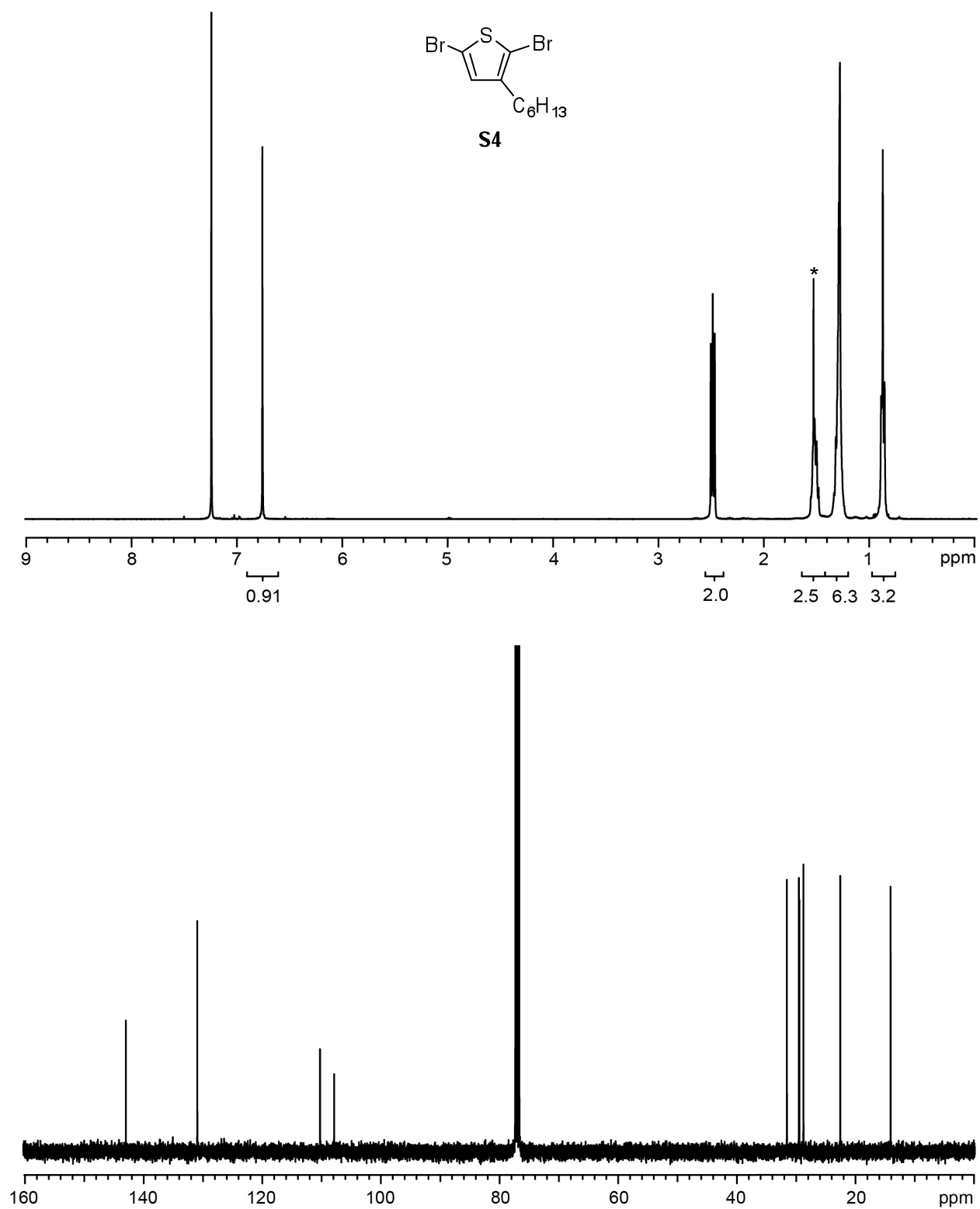


**Figure S2.** <sup>1</sup>H and <sup>13</sup>C NMR spectra for **S2**.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (dd, *J* = 5.2, 2.4 Hz, 1H), 7.52 (br s, 1H), 7.19 (d, *J* = 5.2 Hz, 1H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.60 (m, 2H), 1.29 (br m, 6H), 0.87 (t, *J* = 7.2 Hz, 3H). The satellite peaks on the signals at 8.0-7.4 ppm arise from H-Se coupling. The symbol \* denotes residual water in the CDCl<sub>3</sub>. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 145.31, 131.48, 129.66, 123.79, 31.93, 31.71, 30.37, 29.03, 22.64, 14.14.

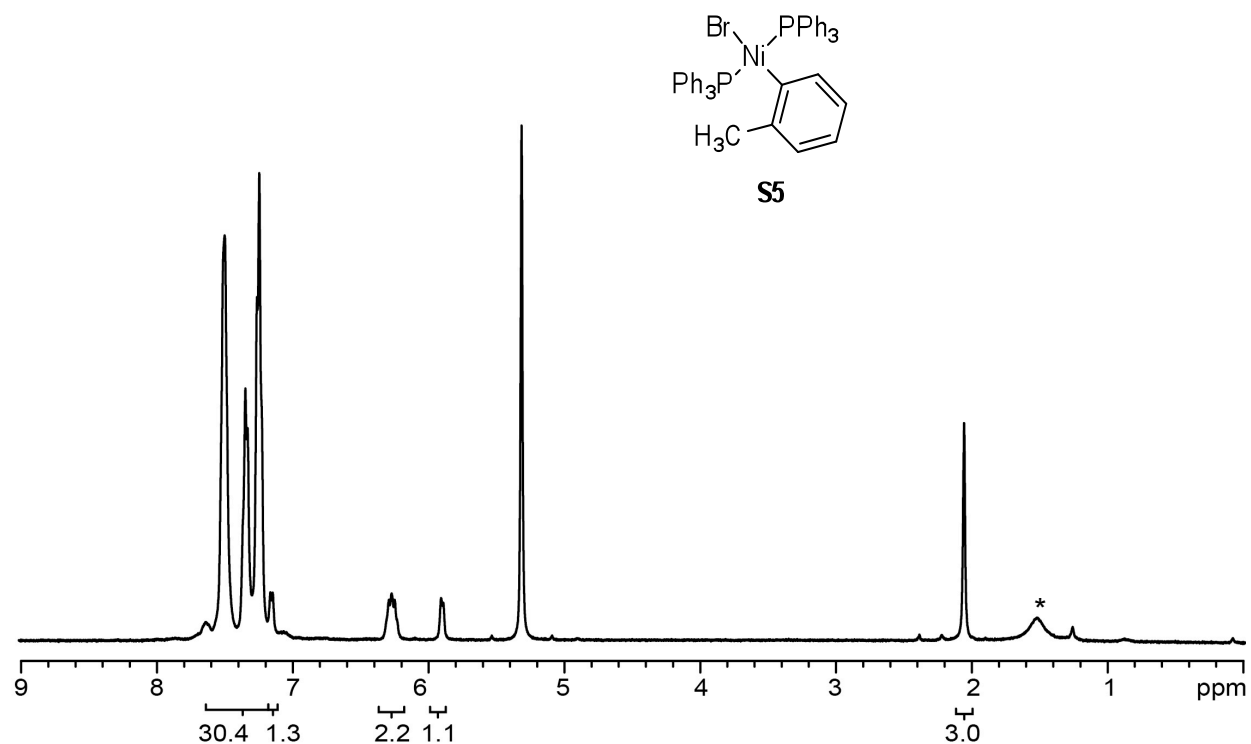


**Figure S3.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for **S3**.  
 $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.97 (s, 1H), 2.47 (t,  $J = 7.6$  Hz, 2H), 1.51 (m, 2H), 1.28 (br, 6H), 0.87 (t,  $J = 7.2$  Hz, 3H). The symbol \* denotes residual water in the  $\text{CDCl}_3$ .  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.90, 134.22, 113.53, 110.98, 31.57, 30.63, 29.49, 28.78, 22.56, 14.09.

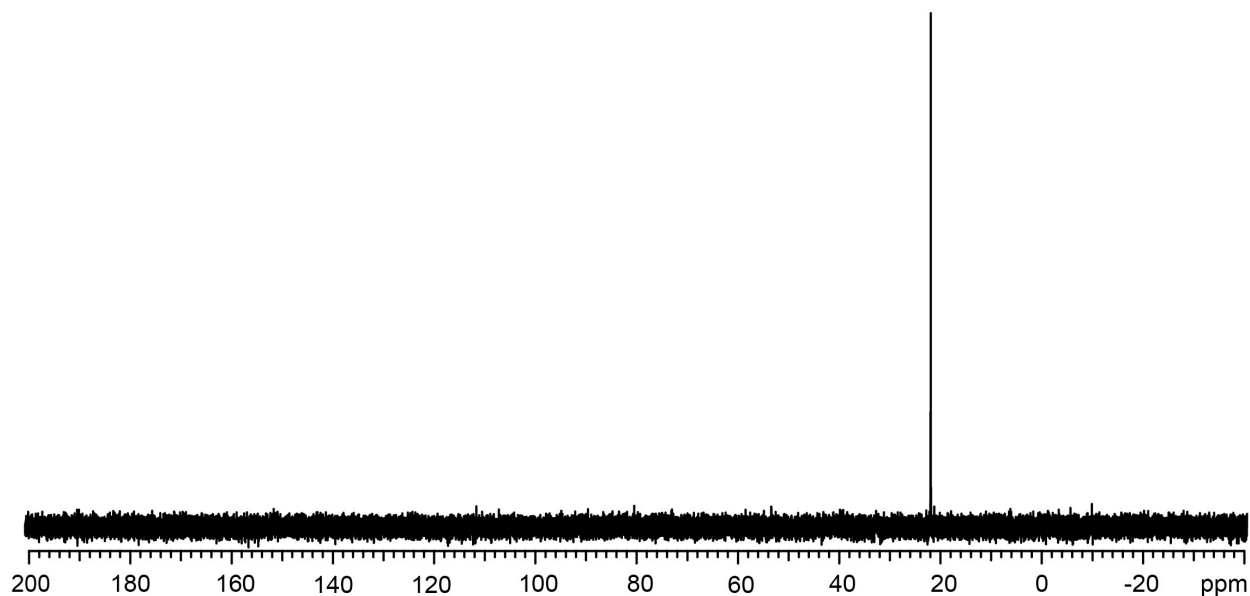


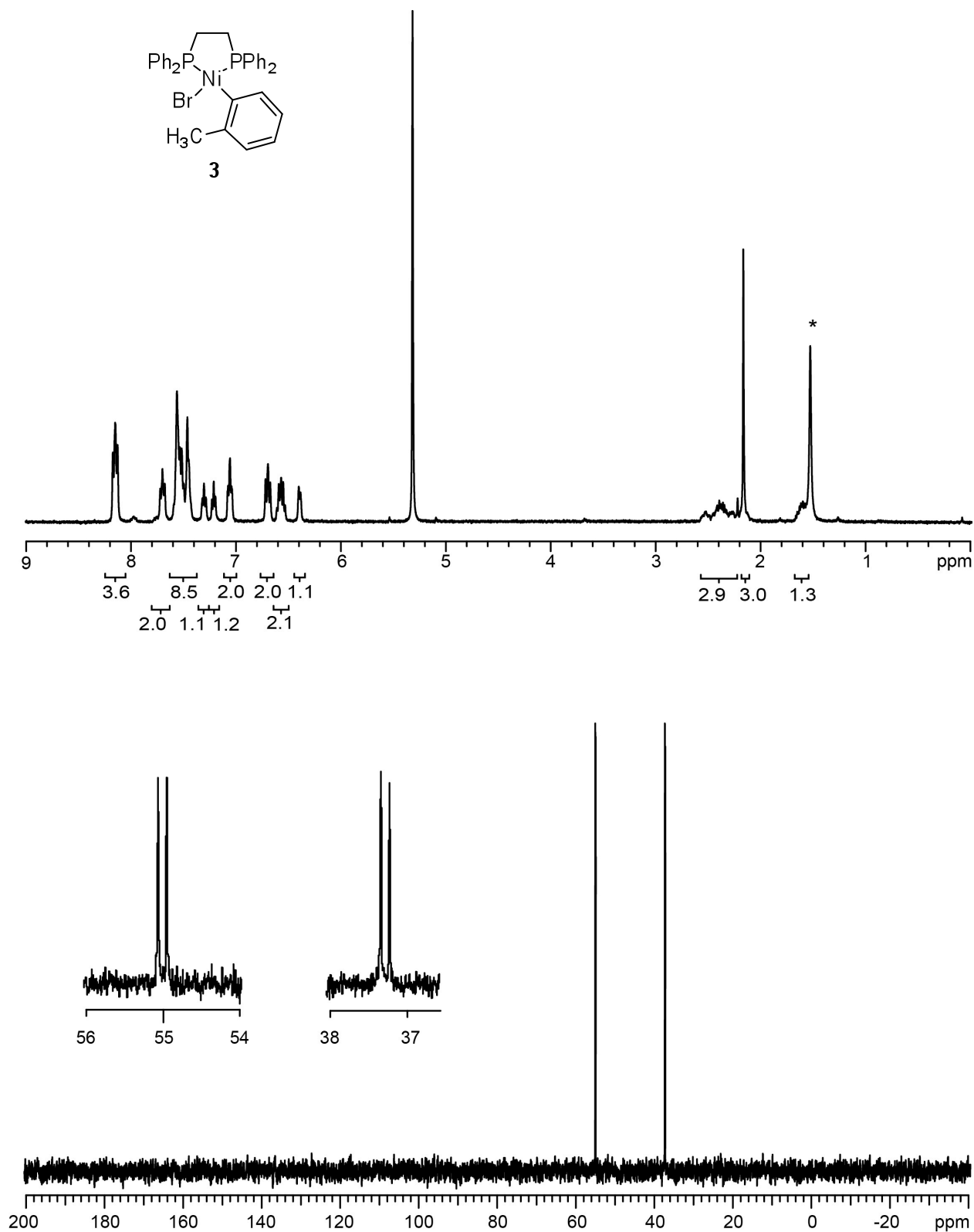
**Figure S4.** <sup>1</sup>H and <sup>13</sup>C NMR spectra for **S4**.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 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>) δ 142.98, 130.94, 110.26, 107.89, 31.54, 29.53, 29.46, 28.76, 22.55, 14.06.



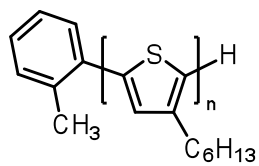
**Figure S5.**  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra for **S5**.  
 $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.50-7.20 (br, 30H), 7.15 (m, 1H), 6.27 (m, 2H), 5.91 (m, 1H), 2.06 (br, 3H).  
 The symbol \* denotes residual water in the  $\text{CD}_2\text{Cl}_2$ .  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  21.9 (s).



