

## Supporting Information

# Facile Synthesis of ABA Triblock Copolymer Containing Regioregular Poly(3-Hexylthiophene) and Polystyrene Segments via Linking Reaction of Poly(styryl)lithium

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### Experimental

**Materials.** All reagents were purchased from Sigma-Aldrich Corp. (>99%) and used as received unless otherwise stated. Tetrahydrofuran (THF, 99.5%, Wako Chemicals Co., Ltd.) for the GRIM polymerization was refluxed over sodium benzophenone under N<sub>2</sub> for 2 h, then distilled just before use. Benzene (99%) was washed with concentrated sulfuric acid twice, distilled water once, 5% aqueous sodium hydroxide (NaOH) twice, and then distilled water twice. It was pre-dried over calcium chloride and then over phosphorous pentoxide. Finally, it was distilled from 1,1-diphenylhexyllithium (DPHLi) on a high vacuum line (10<sup>-6</sup> Torr). *sec*-Butyllithium (*sec*-BuLi, 1.3 M in cyclohexane) was used after diluting with dry heptane distilled from DPHLi. Styrene (>99%) was washed with 5% aqueous NaOH and distilled water three times, then dried over magnesium sulfate overnight. After the filtration, it was

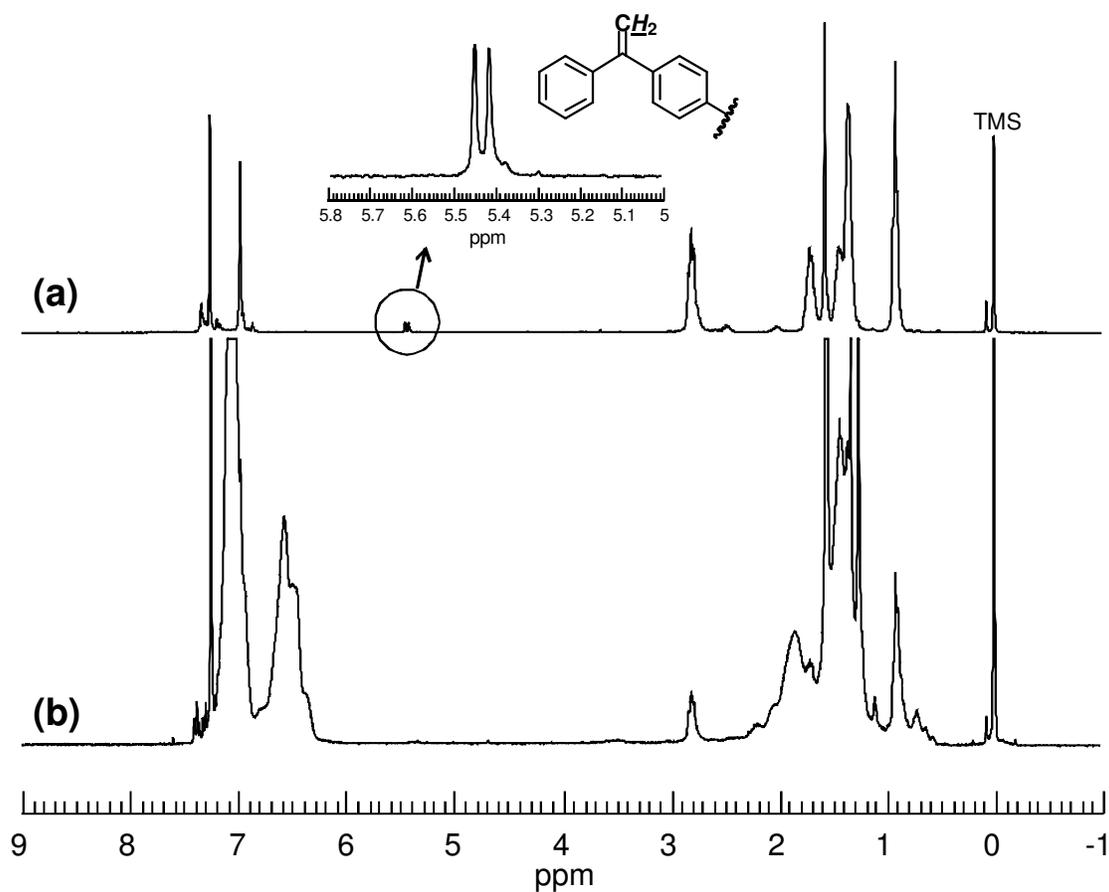
pre-distilled from calcium hydride under the reduced pressure, and then distilled from 5% dibutylmagnesium on the vacuum line. It was stored at  $-30\text{ }^{\circ}\text{C}$  in sealed glass ampoules with breakseals after diluting with dry benzene. 2-Bromo-3-hexyl-5-iodothiophene<sup>1</sup> and 1-[4-(3-bromopropyl)phenyl]-1-phenylethylene<sup>2</sup> were synthesized according to the previous papers.

