
School of Natural Sciences and Mathematics

2012-12-06

*Synthesis and Characterization of a Polyisoprene-*b*-
polystyrene-*b*-poly(3-hexylthiophene) Triblock
Copolymer*

UTD AUTHOR(S): Hein Q. Nguyen, Mahesh P. Bhatt, Elizabeth A.
Rainbolt and Mihaela C. Stefan

©2013 The Royal Society of Chemistry. This article may not be further
made available or distributed.

Synthesis and characterization of a polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) triblock copolymer†

Cite this: *Polym. Chem.*, 2013, **4**, 462

Received 20th November 2012
Accepted 5th December 2012

Hien Q. Nguyen, Mahesh P. Bhatt, Elizabeth A. Rainbolt and Mihaela C. Stefan*

DOI: 10.1039/c2py21009f

www.rsc.org/polymers

A polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) triblock copolymer was synthesized by anionic coupling of *living* polyisoprene-*b*-polystyryl lithium with allyl-terminated poly(3-hexylthiophene). The triblock copolymer retained the opto-electronic properties and morphology found in the poly(3-hexylthiophene) homopolymer despite the insulating polyisoprene and polystyrene blocks, making it potentially useful as an elastomeric semiconducting material.

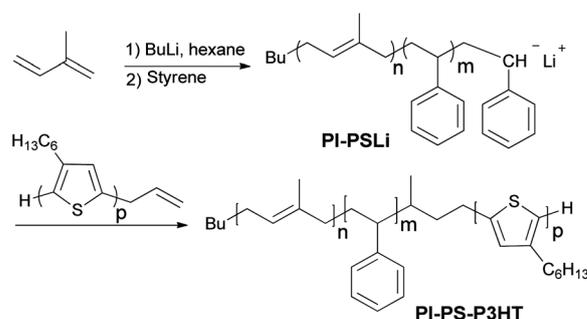
Regioregular poly(3-hexylthiophene) (P3HT) is one of the most studied semiconducting polymers for organic electronics applications.¹ Various cross-coupling polymerization methods have been employed for the synthesis of P3HT.^{2–6} Grignard metathesis (GRIM) polymerization is the most versatile method for the synthesis of P3HT due to its quasi-*living* nature which allows the large scale synthesis of polymers with well-defined molecular weights and functional end groups.^{7,8} Moreover, GRIM has been successfully employed for the *in situ* end-group functionalization of P3HT to generate allyl-terminated P3HT which was used as a precursor for the synthesis of block copolymers containing P3HT.^{9,10}

Controlled radical polymerization (CRP) methods have been extensively employed for the synthesis of various P3HT rod-coil block copolymers.² Furthermore, anionic, cationic, ring-opening, and ring-opening metathesis polymerizations have also been used for the synthesis of P3HT rod-coil block copolymers.² Synthesis of P3HT block copolymers by a combination of GRIM and anionic polymerizations is particularly attractive due to the *living* nature of both methods, which enables the generation of block copolymers with tunable molecular weights and compositions.^{11–18} Block copolymers of rod-like P3HT and coil-like polystyrene,^{11,15,16} poly(methyl methacrylate),^{13,18} poly(2-vinylpyridine),¹² poly-

(4-vinyltriphenylamine),¹⁴ and polyisoprene¹⁵ have been synthesized by a combination of cross-coupling and anionic polymerizations.

We are reporting here for the first time the synthesis and opto-electronic properties of a triblock copolymer containing polyisoprene (PI), polystyrene (PS), and P3HT. This copolymer combines the good optoelectronic properties of P3HT with the elastomeric nature of polyisoprene and potentially can be used as an actuating material for artificial muscle applications.

A polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) (PI-PS-P3HT) triblock copolymer was synthesized by addition of *living* polyisoprene-*b*-polystyryl lithium to the allyl-terminated P3HT as shown in Scheme 1. The allyl-terminated P3HT was synthesized by *in situ* addition of allyl magnesium bromide to the nickel-terminated polymer, which produced a polymer with Br/allyl and H/allyl end-groups ($DP_n = 20$).^{11,19,20} Prior to the anionic coupling reaction the bromine end-group was reduced by magnesium halogen exchange to generate the H/allyl P3HT polymer.¹¹ This step is necessary to prevent the possible lithium bromine exchange side reaction that can take place during the coupling step. The polyisoprene-*b*-polystyrene (PI-PS) diblock copolymer was prepared by *living* anionic polymerization in moisture and oxygen free cyclohexane according to a previously described method.^{11,21} The allyl-terminated P3HT was transferred to the reaction flask containing



Scheme 1 Synthesis of polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) (PI-PS-P3HT) ($M_n = 7170 \text{ g mol}^{-1}$).