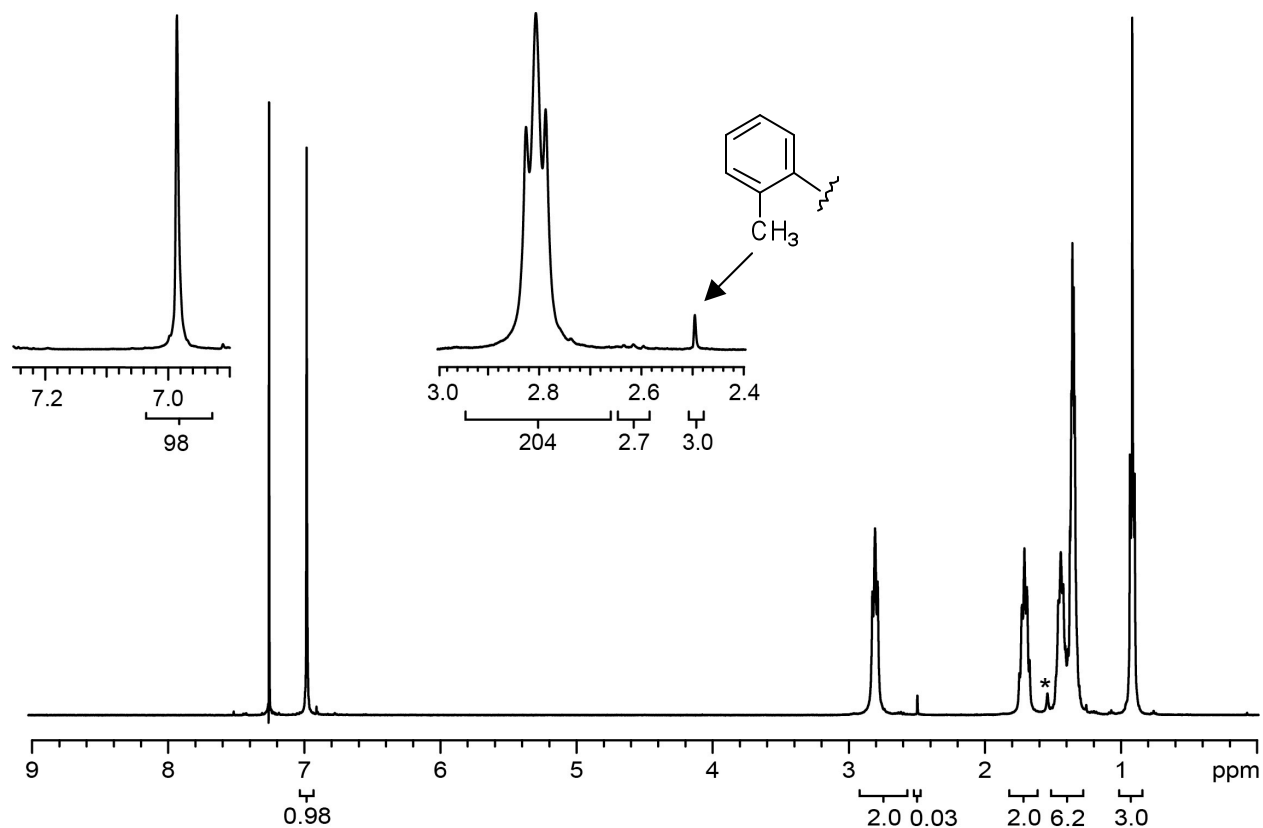


**Figure S8.** <sup>1</sup>H and <sup>31</sup>P NMR spectra for **3**.

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

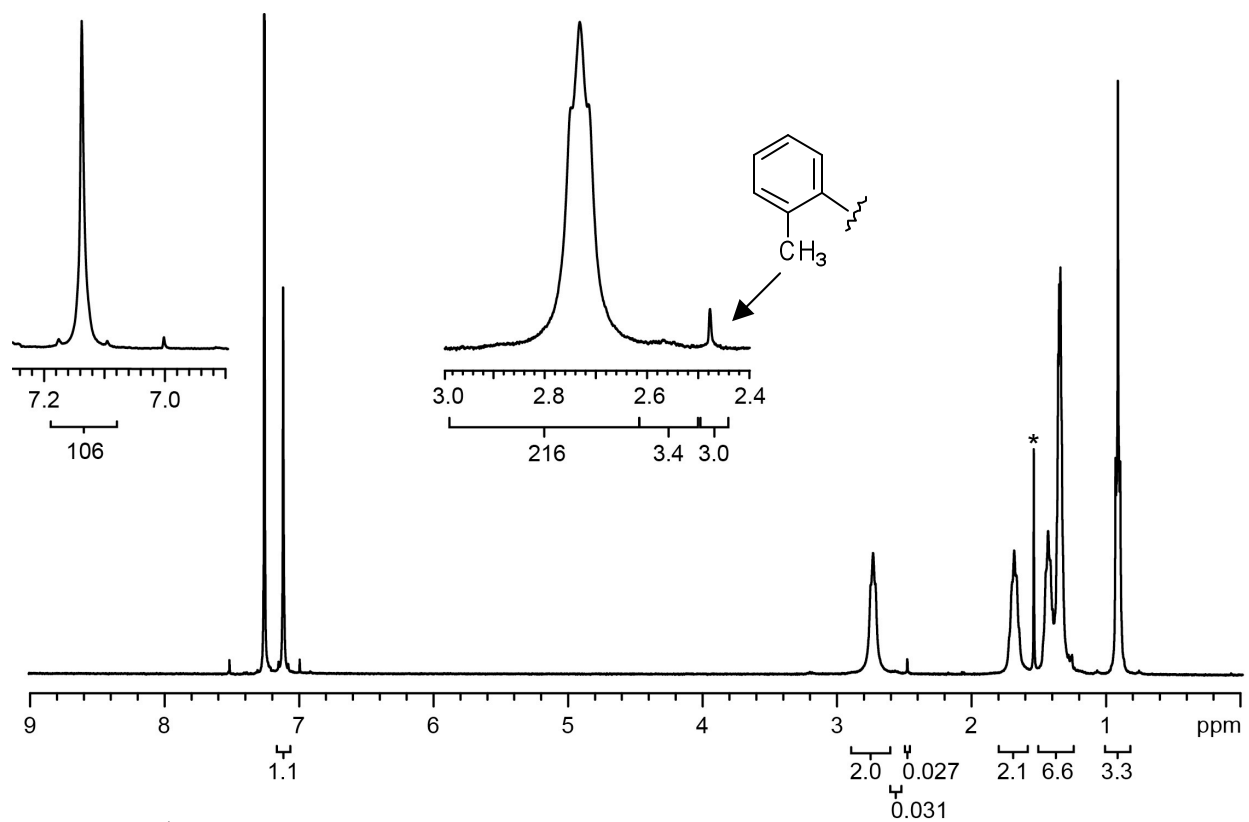
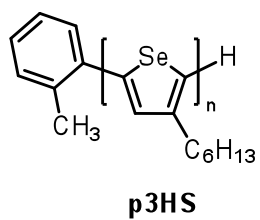


**p3HT**



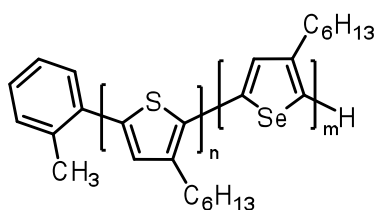
**Figure S9.**  $^1\text{H}$  NMR spectrum for **p3HT**.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.98 (s, 1H), 2.81 (br, 2H), 1.71 (br, 2H), 1.44-1.36 (br, 6H), 0.92 (br, 3H). Integrations in the insets are normalized to 100-fold that of the full-scale image.

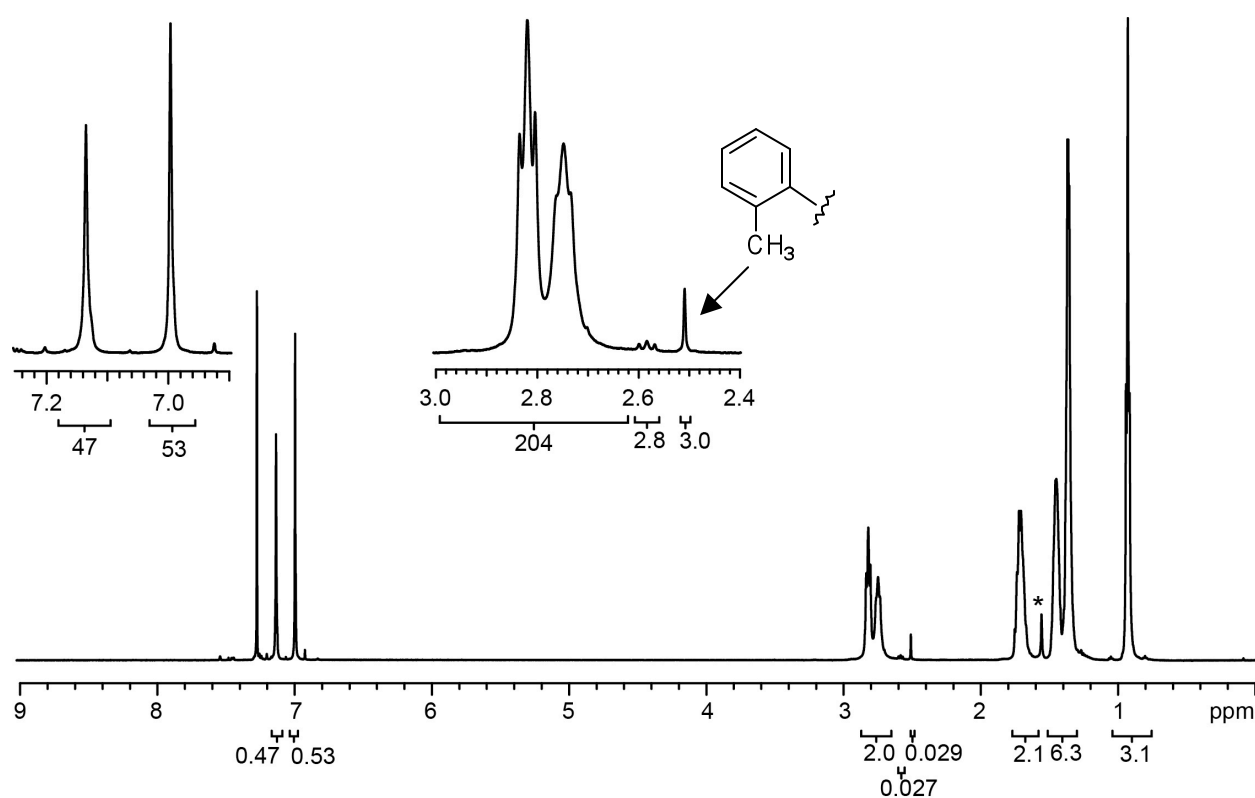


**Figure S10.**  $^1\text{H}$  NMR spectrum for **p3HS**.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12 (s, 1H), 2.74 (br, 2H), 1.69 (br, 2H), 1.43-1.35 (br, 6H), 0.92 (br, 3H). Integrations in the insets are normalized to 100-fold that of the full-scale image.



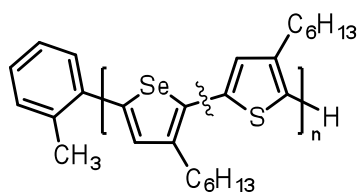
**p(3HT-*block*-3HS)**



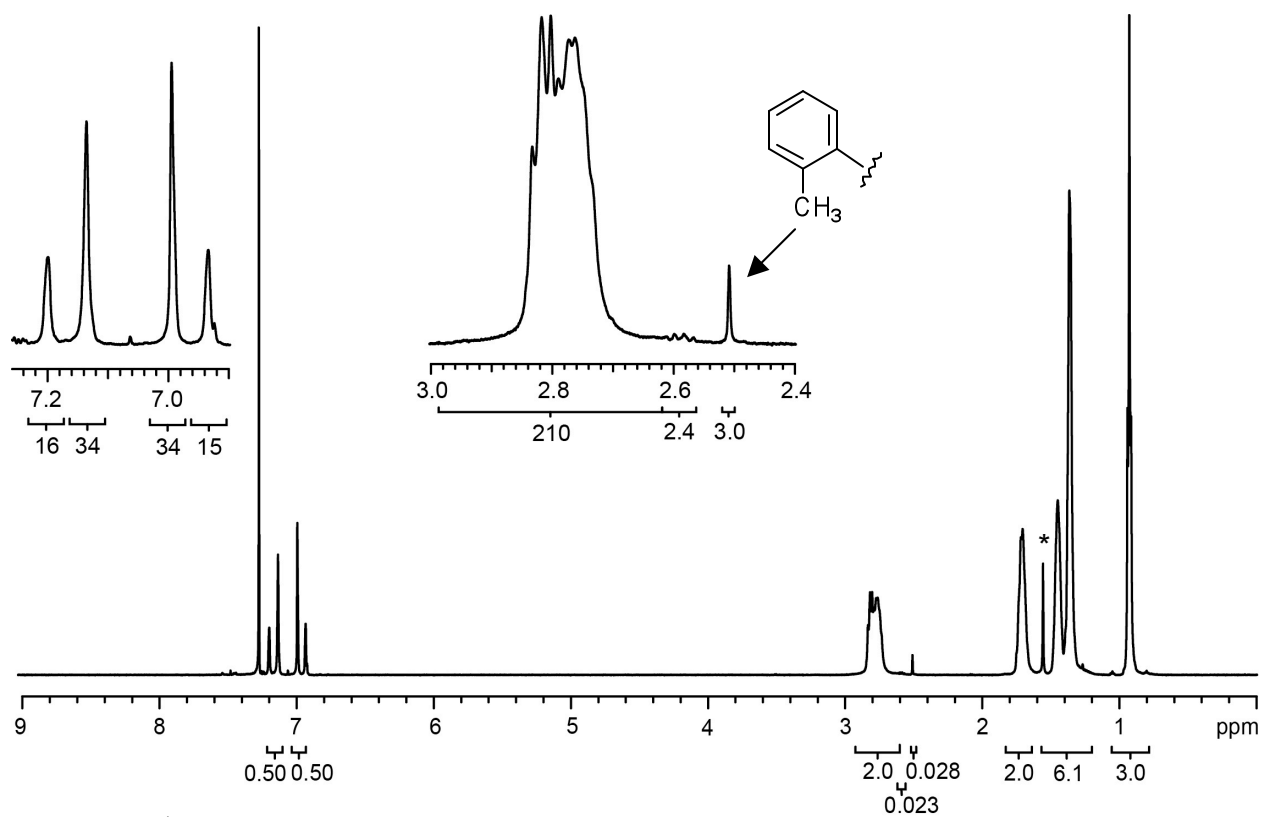
**Figure S11.**  $^1\text{H}$  NMR spectrum for the block copolymer.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12 (s, 0.5H), 6.98 (s, 0.5H), 2.82-2.74 (br, 2H), 1.71 (br, 2H), 1.44-1.35 (br, 6H), 0.91 (br, 3H). Integrations in the insets are normalized to 100-fold that of the full-scale image.



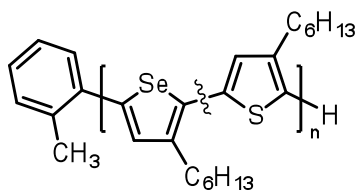


**p(3HT-*g*-3HS)**

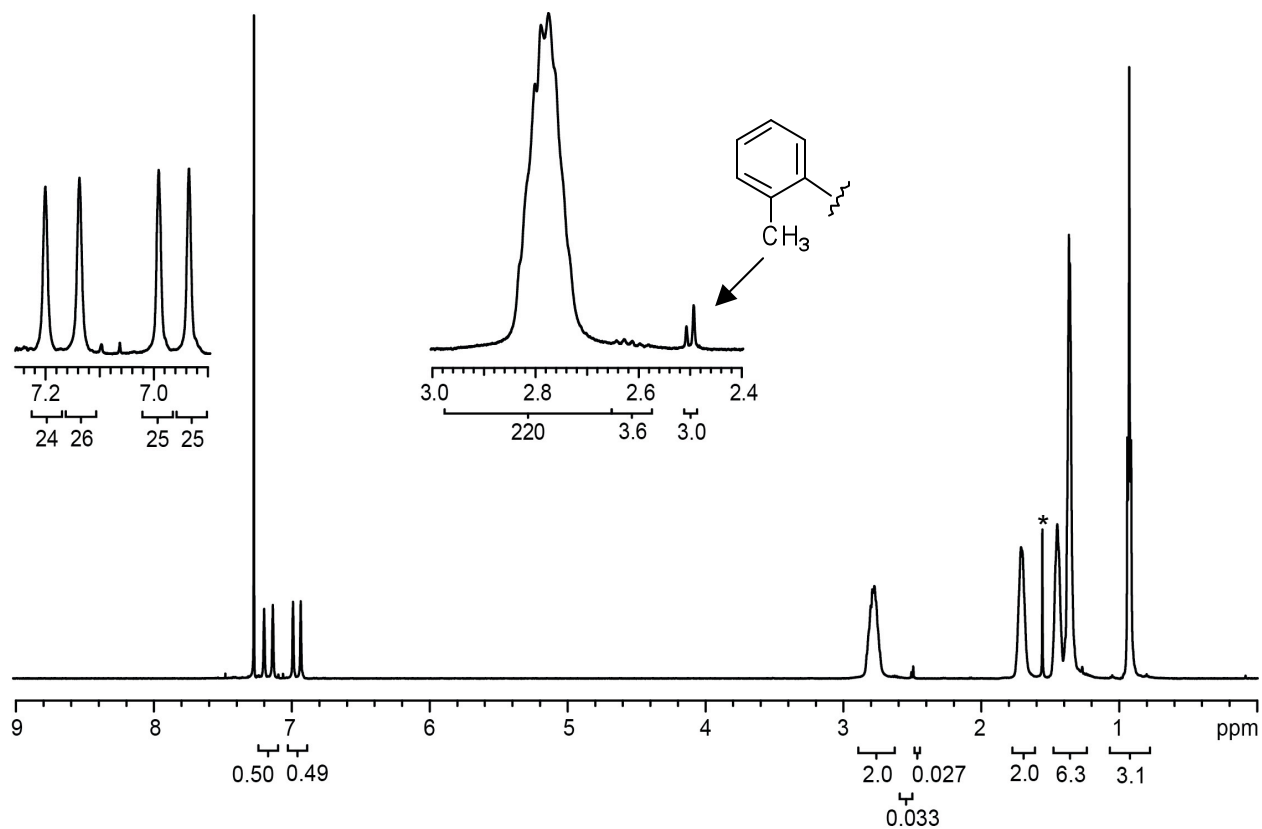


**Figure S12.**  $^1\text{H}$  NMR spectrum for the gradient copolymer.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18 (s, 0.16H), 7.12 (s, 0.34H), 6.98 (s, 0.34H), 6.92 (s, 0.16H), 2.78 (br, 2H), 1.71 (br m, 2H), 1.44-1.35 (br, 6H), 0.91 (br, 3H). Integrations in the insets are normalized to 100-fold that of the full-scale image.