**Synthesis of  $\alpha,\omega$ -Ends DPE-Functionalized P3HT (1).** Isopropylmagnesium chloride (2.0 M in THF, 0.477 mL, 0.954 mmol) was added to a dry THF solution (18 mL) of lithium chloride (0.120 g, 2.83 mmol) and 2-bromo-3-hexyl-5-iodothiophene (0.324 g, 0.867 mmol) at  $0\text{ }^{\circ}\text{C}$ . Then, a suspension of [1,3-bis(diphenylphosphino)propane]nickel(II) dichloride ( $\text{Ni}(\text{dppp})\text{Cl}_2$ ) (0.016 g, 0.0295 mmol) in dry THF (5.0 mL) was added to the mixture and stirred at room temperature for 10 min. The monomer conversion was found to be 95% by comparing the peak areas of polymer and monomer in the GPC trace. Finally, a THF solution (1.5 mL) of a mixture of 1-hexene (0.009 mL, 0.0720 mmol) and 1-[4-(3-bromomagnesiopropyl)phenyl]-1-phenylethylene which was prepared by magnesium (50 mg, 2.06 mmol) and 1-[4-(3-bromopropyl)phenyl]-1-phenylethylene (0.100g, 0.332 mmol) was *in-situ* added to the polymerization solution and stirred for 30 min. Then, 5N-HCl was added for quenching, followed by pouring the solution into methanol/water (200 mL/100 mL) to precipitate the polymer. The polymer was purified by Soxhlet extraction using methanol, acetone, and chloroform, followed by freeze-drying from its absolute benzene solution three times under the high vacuum condition ( $10^{-6}$  Torr) to afford  $\alpha,\omega$ -ends DPE-functionalized P3HT as a purple solid (**1**, 0.110 g, 70%).

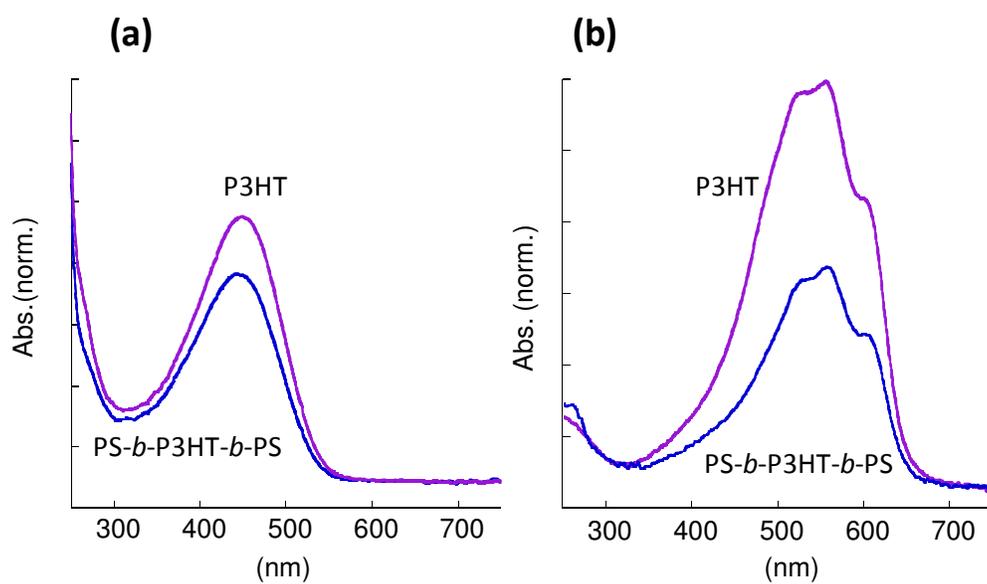
**Synthesis of PS-*b*-P3HT-*b*-PS.** The block copolymer was synthesized by using a standard high vacuum technique. A benzene solution (2.8 mL) of styrene (0.799 g, 7.67 mmol) was added to *sec*-BuLi (0.136 mmol) and stirred at room temperature for 2 h. A one-third portion of the solution was added to a benzene solution (7 mL) of **1** (0.073 g, 0.0104 mmol). After reacting at  $40\text{ }^{\circ}\text{C}$  for 24 h, the solution was poured into a mixture of methanol/water (90 mL/10 mL) to precipitate the polymer. The polymer was purified by fractional precipitation using cyclohexane/hexane several times to afford PS-*b*-

P3HT-*b*-PS as a purple solid (0.108 g, 55%).