University of Texas at Dallas, Department of Chemistry, 800 West Campbell Road, Richardson, TX 75080, USA. E-mail: mihaela@utdallas.edu; Fax: +1 972-883-2925; Tel: +1 972-883-6581

† Electronic supplementary information (ESI) available: Experimental section, TMAFM images, and OFET data. See DOI: 10.1039/c2py21009f

the *living* polyisoprene-*b*-polystyrene lithium and allowed to react for 10 minutes at 40 °C. The final copolymer was precipitated in methanol and washed with cold cyclohexane to remove the unreacted PI-PS diblock copolymer. The complete disappearance of the allyl protons in the ^1H NMR spectrum of the copolymer confirmed the successful coupling reaction. The composition of the synthesized PI-PS-P3HT triblock copolymer was estimated from the ^1H NMR analysis (Fig. S1, ESI †). The PI-PS-P3HT triblock copolymer contained 31.5 mol% PI, 44.2 mol% PS, and 24.3 mol% P3HT as estimated from the integration of methylene protons of the P3HT block *vs.* the vinyl protons of PI and the aromatic protons of PS blocks. The PI block contained $\sim 95\%$ 1,4-units (*cis* and *trans*) and $\sim 5\%$ 3,4-units.

The UV-vis absorbance spectra of the PI-PS-P3HT triblock copolymer were recorded both in chloroform solution and film deposited from chloroform (Fig. 1). The PI-PS-P3HT triblock copolymer displayed an absorption maximum at 450 nm for solution and 533 nm for the film, which is due to the π - π^* transition of P3HT. The absorbance maximum of the film bathochromically shifted to 533 nm which indicates increased ordering and enhanced interchain packing of PI-PS-P3HT in a solid state. The UV-vis spectrum of the film also shows two vibronic peaks at 550 and 605 nm which are due to the interchain π - π interaction.^{19,20} The absorbance maximum measured for the PI-PS-P3HT triblock copolymer is comparable to that of the P3HT homopolymer which indicates that the presence of insulating PI and PS blocks does not affect the effective conjugation length of the P3HT semiconducting segment.²²

The thin film X-ray diffraction pattern was obtained for PI-PS-P3HT (Fig. 2). The PI-PS-P3HT copolymer shows a first order reflection (100) at $2\theta = 5.41^\circ$ ($d = 16.32 \text{ \AA}$) corresponding to the lamellar planes formed by the side-by-side stacking of the P3HT. The diffraction pattern also shows higher order reflection peaks (200) ($2\theta = 10.88^\circ$) and (300) ($2\theta = 16.39^\circ$) of P3HT corresponding to d -spacings of 8.1 \AA and 5.4 \AA , respectively. The P3HT homopolymer shows one additional peak at $2\theta = 24^\circ$ which is due to the π -stacking of polymer backbones.^{22,23} The absence of the peak at $2\theta = 24^\circ$ for the PI-PS-P3HT triblock copolymer is most likely due to the presence of PI and PS insulating blocks which can affect the P3HT π -stacking. However, the presence of the lamellar packing peak at

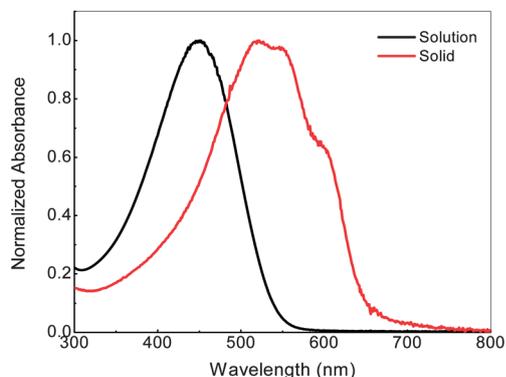


Fig. 1 UV-vis spectra of polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) (PI-PS-P3HT).