**p(3HT-co-3HS)**



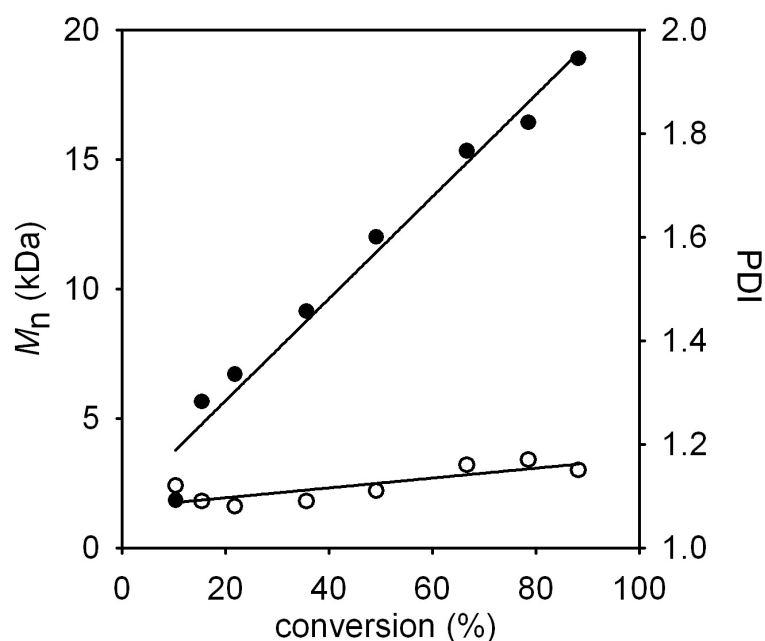
**Figure S13.**  $^1\text{H}$  NMR spectrum for the random copolymer.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18 (s, 0.25H), 7.12 (s, 0.25H), 6.98 (s, 0.25H), 6.92 (s, 0.25H), 2.77 (br, 2H), 1.70 (br, 2H), 1.44-1.35 (br, 6H), 0.91 (br, 3H). Integrations in the insets are normalized to 100-fold that of the full-scale image.

## V. $M_n$ and PDI versus Conversion

*General procedure for obtaining plots of  $M_n$  and PDI versus conversion:*

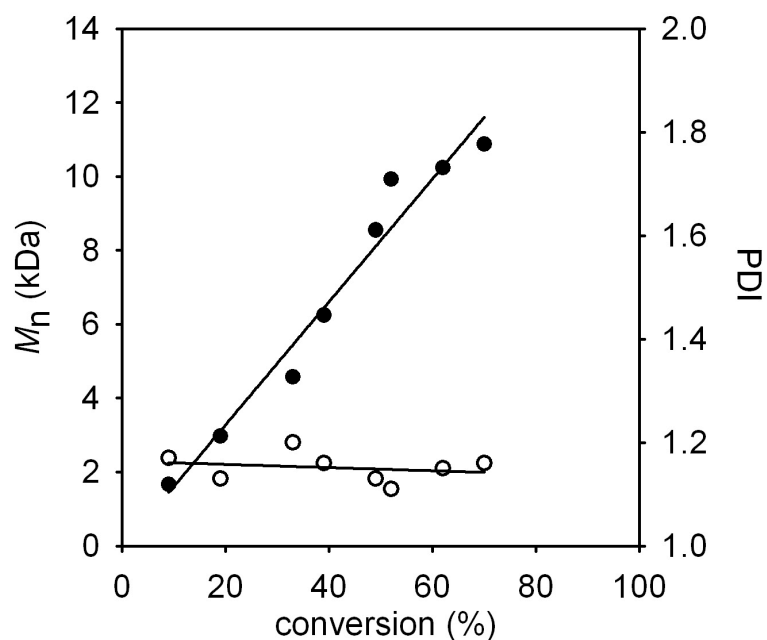
An oven-dried 50 mL Schlenk flask equipped with a stir bar and a septum was evacuated and cooled under vacuum. Once cool, the flask was filled with  $N_2$  and re-evacuated: this process was repeated twice and the flask was filled with  $N_2$ . THF (10 mL) was added to the flask and cooled to 0 °C. Then, monomers **1** and **2** (see pg S5-S6) and a  $C_{22}H_{46}$  solution (0.5 mL, 0.1 M in THF) were added by syringe and the solution was stirred for 1 min. A ~ 0.2 mL aliquot was withdrawn via syringe and quenched with HCl (~ 1 mL, 5 M). GC analysis afforded the initial ratio of monomer to internal standard peak areas. Then the catalyst solution (5 mM, see pg S6) was added to the reaction. Aliquots (~0.2 mL) were taken from the reaction periodically via syringe and quenched with 5 M aq HCl (~ 1 mL). Each aliquot was then extracted with  $CHCl_3$  (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  $C_{22}H_{46}$  peak.



**Table S1.** Data plotted in Fig. S14.

conv. %	$M_n$ (kDa)	PDI
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

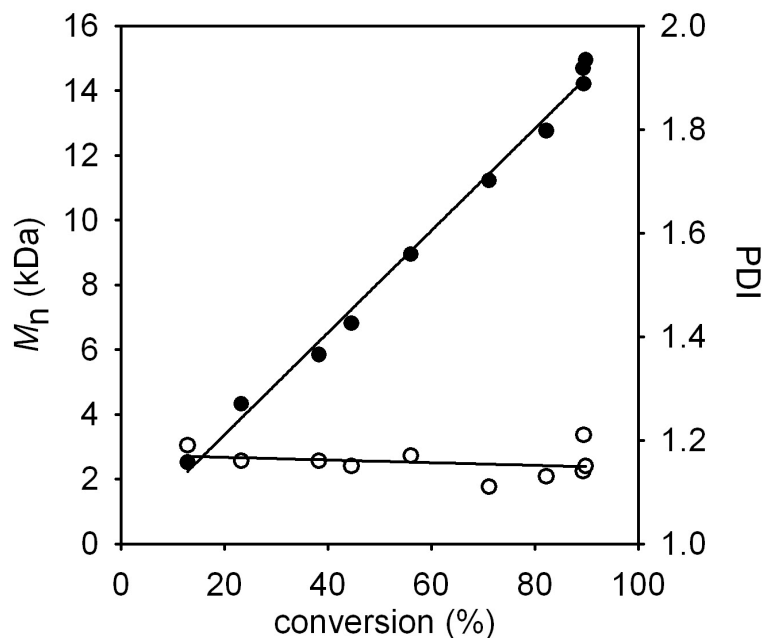
**Figure S14.** Plot of  $M_n$  (●) and PDI (○) versus conversion for the homopolymerization of **2** with catalyst **3**, at 0 °C in THF. Conditions:  $[2]_0 = 0.03$  M,  $[1]_0/[3]_0 = 100$ .



**Table S2.** Data plotted in Fig. S15.

conv. %	$M_n$ (kDa)	PDI
9.0	1.7	1.17
18.7	3.0	1.13
32.7	4.6	1.20
39.0	6.2	1.16
49.3	8.6	1.13
52.0	9.9	1.11
62.3	10.2	1.15
70.0	10.9	1.16

**Figure S15.** Plot of  $M_n$  (●) and PDI (○) versus conversion for polymerization of **1** with catalyst **3**, at 0 °C in THF. After ~70% conversion, the polymer precipitated from solution. Conditions:  $[1]_0 = 0.01$  M,  $[1]_0/[3]_0 = 50$ .

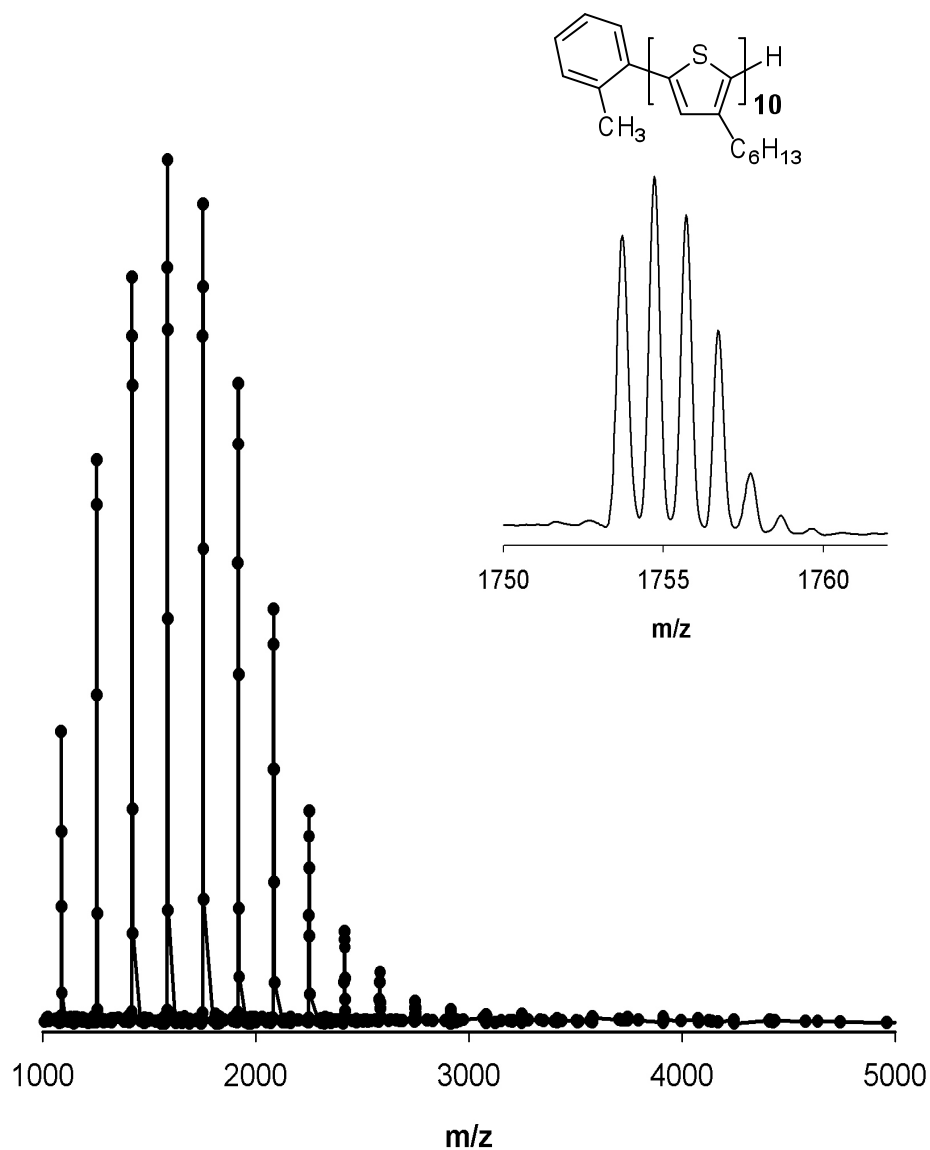


**Table S3.** Data plotted in Fig. S16

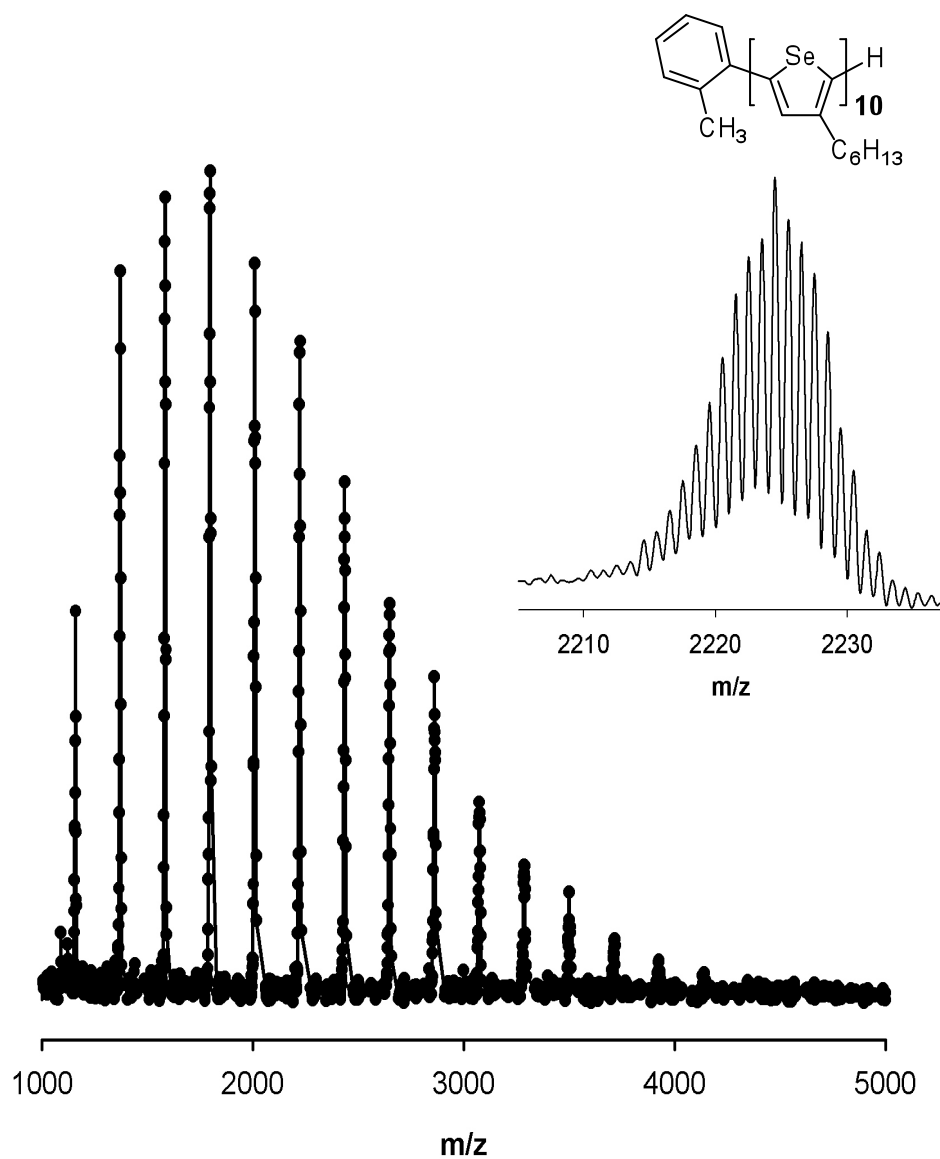
conv. (%)	$M_n$ (kDa)	PDI
12.8	2.5	1.19
23.2	4.3	1.16
38.2	5.8	1.16
44.5	6.8	1.15
56.0	8.9	1.17
71.1	11.2	1.11
82.2	12.8	1.13
89.3	14.7	1.14
89.4	14.2	1.21
89.8	14.9	1.15

**Figure S16.** Plot of  $M_n$  (●) and PDI (○) versus conversion for the copolymerization of **1** and **2** with catalyst **3** at 0 °C in THF. The comonomer mole ratio was ~1:1. The conversion refers to the overall conversion of **1** and **2**. Conditions:  $[1+2]_0 = 0.02$  M,  $[1+2]_0/[3]_0 = 100$ .