**Measurements.** Molecular weights (MWs) and polydispersity indices (PDIs) were measured by GPC on a Jasco GULLIVER 1500 equipped with a pump, an absorbance detector (UV,  $\lambda = 254$  nm), and three polystyrene gel columns based on a conventional calibration curve using polystyrene standards. Chloroform was used as a carrier solvent at a flow rate of 1.0 mL/min at room temperature. Absolute MWs were measured with a HPLC system equipped with a pump, refractometer (RI), absorbance detector (UV,  $\lambda = 254$  nm), online right angle laser light scattering (RALLS) detector ( $\lambda = 670$  nm), sample processor, and polystyrene gel columns connected in the following series: 650, 200, and 75 Å. THF was used as a carrier solvent at a flow rate of 1.0 mL/min at room temperature.  $^1\text{H}$  NMR was recorded on a Bruker DPX (300 MHz) in chloroform-*d* calibrated to tetramethylsilane as an internal standard ( $\delta_{\text{H}}$  0.00). Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF MS) spectra were recorded on a Shimadzu AXMA-CFR mass spectrometer. The spectrometer was equipped with a nitrogen laser (337 nm) and with pulsed ion extraction. The operation was performed at an accelerating potential of 20 kV by linear-positive ion mode. A 10  $\mu\text{L}$  of the sample polymer solution in THF (5 mg/mL) and a 100  $\mu\text{L}$  of the matrix, 2,2':5'2''-terthiophene (Aldrich) solution in THF (75 mg/mL) were well mixed. A 1  $\mu\text{L}$  aliquot of the final solution was deposited onto a sample target plate and dried in air at room temperature. Mass values were calibrated by the three-point method with insulin plus  $\text{H}^+$  at  $m/z$  5734.62, insulin  $\beta$  plus  $\text{H}^+$  at  $m/z$  3497.96, and  $\alpha$ -cyanohydroxycinnamic acid dimer plus  $\text{H}^+$  at  $m/z$  379.35. Differential scanning calorimetry (DSC) was performed with a Seiko EXSTAR 6000 DSC 6200. The samples were heated at 20  $^\circ\text{C}/\text{min}$  under nitrogen and the second thermograms were recorded. Calibrations were made using indium as a standard. Ultraviolet-visible (UV-vis) absorption spectra of polymer solution in chloroform and thin films were recorded on a Jasco FP-750 spectrometer over a wavelength range of 250–800 nm. Atomic force microscopy (AFM) phase images were taken with a SIT-NT SPA 400 operating in a tapping mode.

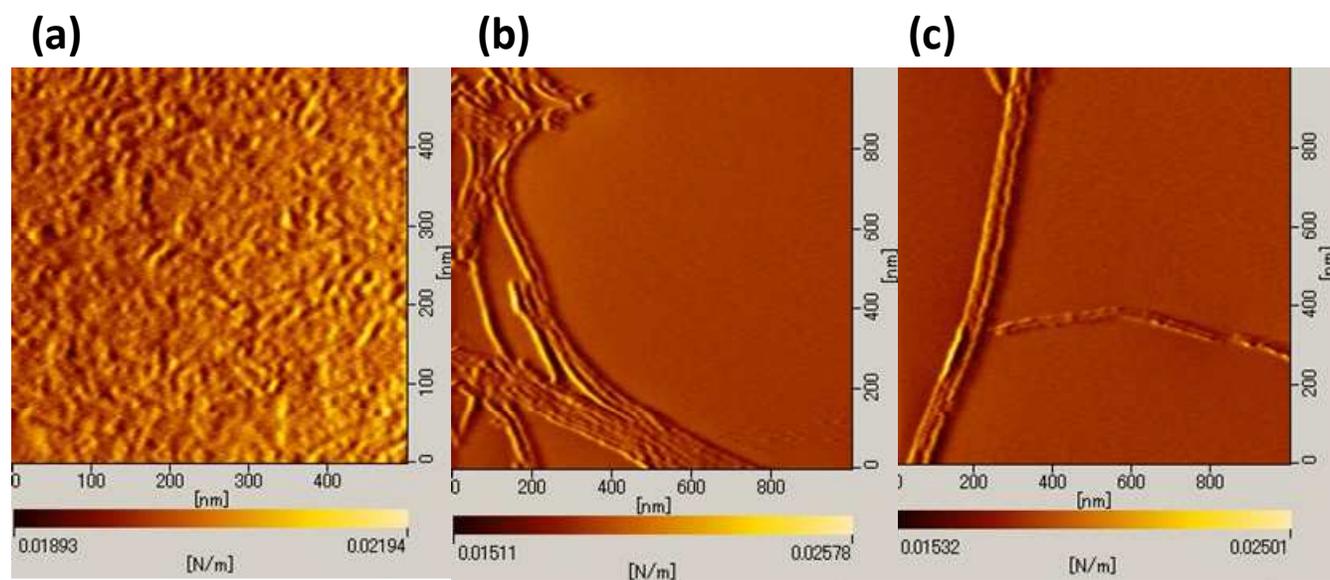


**Figure S1.**  $^1\text{H}$  NMR Spectra of (a)  $\alpha,\omega$ -ends DPE functionalized P3HT (**1**) and (b) the isolated PS-*b*-P3HT-*b*-PS.



**Figure S2.** UV-vis Spectra of the P3HT (purple) and isolated PS-*b*-P3HT-*b*-PS (blue) (a) in chloroform

and (b) in the film state.



**Figure S3.** AFM tapping mode phase images of PS-*b*-P3HT-*b*-PS thin films (a) cast from its toluene solution followed by annealing at 120 °C for 24 h under vacuum and (b), (c) drop-cast from its 1,2-dichlorobenzene solution followed by annealing at 120 °C for 24 h under vacuum.

## References

- (1) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169.
- (2) Sugiyama, K.; Karasawa, Y.; Higashihara, T.; Zhao, Y.; Hirao, A. *Monatshfte fure Chemie* **2006**, *137*, 869-80.