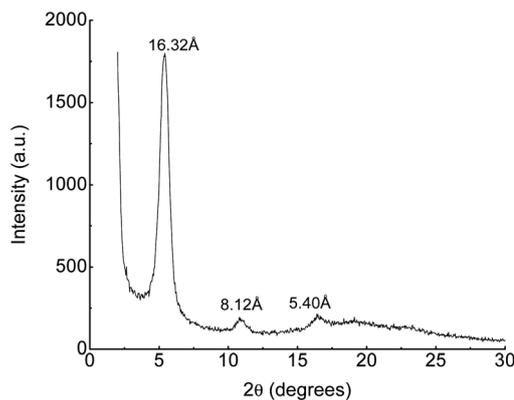


Fig. 2 XRD pattern of polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) (PI-PS-P3HT).

$2\theta = 5.41^\circ$ indicates that the insulating blocks did not disturb the crystalline packing of P3HT.

The surface morphology of PI-PS-P3HT was investigated by tapping mode atomic force microscopy (TMAFM). Thin films of the copolymer were formed by drop-casting of a solution of polymer in toluene on the mica substrate and subsequent evaporation of the solvent. The morphologies of the thin films were investigated before and after annealing at 120 °C (Fig. 3). Nanofibrillar morphology was observed for the PI-PS-P3HT thin film deposited from toluene.^{19,20,23} The observed nanofibrils are shorter and more diluted as compared to P3HT homopolymers. The dilution in nanofibrills observed for the PI-PS-P3HT triblock copolymer is due to the presence of PI and PS insulating blocks and it was previously

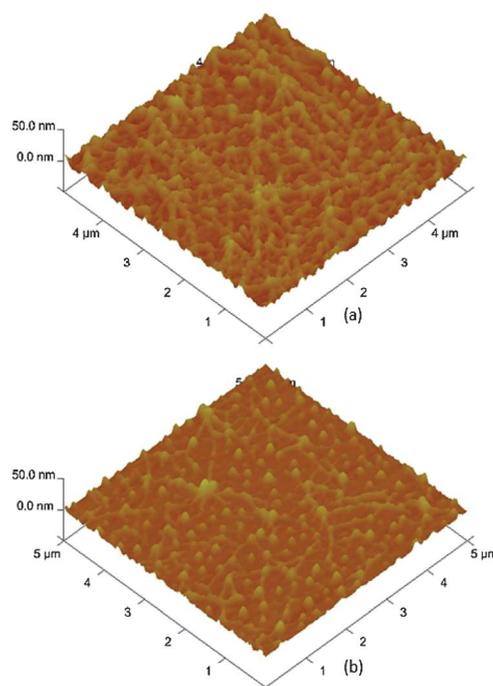


Fig. 3 3D-TMAFM of polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) (PI-PS-P3HT): (a) non-annealed and (b) annealed.

reported for other P3HT block copolymers.^{19,20} Annealing of the film at 120 °C affected the surface morphology of the PI-PS-P3HT diblock copolymer by generating more spherical features (Fig. 3b).

Bottom-gate bottom-contact organic field effect transistors (OFETs) were fabricated and the PI-PS-P3HT triblock copolymer solution in chloroform was deposited on the device by drop-casting. The measurements were performed for both untreated and surface treated silicon dioxide dielectric. Octyltrichlorosilane (OTS) was used for the surface treatment of silicon dioxide dielectric, which has been demonstrated to ensure a better interaction of the hydrophobic polymer with the dielectric. The plot of source-drain current (I_{DS}) versus source-drain voltage (V_{DS}) for the untreated OFET device is shown in Fig. 4 (top). The charge carrier mobility was extracted from a plot of $I_{DS}^{1/2}$ vs. V_{GS} (Fig. 4, bottom).²³ A field-effect mobility of $5.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was measured for the untreated OFET device. A field-effect mobility of $6.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was measured for the OTS treated OFET device (ESI[†]). The measured field-effect mobilities of PI-PS-P3HT are relatively high for a copolymer that contains a large fraction of insulating blocks (24.3 mol% semiconducting P3HT and 75.7 mol% insulating PI and PS).