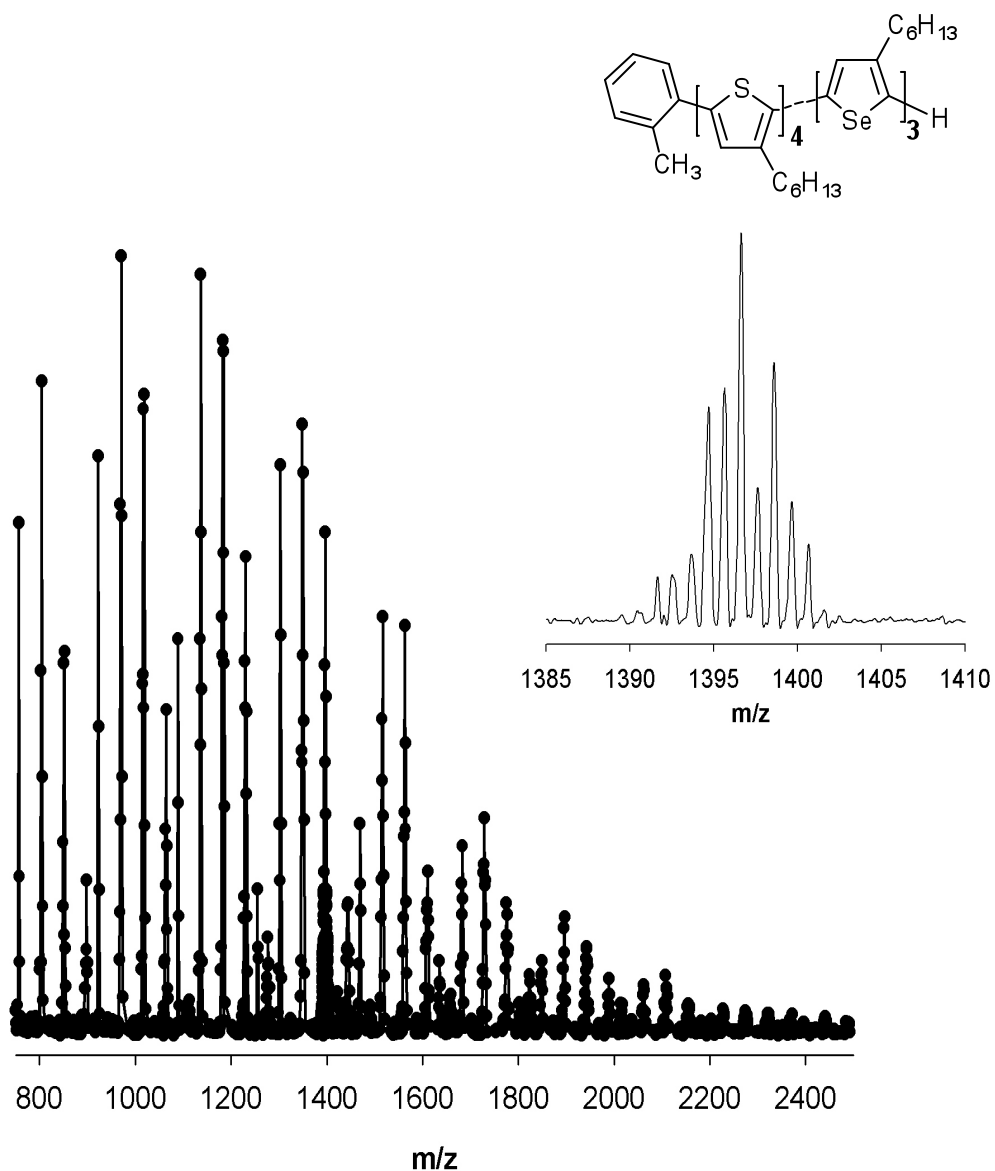
## VI. MALDI-TOF-MS Data



**Figure S17.** MALDI-TOF mass spectra of **o(3HT)**. The observed signals all contain the theoretical monoisotopic exact mass peaks,  $m/z = 92.06 + (n \cdot 166.08)$ , where  $n$  is the degree of polymerization, for the homopolymer containing tolyl/H end groups. The inset shows the isotopic distribution corresponding to the 10-mer. This observed distribution matches the theoretical distribution for the chemical formula  $\text{C}_{107}\text{H}_{148}\text{S}_{10}$ .



**Figure S18.** MALDI-TOF mass spectra of **o(3HS)**. The observed signals all contain the theoretical monoisotopic exact mass peaks,  $m/z = 92.06 + (n \cdot 213.03)$ , where  $n$  is the degree of polymerization, for the homopolymer containing tolyl/H end groups. The inset shows the isotopic distribution corresponding to the 10-mer. This observed distribution matches the theoretical distribution for the chemical formula  $C_{107}H_{148}Se_{10}$ .



**Figure S19.** MALDI-TOF mass spectra of *o*(3HT-*co*-3HS). Peaks assignments are shown in Figure S20 (page S26). The monoisotopic exact masses  $m/z = 92.06 + (166.08 \cdot n + 213.03 \cdot m)$ , where  $m$  and  $n$  are the degrees of polymerization for **1** and **2**, respectively. The inset shows the isotopic distribution corresponding to the 7-mer (where  $n = 4$  and  $m = 3$ ), containing tolyl/H end-groups. This observed distribution matches the theoretical distribution for the chemical formula  $C_{77}H_{106}S_4Se_3$ .

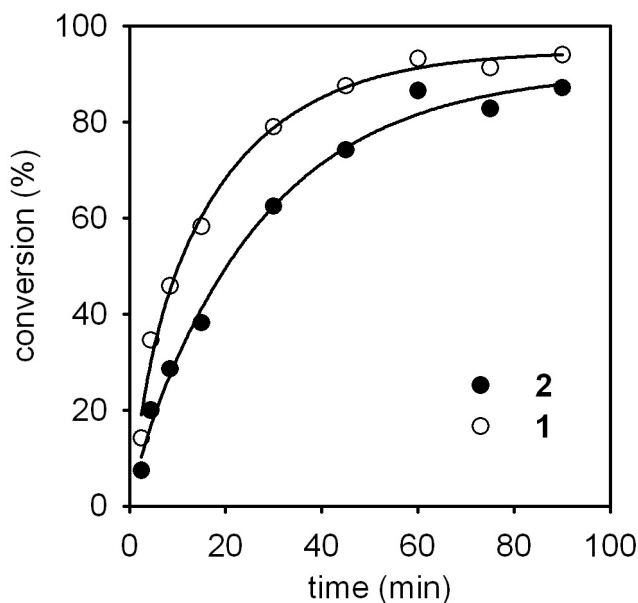




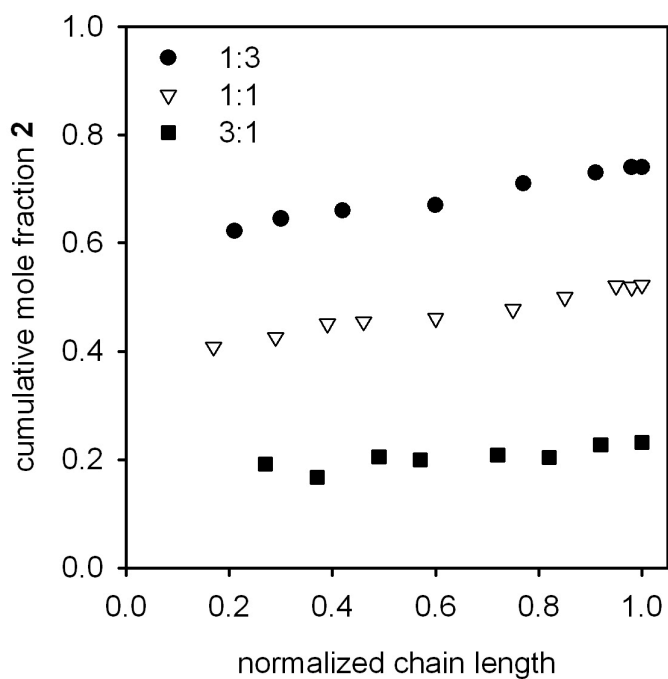
## VII. Batch Copolymerizations Procedure and Data

### *General procedure for conducting batch copolymerizations:*

An oven-dried 50 mL Schlenk flask equipped with a stir bar and a septum was evacuated and cooled under vacuum. Once cool, the flask was filled with N<sub>2</sub> and re-evacuated: this process was repeated twice and the flask was filled with N<sub>2</sub>. THF (10 mL) was added to the flask and cooled to 0 °C. **1**, **2** (see pg S6) of varying ratios ( $[1 + 2]_{\text{total}} = 0.02 \text{ M}$ ) and C<sub>22</sub>H<sub>46</sub> solution (0.5 mL, 0.2 M in THF) were added by syringe and the solution stirred for 1 min. An aliquot (~0.2 mL) was withdrawn via syringe and quenched with 5 M aq HCl (~1 mL). GC analysis afforded the initial ratio of monomer to internal standard peak areas. Then, a catalyst **3** solution was added to the reaction. Aliquots (~0.2 mL) were taken from the reaction periodically via syringe and quenched with 5 M aq HCl (~1 mL). Each aliquot was then extracted with CHCl<sub>3</sub> and the solvent removed in vacuo. The samples were then dissolved in THF (~1 mL), divided and analyzed by GC and GPC to determine the cumulative mole fraction, conversion, molecular weight and polydispersity indices. Values of cumulative mole fraction of **2** shown in Figure S22 are based on the conversion data. Analysis of representative aliquots by <sup>1</sup>H NMR gave the same cumulative mole fraction, and GC conversion data were used because the experiment is more facile.



**Figure S21.** Plot of monomer conversion versus time for the copolymerization of **1** and **2** with catalyst **3** at 0 °C in THF. The comonomer mole ratio was ~1:1.



**Figure S22.** Plot of the cumulative mole fraction of **2** in the copolymer versus the normalized chain length for a series of batch copolymerizations in which the initial feed ratios of **2:1** = 1:3, 1:1, and 3:1. The normalized chain length =  $DP/DP_{\text{final}}$ .

**Table S5.** Data plotted in Fig. SX

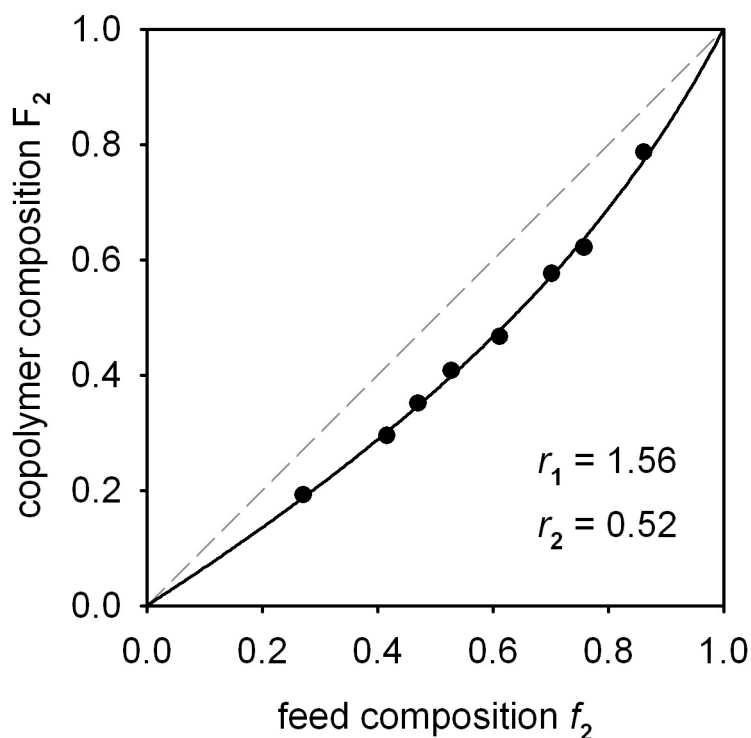
ratio 2:1	cuml.mol fraction 2	norm. chain length
1:3	0.622	0.20
	0.645	0.30
	0.661	0.41
	0.673	0.59
	0.712	0.77
	0.727	0.91
	0.744	1.00
	0.740	0.98
	0.740	0.98
1:1	0.408	0.16
	0.426	0.28
	0.451	0.38
	0.455	0.45
	0.461	0.59
	0.478	0.74
	0.500	0.85
	0.519	0.98
	0.523	1.00
3:1	0.192	0.27
	0.167	0.37
	0.205	0.49
	0.200	0.57
	0.208	0.72
	0.204	0.82
	0.227	0.92
	0.232	1.00

## VIII. Reactivity Ratios

*General procedure for determining reactivity ratios:*

A series of batch copolymerizations were carried out as described on page S27, with various initial feed compositions of the two comonomers. The cumulative mole fraction of **2** in the copolymer ( $F_2$ ) at low conversion (~10%) was plotted versus the initial mole fraction of comonomer **2** in the feed ( $f_2$ ). These data were then fit to the Mayo-Lewis copolymerization equation (eq 1) by a non-linear least-squares regression in SigmaPlot 10.

$$F_2 = \frac{r_2 f_2^2 + f_2(1 - f_2)}{r_2 f_2^2 + 2f_2(1 - f_2) + r_1(1 - f_2)^2} \quad (\text{eq 1})$$



**Figure S22.** Plot of the thiophene mole fraction in the copolymer ( $F_2$ ) versus the mole fraction of **2** in the feed ( $f_2$ ) for a series of batch copolymerizations with various initial comonomer feed compositions. The best fit with the Mayo-Lewis equation was obtained where  $r_1 = 1.56 \pm 0.08$  and  $r_2 = 0.52 \pm 0.03$ .

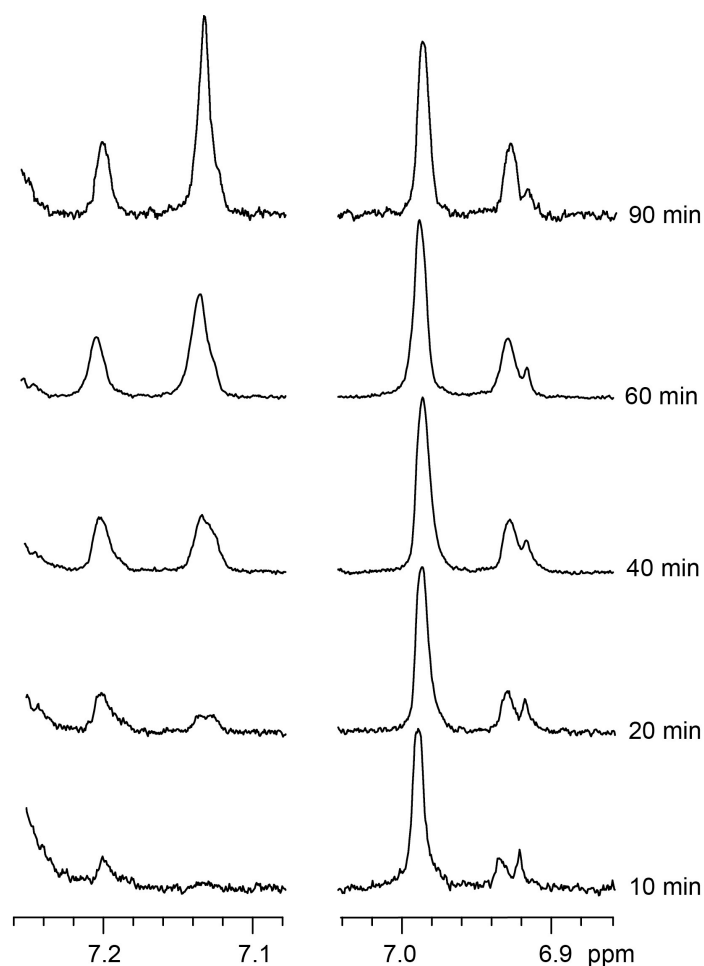
**Table S6.** Data plotted in Figure S22.