Electrical conductivity measurements were conducted on thin polymer films by the standard four-point probe method under ambient conditions. The average value of the conductivity measured was $2 \times 10^{-2} \text{ S cm}^{-1}$ on a thin film with a thickness of 0.32 μm . A conductivity of 2 S cm^{-1} was previously reported for a PI-P3HT diblock copolymer containing 35 mol% P3HT which had a DP_n of the semiconducting P3HT segment of ~ 40 .²⁴ The relatively low conductivity measured for the PI-PS-P3HT triblock copolymer is

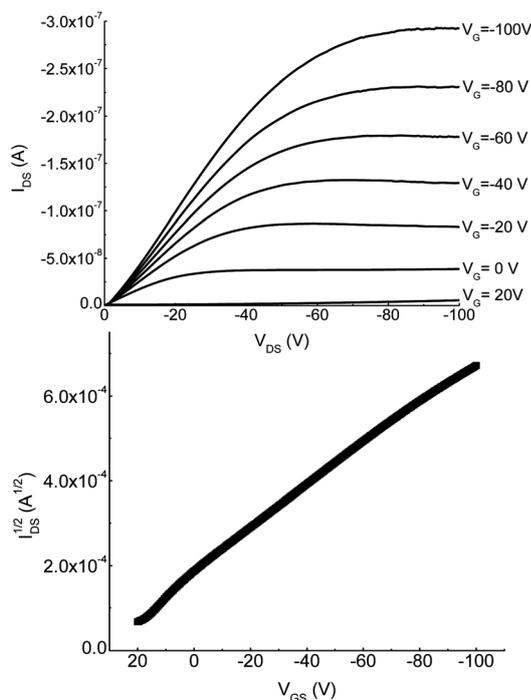


Fig. 4 Current–voltage characteristics of polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) (PI-PS-P3HT) on an untreated OFET device; top: output curves at different gate voltages; bottom: transfer curves at $V_{DS} = -100 \text{ V}$ ($\mu = 5.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $V_T = 19.0 \text{ V}$, on/off ratio = 10^2 , $W = 475 \mu\text{m}$, $L = 20 \mu\text{m}$).

due to the low content of the semiconducting P3HT block (24.3 mol %) and to the low DP_n of the P3HT block ($DP_n = 20$).

In summary, a novel triblock copolymer containing semiconducting P3HT and coil-like polyisoprene and polystyrene was synthesized by a combination of *living* GRIM and anionic coupling. This triblock copolymer has excellent field-effect mobility despite its high content of insulating polyisoprene and polystyrene. The mechanical properties of this elastomeric semiconducting polymer are currently under investigation.

Financial support for this project from NSF (Career DMR-0956116) and Welch Foundation (AT-1740) is gratefully acknowledged. We gratefully acknowledge the NSF-MRI grant (CHE-1126177) used to purchase the Bruker AVANCE III 500 NMR instrument.

Notes and references

- 1 *Handbook of Thiophene-based Materials: Applications in Organic Electronics and Photonics*, ed. I. F. Perepichka and D. F. Perepichka, 2009.
- 2 M. C. Stefan, M. P. Bhatt, P. Sista and H. D. Magurudeniya, *Polym. Chem.*, 2012, **3**, 1693–1701.
- 3 A. Kiriya, V. Senkovskyy and M. Sommer, *Macromol. Rapid Commun.*, 2011, **32**, 1503–1517.
- 4 M. He, W. Han, J. Ge, Y. Yang, F. Qiu and Z. Lin, *Energy Environ. Sci.*, 2011, **4**, 2894–2902.
- 5 K. Okamoto and C. K. Luscombe, *Polym. Chem.*, 2011, **2**, 2424–2434.
- 6 I. M. Osaka and R. D. McCullough, *Acc. Chem. Res.*, 2008, **41**, 1202–1214.
- 7 M. C. Iovu, E. E. Sheina, R. R. Gil and R. D. McCullough, *Macromolecules*, 2005, **38**, 8649–8656.
- 8 A. Yokoyama, R. Miyakoshi and T. Yokozawa, *Macromolecules*, 2004, **37**, 1169–1171.
- 9 M. Jeffries-El, G. Sauve and R. D. McCullough, *Adv. Mater.*, 2004, **16**, 1017–1019.
- 10 M. Jeffries-El, G. Sauve and R. D. McCullough, *Macromolecules*, 2005, **38**, 10346–10352.
- 11 M. C. Iovu, M. Jeffries-El, R. Zhang, T. Kowalewski and R. D. McCullough, *J. Macromol. Sci., Part A: Pure Appl. Chem.*, 2006, **43**, 1991–2000.
- 12 C.-A. Dai, W.-C. Yen, Y.-H. Lee, C.-C. Ho and W.-F. Su, *J. Am. Chem. Soc.*, 2007, **129**, 11036–11038.
- 13 T. Higashihara and M. Ueda, *React. Funct. Polym.*, 2009, **69**, 457–462.
- 14 T. Higashihara and M. Ueda, *Macromolecules*, 2009, **42**, 8794–8800.
- 15 H. Lim, K.-T. Huang, W.-F. Su and C.-Y. Chao, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 3311–3322.
- 16 A. Takahashi, Y. Rho, T. Higashihara, B. Ahn, M. Ree and M. Ueda, *Macromolecules*, 2010, **43**, 4843–4852.
- 17 H. C. Moon, A. Anthonyssamy, Y. Lee and J. K. Kim, *Macromolecules*, 2010, **43**, 1747–1752.
- 18 H. C. Moon, A. Anthonyssamy, J. K. Kim and A. Hirao, *Macromolecules*, 2011, **44**, 1894–1899.
- 19 M. G. Alemseghed, S. Gowrisanker, J. Servello and M. C. Stefan, *Macromol. Chem. Phys.*, 2009, **210**, 2007–2014.

- 20 M. G. Alemseghed, J. Servello, N. Hundt, P. Sista, M. C. Biewer and M. C. Stefan, *Macromol. Chem. Phys.*, 2010, **211**, 1291–1297.
- 21 F. Schue, D. J. Worsfold and S. Bywater, *Macromolecules*, 1970, **3**, 509–513.
- 22 N. Hundt, Q. Hoang, H. Nguyen, P. Sista, J. Hao, J. Servello, K. Palaniappan, M. Alemseghed, M. C. Biewer and M. C. Stefan, *Macromol. Rapid Commun.*, 2011, **32**, 302–308.
- 23 M. P. Bhatt, P. Sista, J. Hao, J. Hundt, M. C. Biewer and M. C. Stefan, *Langmuir*, 2012, 12762–12770.
- 24 M. C. Iovu, C. R. Craley, M. Jeffries-EL, A. B. Krankowski, R. Zhang, T. Kowalewski and R. M. McCullough, *Macromolecules*, 2007, **40**, 4733–4735.

Electronic Supplementary Information
**Synthesis and Characterization of Polyisoprene-*b*-Polystyrene-*b*-
Poly(3-Hexylthiophene) Triblock Copolymer**

Hien Q. Nguyen, Mahesh P. Bhatt, Elizabeth A. Rainbolt, Mihaela C. Stefan*

Table of Contents

Experimental	2
Materials	2
Synthesis of polyisoprene- <i>b</i> -polystyrene- <i>b</i> -poly(3-hexylthiophene)	2
Field effect mobility measurements	3
Tapping mode atomic force microscopy	5
X-ray diffraction studies	5
Electrical conductivity measurements	5
Height and phase TMAFM of PI-PS-P3HT	6
Current voltage characteristic of PI-PS-P3HT on untreated OFET	7
Current voltage characteristic of PI-PS-P3HT on treated OFET	7

Experimental

Materials

All reactions were conducted under pre-purified nitrogen, using oven-dried glassware. Commercial chemicals, purchased from Aldrich Chemical Co., Inc., were used without further purification unless otherwise noted. All solvents were freshly distilled prior to use. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Chloroform was distilled and collected over molecular sieves. Allyl-terminated poly(3-hexylthiophene) was synthesized according to previously published procedure.¹

¹H NMR spectra of the polymers were recorded on a Bruker Advance III 500 MHz spectrometer at 30 °C. ¹H NMR data are reported in parts per million as chemical shift relative to tetramethylsilane (TMS) as the internal standard. Spectra were recorded in CDCl₃.