$f_2$	$F_2$
0.272	0.192
0.416	0.295
0.470	0.351
0.528	0.408
0.612	0.467
0.702	0.576
0.758	0.622
0.862	0.787

## IX. Semi-Batch Copolymerization Procedures and Data

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

A 50 mL Schlenk flask equipped with a stir bar and three-way adapter equipped with a septum was evacuated and cooled under vacuum. Once cool, the flask was filled with N<sub>2</sub> and re-evacuated: this process was repeated twice and the flask filled with N<sub>2</sub>. THF (10 mL) was added to the flask and cooled to 0 °C. Monomer **2** (15 mL, 0.01M) and C<sub>22</sub>H<sub>46</sub> solution (0.1 mL, 0.1 M) were added by syringe and the solution stirred for 1 min. Then **1** (3 mL, 0.05 M) was taken up into a syringe, the needle was inserted through the three-way adapter and the syringe placed in a syringe pump. Then catalyst **3** (0.6 mL, 5 mM) was added to the reaction and the syringe pump was activated to deliver 0.04 mL/min. Aliquots (~0.2 mL) were taken from the reaction via syringe 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 GPC analysis. The remaining portions of each aliquot were then precipitated from MeOH (4 mL). The precipitate was then collected, dried under vacuum and taken up in CDCl<sub>3</sub> for <sup>1</sup>H NMR analysis to determine the mole fraction of **1** in the copolymer.



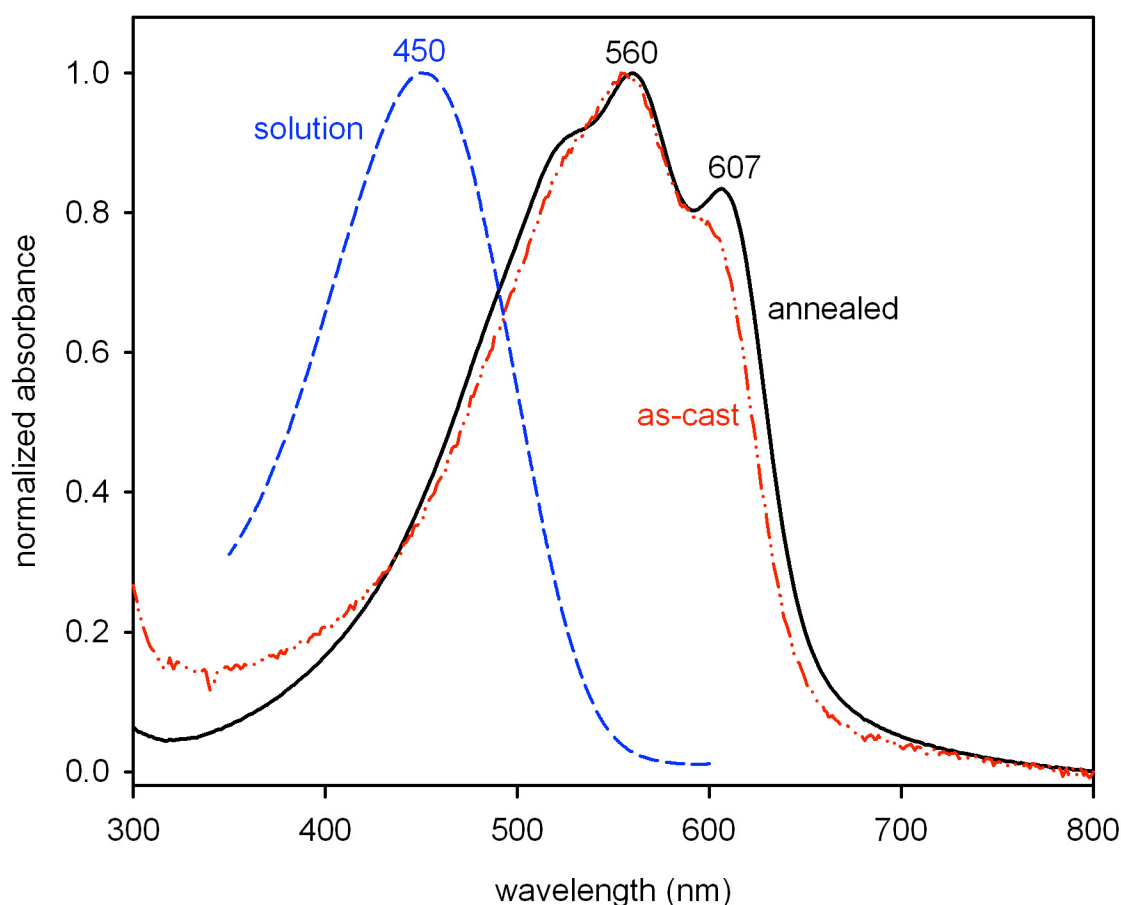
**Figure S23.** Representative <sup>1</sup>H NMR spectra in the aromatic region for successive aliquots drawn during the semi-batch polymerization procedure. The relative peak integrated areas corresponding to repeat units of **1** and **2** are then plotted versus the normalized chain length (by GPC).

## X. UV/Vis Spectra

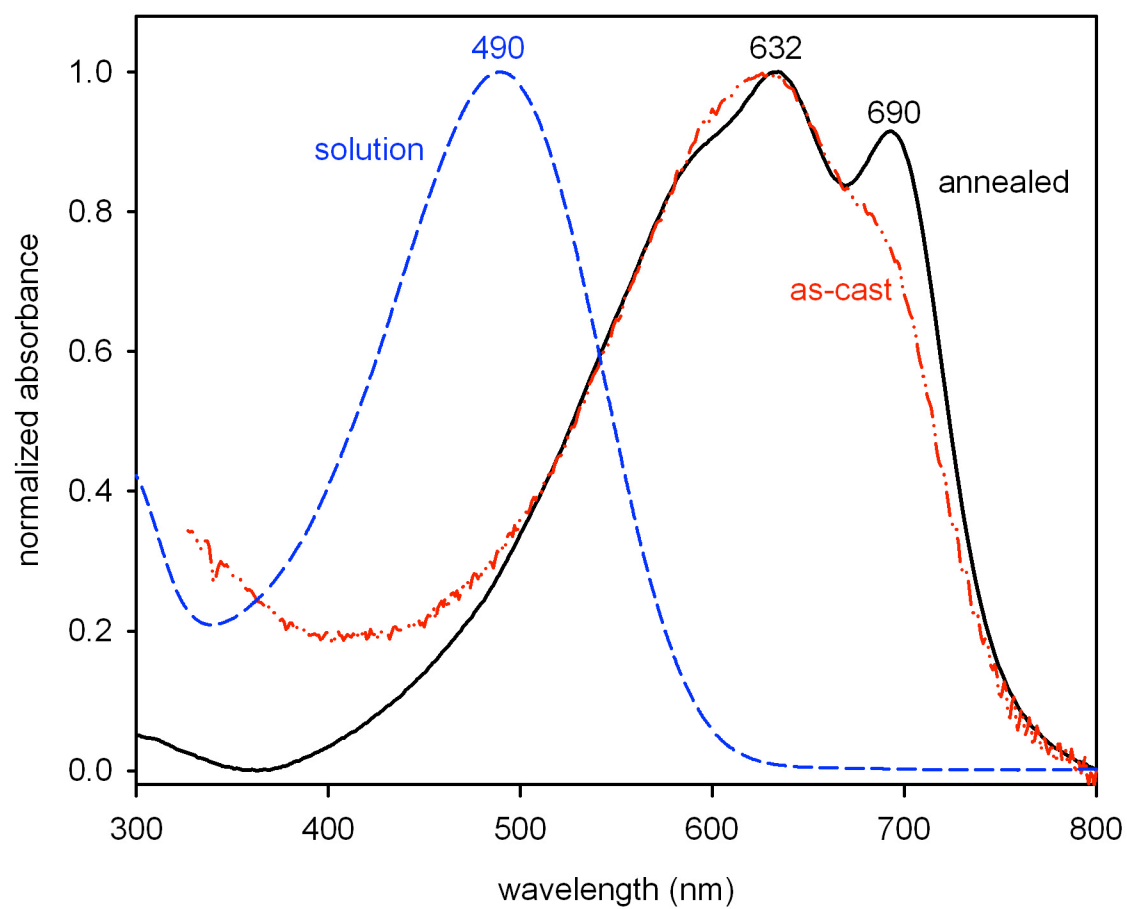
*Solution:* Polymer solutions in chloroform were diluted to 10  $\mu\text{M}$  in quartz cuvettes and steady state absorbance was taken from 300-600 nm after background subtraction.

*As-cast:* Polymer samples (~5 mg) were dissolved in chlorobenzene upon heating, filtered through a 0.2  $\mu\text{m}$  PTFE filter onto a glass slide, and spin-coated at 1000 rpm for 1 min. The glass slides were previously rinsed with methanol dried with a heat gun and cooled under a stream of nitrogen. The films were mounted in a spectrophotometer and absorbance collected from 300-800 nm after background subtraction.

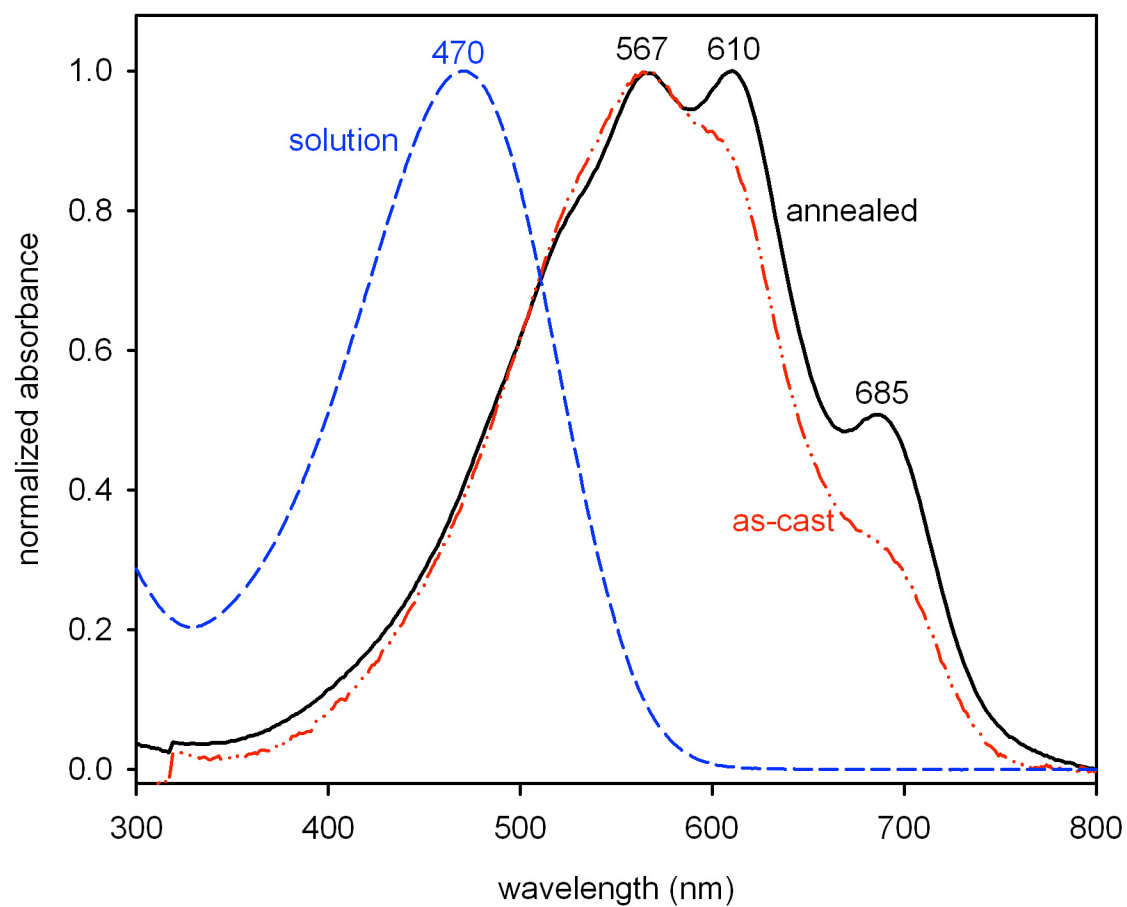
*Annealed:* The thin films were placed in a vacuum oven and the pressure was reduced to 0.04 torr. The oven was heated to 280  $^{\circ}\text{C}$ , cooled to 220  $^{\circ}\text{C}$  and held for 1 hr before gradual cooling to rt. The oven was then refilled with nitrogen and the samples analyzed by UV-vis.



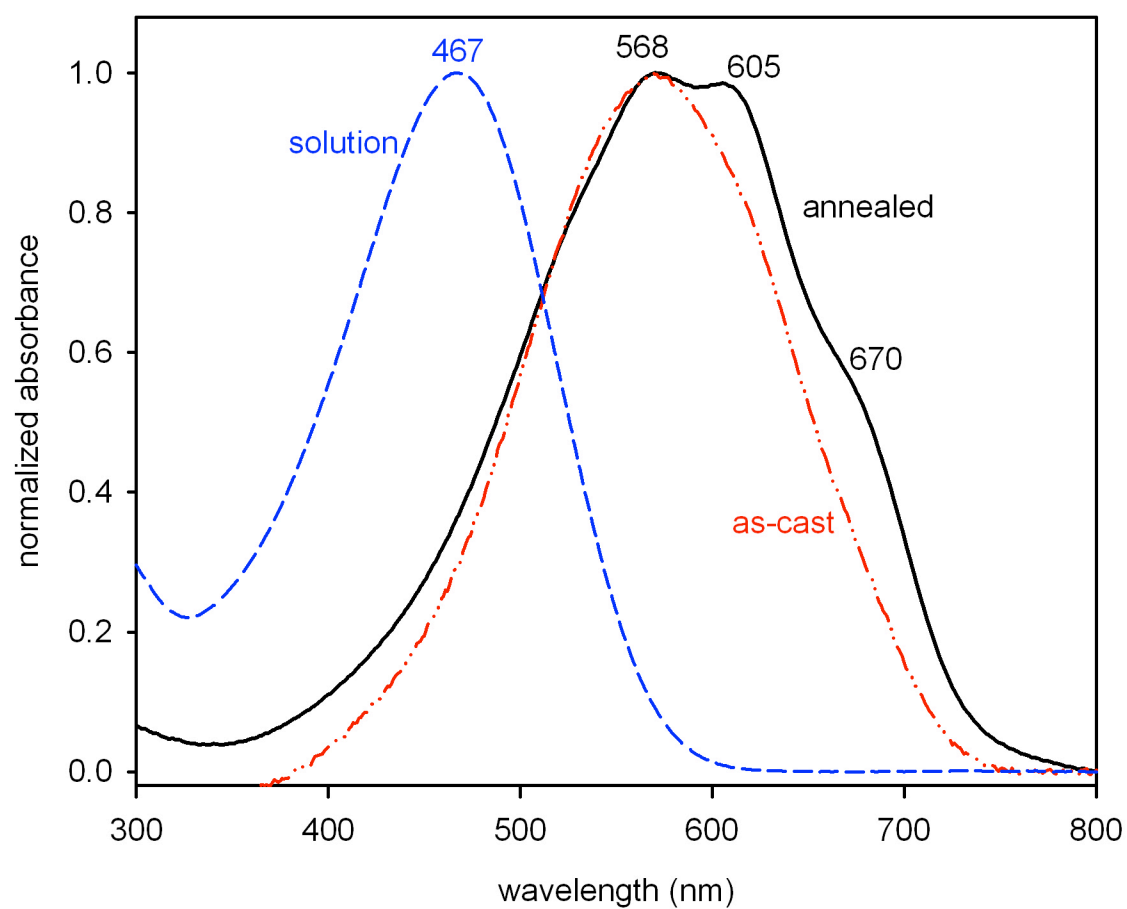
**Figure S24.** UV-vis absorbance spectra of the homopolymer **P3HT** in  $\text{CHCl}_3$  (blue dashed line), and in the thin film as-cast (red dotted-dashed line) and after isothermal recrystallization (solid line).



**Figure S25.** UV-vis absorbance spectra of the homopolymer **P3HS** in  $\text{CHCl}_3$  (blue dashed line), and in the thin film as-cast (red dotted-dashed line) and after isothermal recrystallization (solid line).