The polyisoprene-*b*-polystyrene segment was prepared by *living* anionic polymerization in moisture and oxygen free cyclohexane, according to the previously described method.²

Allyl-terminated poly(3-hexylthiophene): ¹H NMR (500 MHz, CDCl₃): δ_H 0.9 (t, 3H), 1.35-1.43 (m, 6H), 1.69 (t, 2H), 2.80 (t, 2H), 3.49 (d, 2H), 5.11 (m, 2H), 5.98 (m, 1H) 6.95 (s, 1H), DP_n=20; SEC: M_n=4500 g/mol; PDI = 1.25.¹

Polyisoprene-*b*-polystyrene: ¹H NMR (500 MHz, CDCl₃): δ_H 1.4 (t, *J* = 7 Hz, 3H), 1.53 (s, 3H), 1.61 (s, 3H), 1.67 (s, 3H), 2.0 (m, 2H) 4.7 (m, 1H), 5.1 (m, 1H), 6.5 (m, 2H) 7.1 (m, 3H), SEC: M_n=3700 g/mol; PDI = 1.20.

Synthesis of polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) (PI-PS-P3HT)

Polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) (PI-PS-P3HT) triblock copolymer was synthesized by reacting the allyl-terminated poly(3-hexylthiophene) (M_n=4500 g/mol; DP_n(NMR)=20) as a solution in dry THF (5 mL) with the *living* polyisoprene-*b*-polystyryl lithium (M_n(SEC)=3320 g/mol) in cyclohexane. The coupling reaction was allowed to proceed for 10 min at 40°C. The coupling reaction was performed in a glove box under nitrogen atmosphere. The copolymer was precipitated in methanol and washed with cold cyclohexane to remove the unreacted polyisoprene-*b*-polystyrene diblock copolymer. The composition of the block copolymer was estimated from ¹H NMR spectrum by integrating protons *a* vs protons *c* and *e* (Figure S1). The triblock copolymer contained 24.3 mol% regioregular poly(3-hexylthiophene), 31.5 mol% polyisoprene, and 44.2 mol% polystyrene. SEC: M_n=7170 g/mol; PDI = 1.50.