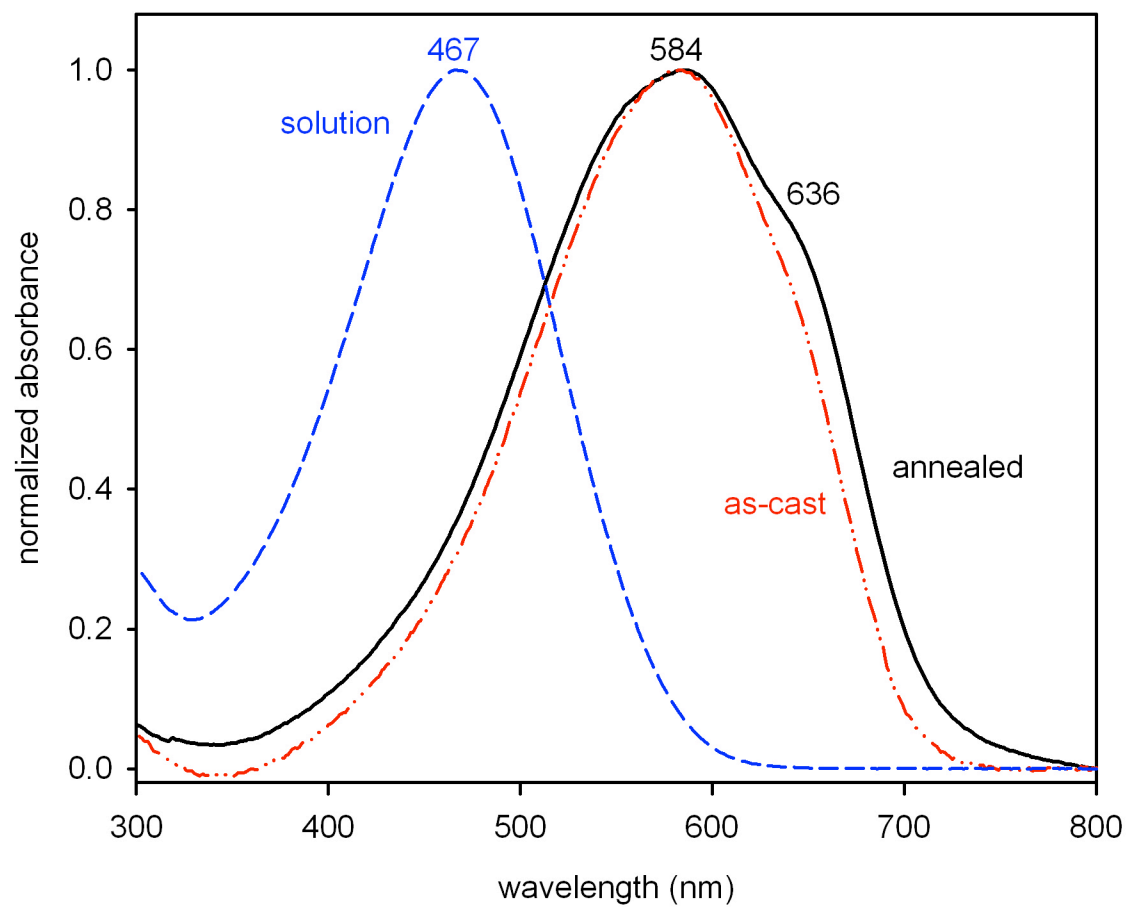


**Figure S26.** UV-vis absorbance spectra of the **block** copolymer in  $\text{CHCl}_3$  (blue dashed line), and in the thin film as-cast (red dotted-dashed line) and after isothermal recrystallization (solid line).

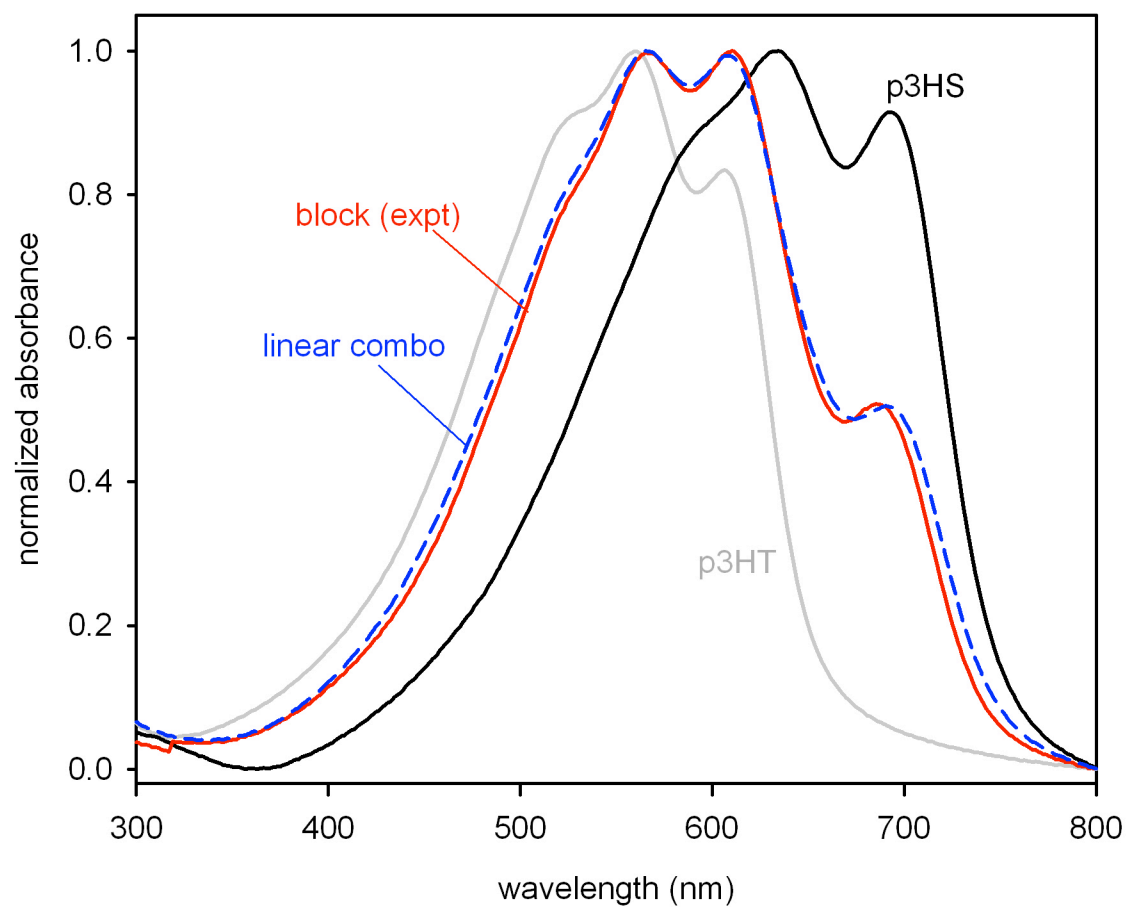


**Figure S27.** UV-vis absorbance spectra of the **gradient** copolymer in  $\text{CHCl}_3$  (blue dashed line), and in the thin film as-cast (red dotted-dashed line) and after isothermal recrystallization (solid line).





**Figure S28.** UV-vis absorbance spectra of the **random** copolymer in  $\text{CHCl}_3$  (blue dashed line), and in the thin film as-cast (red dotted-dashed line) and after isothermal recrystallization (solid line).

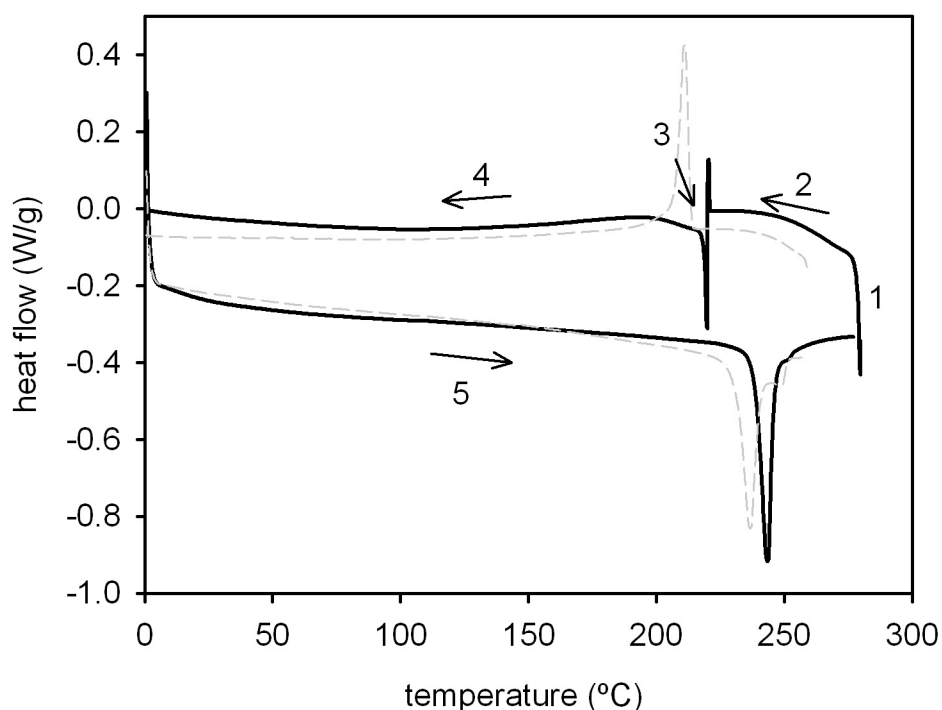


**Figure S29.** Comparison of UV-vis absorbance spectra for the block copolymer (red) with the corresponding homopolymers P3HT (grey) and P3HS (black), each after isothermal recrystallization. The linear combination (blue dotted line) of the spectra for P3HT and P3HS closely matches the observed spectra of the block copolymer.

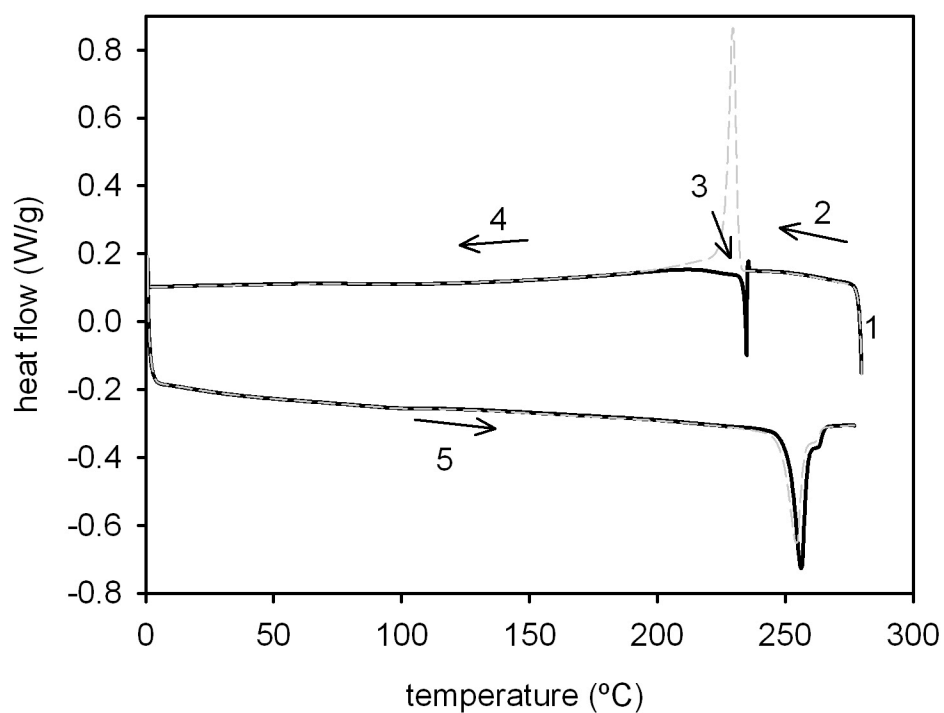
## XI. Differential Scanning Calorimetry (DSC)

Samples (2-5 mg) were sealed in aluminum pans as described on page S2. DSC scans for each polymer were then performed using the following protocol. Thermograms are shown with black lines in the figures S30-S34, with each step labeled. The dashed grey line in the figures are the thermograms with non-isothermal crystallization exotherms observed.

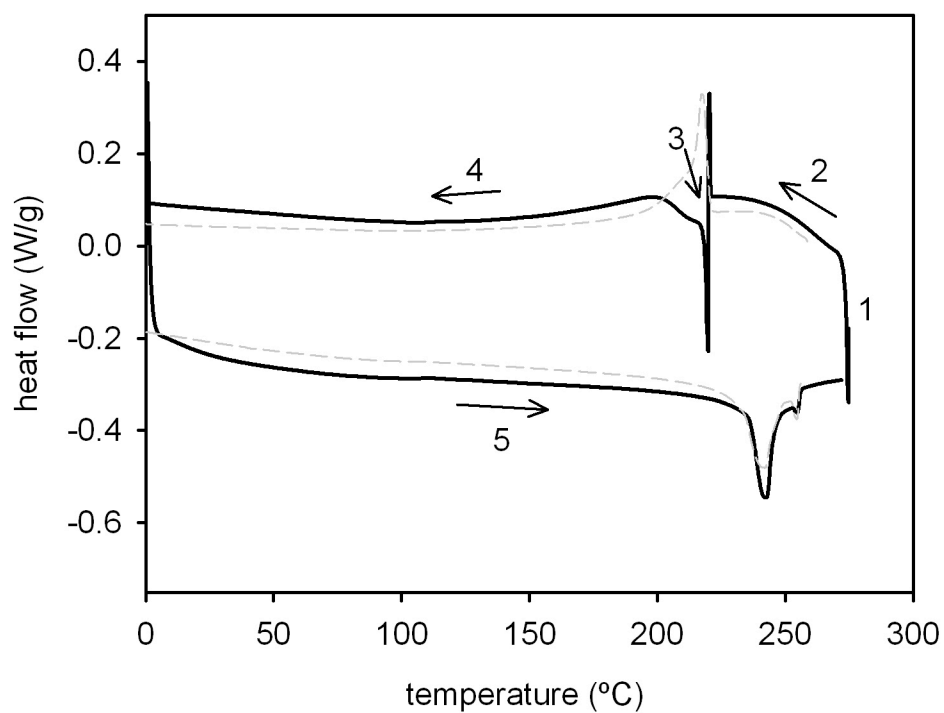
1. Equilibrate at 280 °C
2. Ramp temperature to 220 °C (230 °C for p3HS) at 10 °C/min
3. Isothermal at 220 °C (230 °C for p3HS) for 1 h
4. Ramp temperature to 0 °C at 10 °C/min
5. Ramp temperature to 280 °C at 10 °C/min



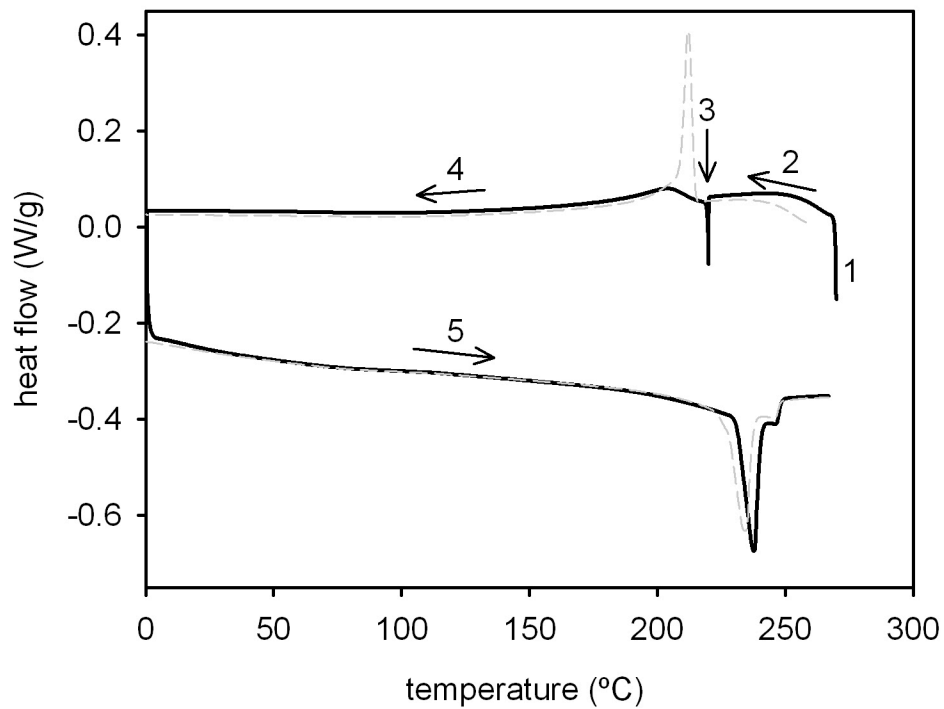
**Figure S30.** DSC thermogram for the **P3HT** homopolymer.  $T_m = 243$  °C.  $\Delta H_m = 26$  J/g (~70% degree of crystallinity<sup>2</sup>).



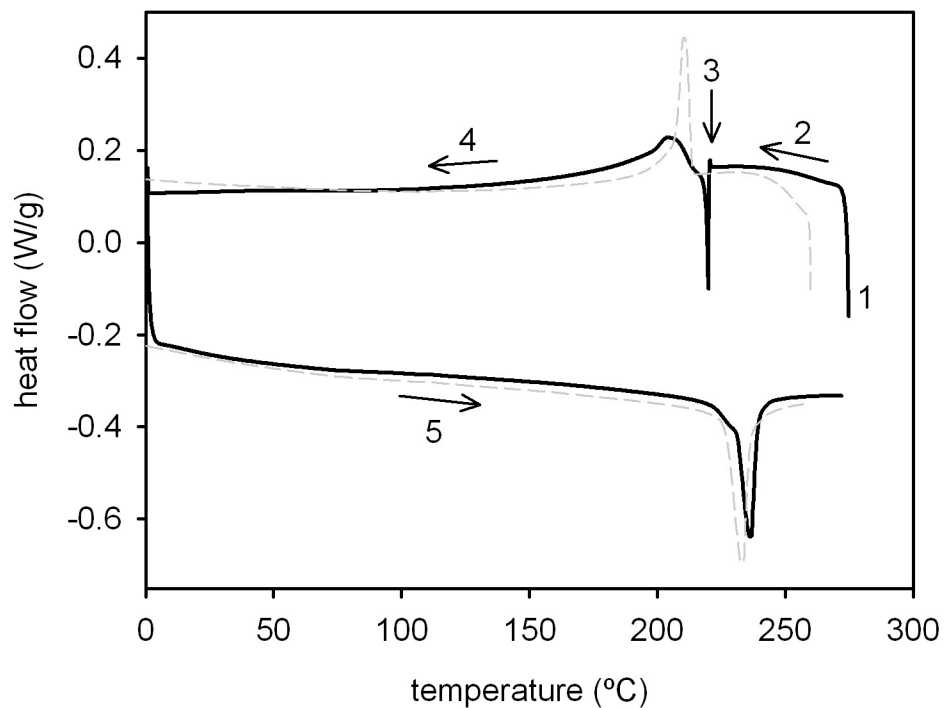
**Figure S31.** DSC thermogram of the **P3HS** homopolymer.  $T_m = 256\text{ °C}$ .  $\Delta H_m = 18\text{ J/g}$ .



**Figure S32.** DSC thermogram of the **block** copolymer.  $T_m = 242\text{ °C}$ .  $\Delta H_m = 20\text{ J/g}$ .

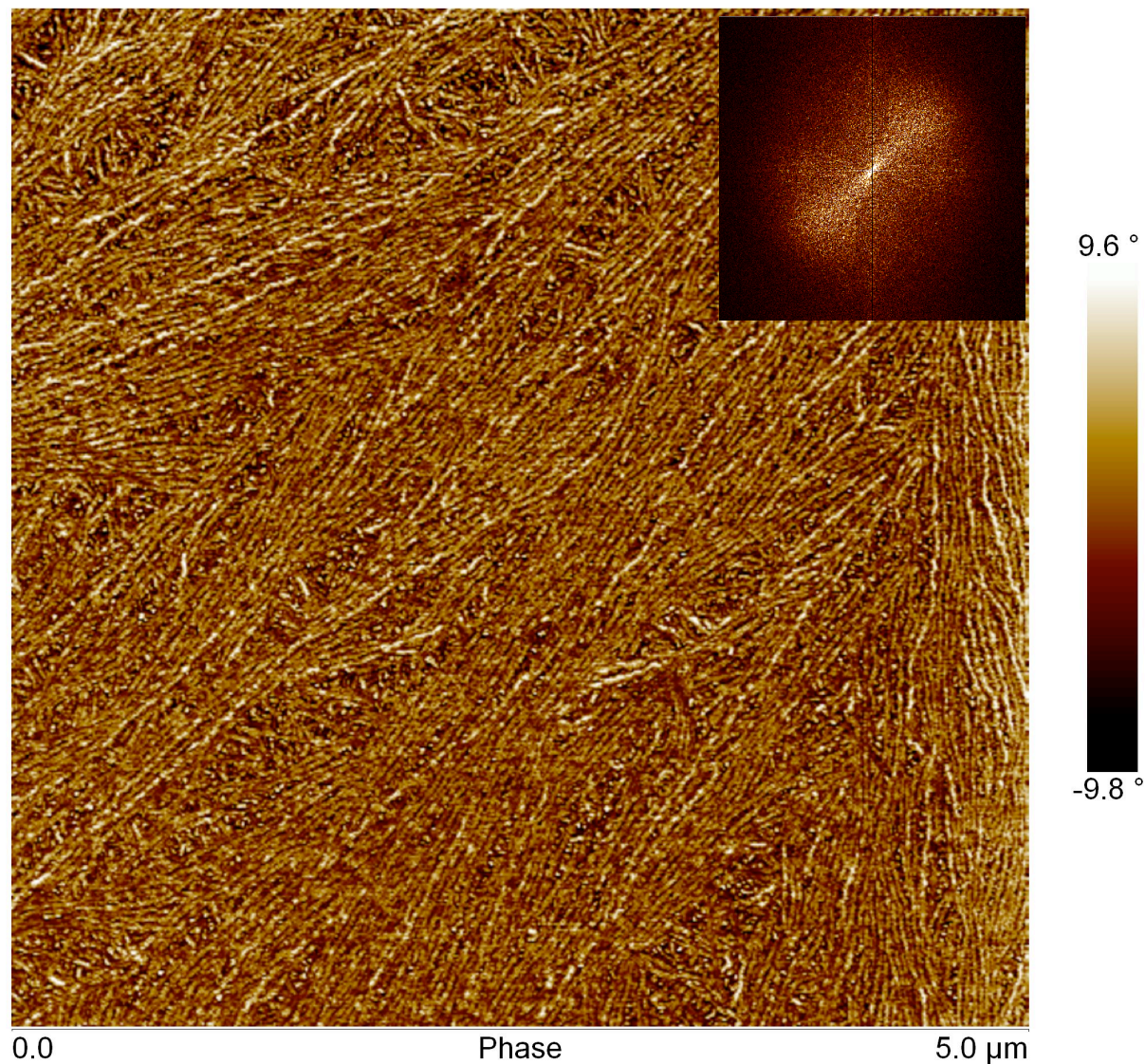


**Figure S33.** DSC thermogram of the **gradient** copolymer.  $T_m = 238\text{ }^{\circ}\text{C}$ .  $\Delta H_m = 18\text{ J/g}$ .



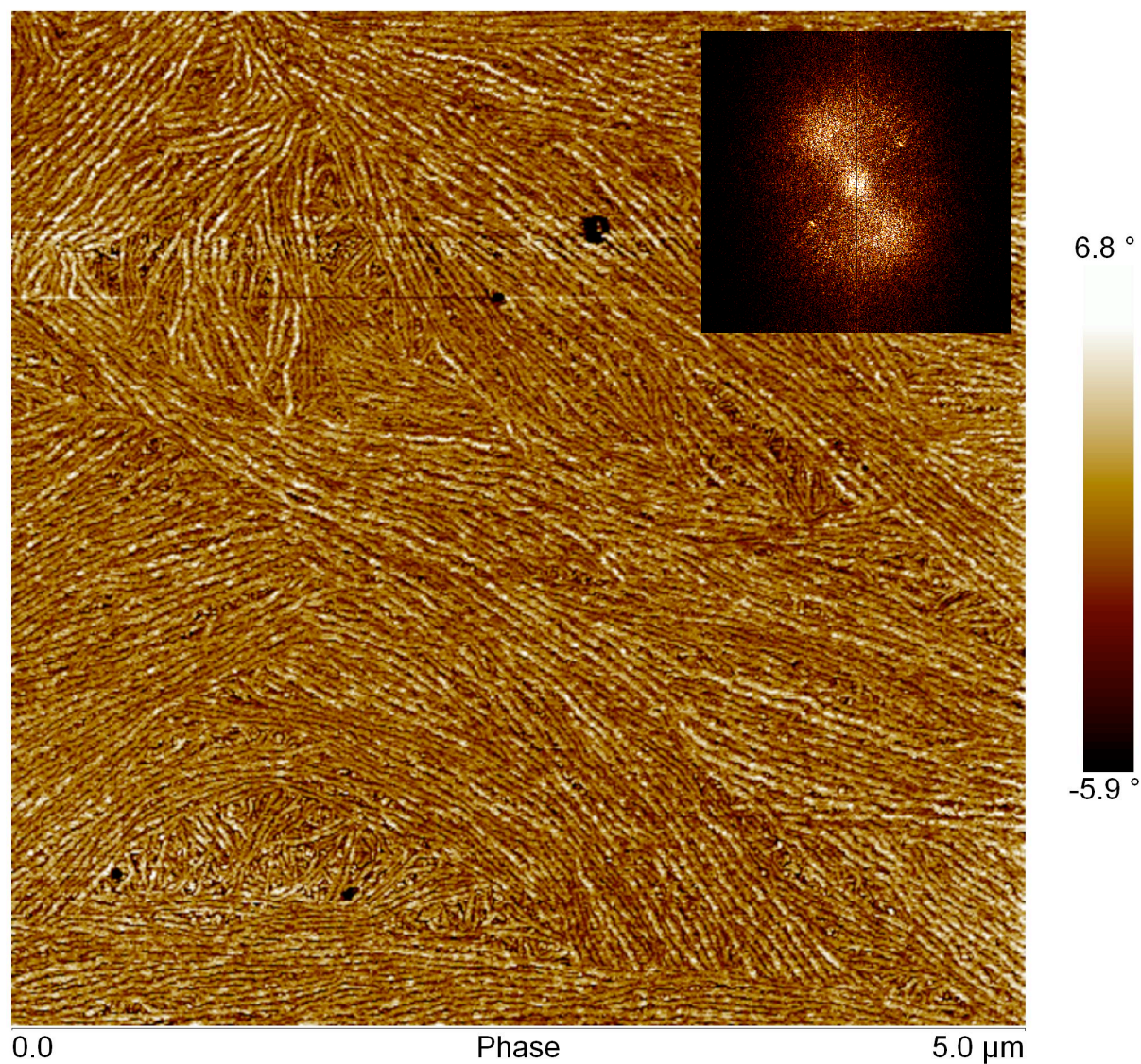
**Figure S34.** DSC thermogram of the **random** copolymer.  $T_m = 236\text{ }^{\circ}\text{C}$ .  $\Delta H_m = 16\text{ J/g}$ .

## XII. Atomic Force Microscopy (AFM) Phase Images



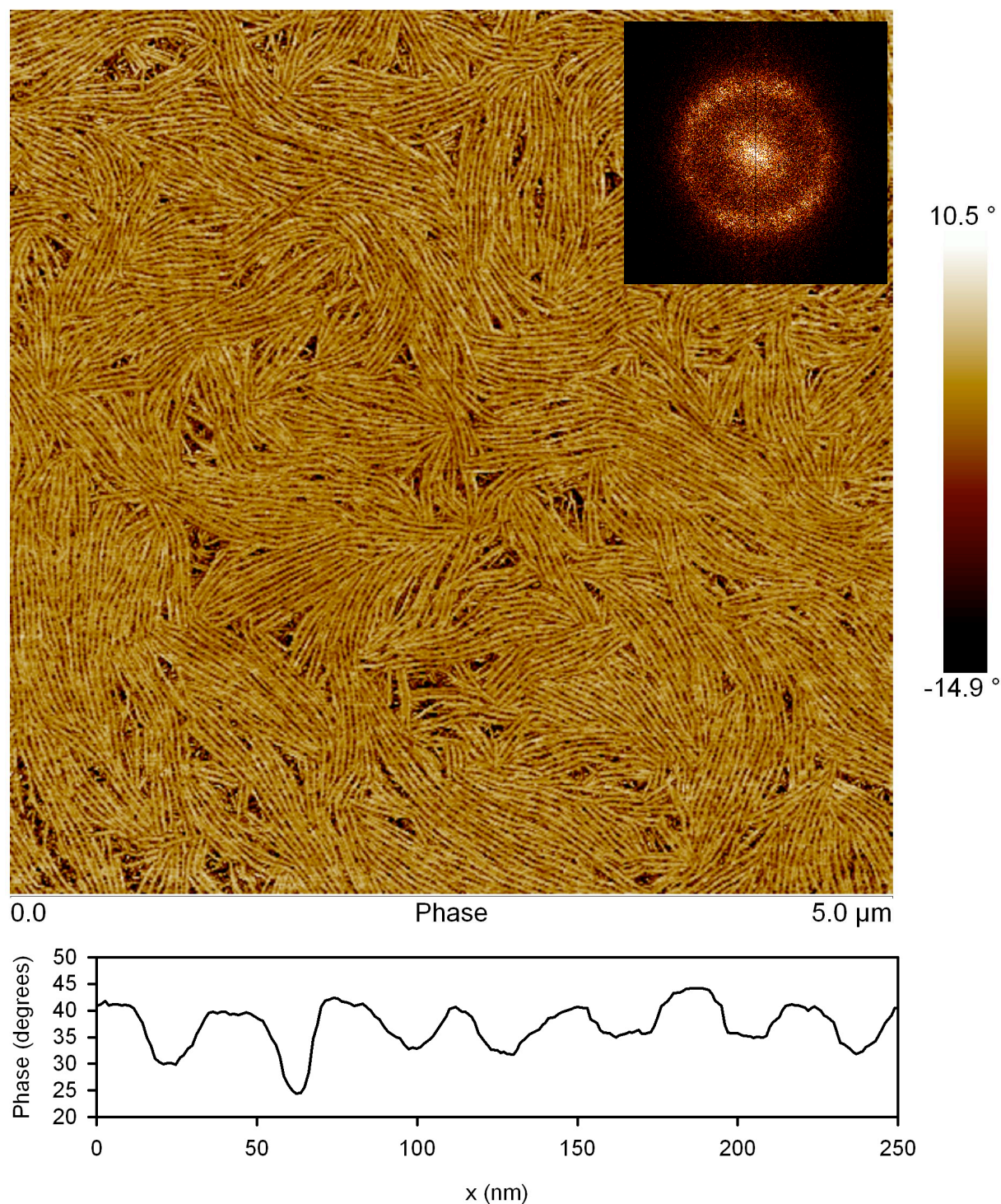
**Figure S35.** Atomic Force Microscopy (AFM) phase image of the homopolymer **p3HT** (as described in general experimental on page S2). Scans were collected in the horizontal direction at a scan rate of 0.5 Hz, with 512 pixels per scan. The inset shows the Fourier transform of the phase image.





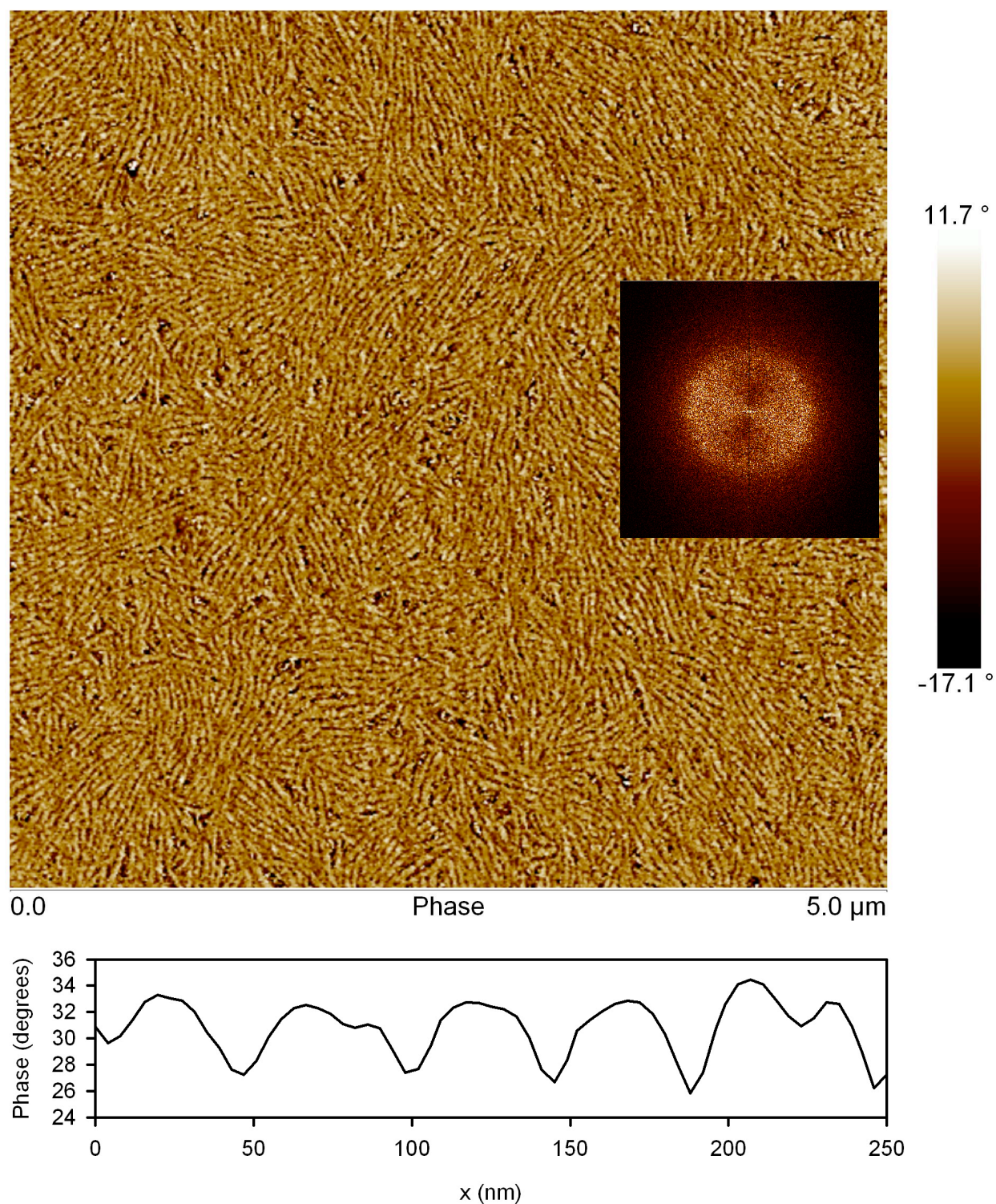
**Figure S36.** Atomic Force Microscopy (AFM) phase image of the homopolymer **p3HS** (as described in general experimental on page S2). Scans were collected in the horizontal direction at a scan rate of 0.5 Hz, with 512 pixels per scan. The inset shows the Fourier transform of the phase image.





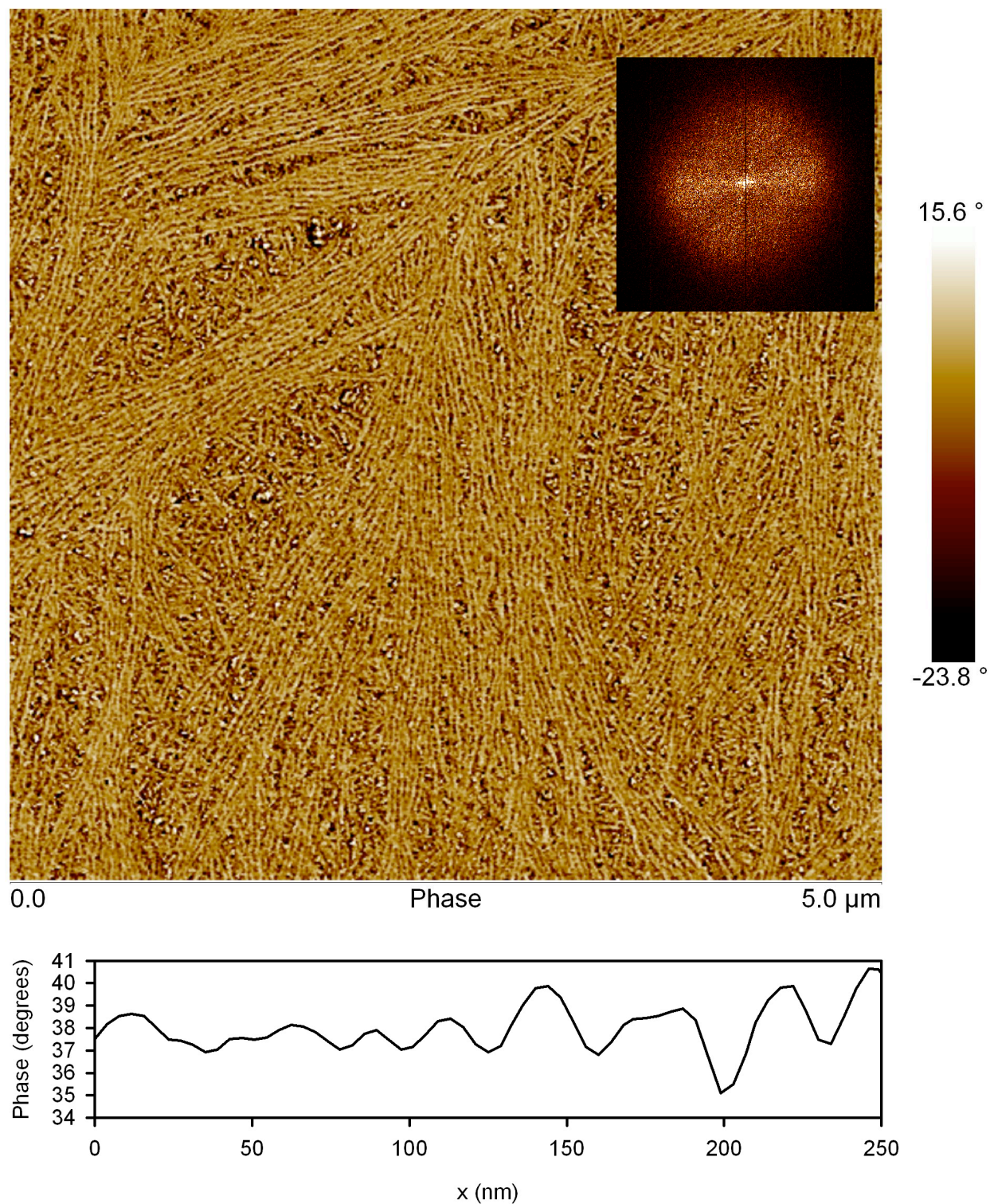
**Figure S37.** Atomic force microscopy (AFM) phase image of the **block** copolymer after isothermal recrystallization (as described in general experimental on page S2). Scans were collected in the horizontal direction at a scan rate of 0.5 Hz, with 512 pixels per scan. The inset shows the Fourier transform of the phase image. Below the image is a side profile taken across a series of adjacent fibers, perpendicular to the fiber direction.





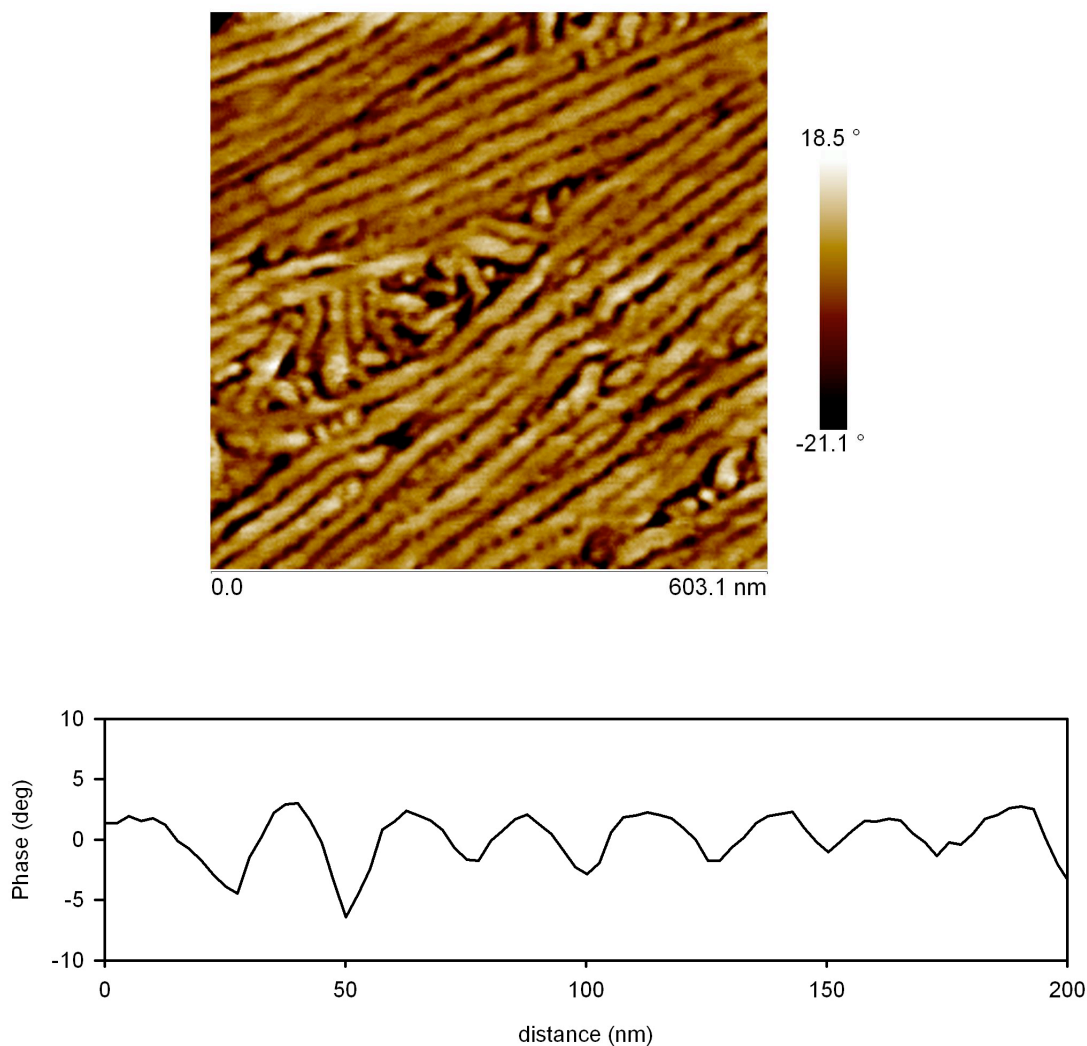
**Figure S38.** Atomic force microscopy (AFM) phase image of the **gradient** copolymer after isothermal recrystallization (as described in general experimental on page S2). Scans were collected in the horizontal direction at a scan rate of 0.5 Hz, with 512 pixels per scan. The inset shows the Fourier transform of the phase image. Below the image is a side profile taken across a series of adjacent fibers, perpendicular to the fiber direction.





**Figure S39.** Atomic force microscopy (AFM) phase image of the **random** copolymer after isothermal recrystallization (as described in general experimental on page S2). Scans were collected in the horizontal direction at a scan rate of 0.5 Hz, with 512 pixels per scan. The inset shows the Fourier transform of the phase image. Below the image is a side profile taken across a series of adjacent fibers, perpendicular to the fiber direction.

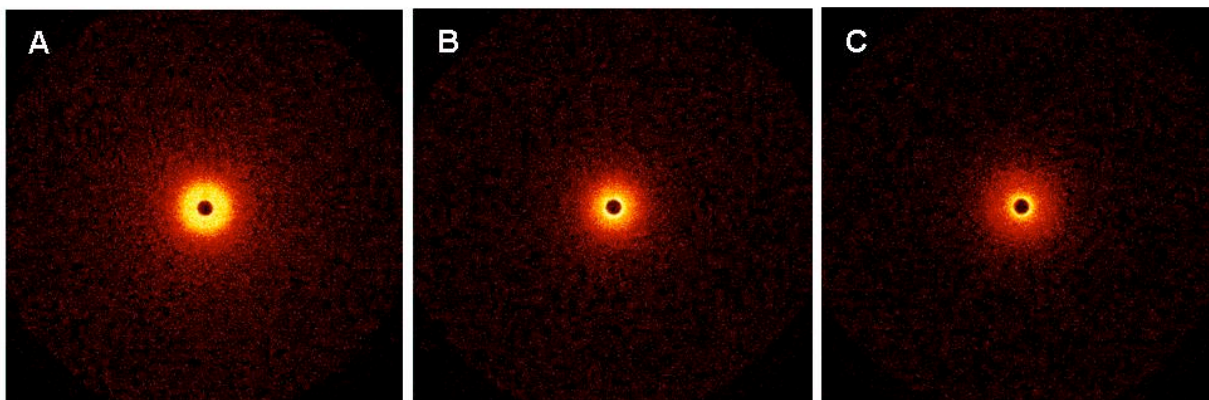
The lower MW gradient copolymer synthesized at 0 °C (GPC:  $M_n = 14.4$  kDa, PDI = 1.10) was also spin-cast and isothermally recrystallized, according to the same procedure described above. The AFM phase image of this thin film is shown below. As expected, the lamellar period is shorter than for the high MW polymers (~20-25 nm).



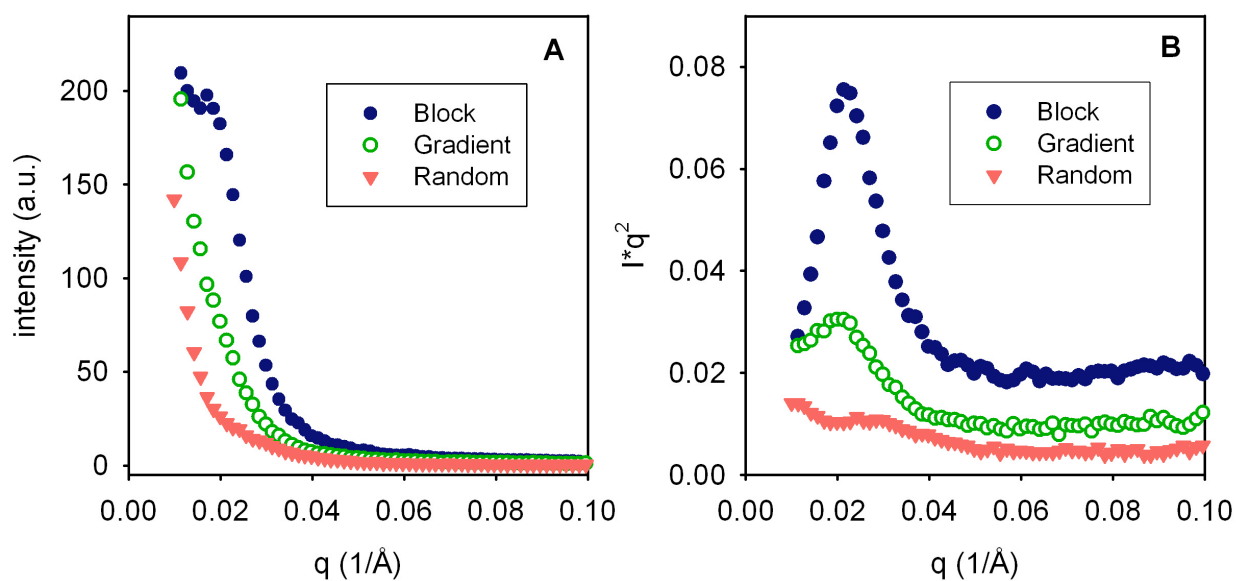
**Figure S40.** Atomic force microscopy (AFM) phase image of the **low MW gradient** copolymer after isothermal recrystallization (as described in general experimental on page S2). Scans were collected in the horizontal direction at a scan rate of 0.5 Hz, with 256 pixels per scan. Below the image is a side profile taken across a series of adjacent fibers, perpendicular to the fiber direction.



### XIII. Small Angle X-ray Scattering



**Figure S41.** Raw data for the SAXS in transmission mode through bulk pellet of the (A) block, (B) gradient, and (C) random copolymer after melt casting and isothermal recrystallization.



**Figure S42.** (A) Plot of scattered X-ray intensity versus the scattering vector  $q$  for the bulk copolymers and (B) plot of the Lorenz-corrected scattering intensities  $Iq^2$  versus  $q$ .

### References

- <sup>1</sup> Hollinger, J.; DiCarmino, P. M.; Karl, D.; Seferos, D. S. *Macromolecules* **2012**, *45*, 3772–3778.
- <sup>2</sup> Kohn, P.; Huettner, S.; Komber, H.; Senkovskyy, V.; Tkachov, R.; Kiri, A.; Friend, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 4790–4805.