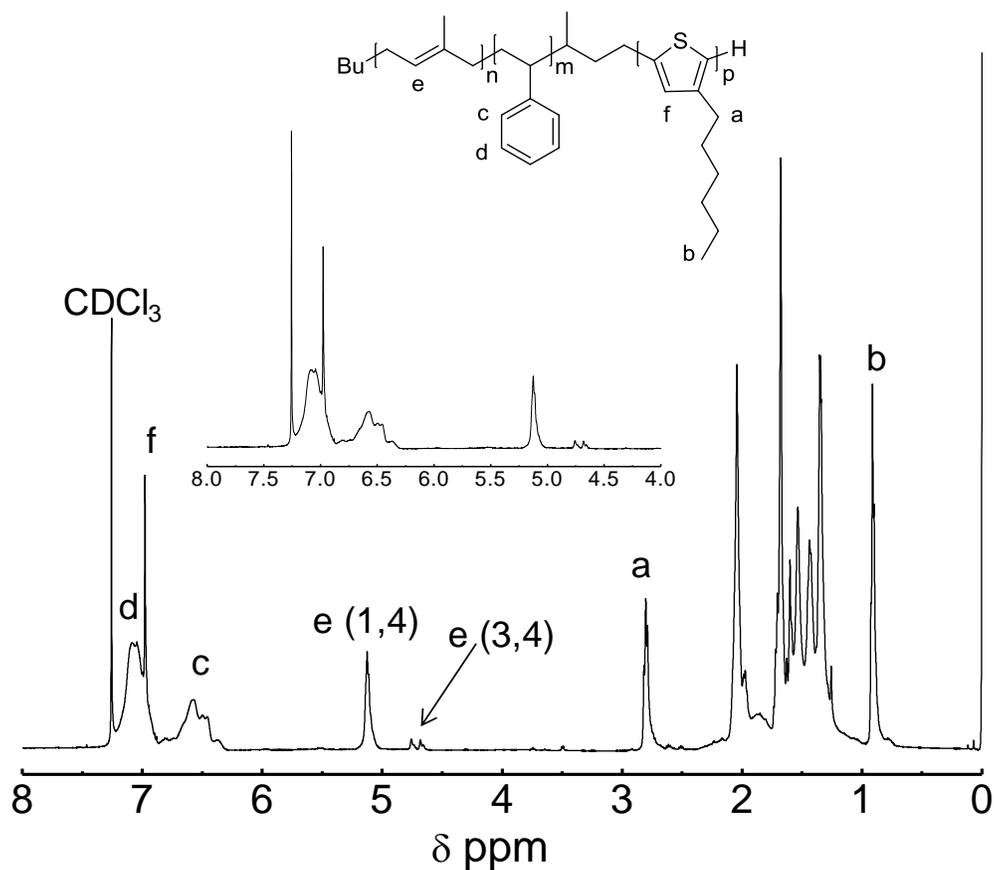


Figure S1. ¹H NMR spectrum of polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) (PI-PS-P3HT) ($M_n=7170$ g/mol)

Field-effect mobility measurements

Field-effect mobility measurements were performed on thin-film transistors with a common bottom-gate, bottom-contact configuration. Highly doped, n-type silicon wafers with a resistivity of 0.001-0.003 Ω cm were used as substrates. Silicon dioxide (SiO₂) was thermally grown at 1000 °C on silicon substrate to obtain a 200 nm thickness. Chromium metal (5 nm) followed by 100 nm of gold were deposited by E-beam evaporation as source-drain contacts. The source-drain pads were formed by photo-lithographically patterning the metal layer. The SiO₂ on the back side of the wafer was etched with buffered oxide etchant (BOE from JT Baker) to generate

the common bottom-gate. The resulting transistors had a channel width of 475 μm and channel lengths varying from 2 to 80 μm . The measured capacitance density of the SiO_2 dielectric was 17 nF/cm^2 . Prior to copolymer deposition, the substrates were cleaned by UV/ozone for 10 min. The devices were then cleaned in air with water, methanol, hexane, chloroform, and dried with nitrogen flow followed by vacuum for 30 minutes at 80 $^\circ\text{C}$. The copolymer films were deposited in air by drop casting 10 μL of a 1.0 mg/mL solution in chloroform and allowed to dry in a Petri dish saturated with chloroform. The devices were then further annealed for 30 min at 120 $^\circ\text{C}$. For the surface treated devices, the devices were cleaned in air with water, methanol, hexane, chloroform, and dried with nitrogen flow, followed by vacuum drying for 30 minutes at 80 $^\circ\text{C}$. The devices were placed in a glass container in a solution of 8×10^{-3} M n-octyltrichlorosilane in dried toluene. The sealed container was placed in a glovebox at ambient temperature for 48 h. After 48 h, the devices were taken out of the glovebox and rinsed with freshly distilled toluene before baking them at 80 $^\circ\text{C}$ for 30 min in a vacuum oven. The devices were allowed to cool under vacuum. The polymer films were deposited in air by drop-casting 4–5 drops of 1 mg/mL of polymer solution (in chloroform) filtered through a 0.2 μm PTFE filter using a 25 μL syringe. The devices were allowed to dry in a Petri dish saturated with chloroform. The devices were annealed under vacuum for 30 min at 120 $^\circ\text{C}$ prior to measurements. The devices were allowed to cool down to room temperature under vacuum after annealing. A Keithley 4200-SCS semiconductor characterization system was used to probe the devices. The probe station used for electrical characterization was a Cascade Microtech Model Summit Microchamber. When measuring current–voltage curves and transfer curves, V_{GS} was scanned from +20 V to –100 V. All the measurements were performed at room temperature in air. A plot of $I_{\text{DS}}^{1/2}$ vs. V_{GS} was obtained in the saturation regime and the field-effect mobilities were calculated using following equation:

$$\mu = \frac{2L}{WC_i} \frac{I_{\text{DS}}}{(V_{\text{GS}} - V_{\text{T}})^2}$$

where I_{DS} is the source-drain current, W is the channel width, L is the channel length, C_i is the capacitance of the dielectric, V_{GS} is the gate voltage, and V_{T} is the threshold voltage.

Tapping mode Atomic Force Microscopy (TMAFM)

TMAFM investigation of thin film morphology was carried out using a Nanoscope IV-Multimode Veeco, equipped with an E-type vertical engage scanner. The AFM images were collected at room temperature in air using silicon cantilevers with nominal spring constant of 42 N/m and nominal resonance frequency of 320 kHz (standard silicon TESP Probes with aluminum coating on backside). A typical value of AFM detector signal corresponding to R.M.S. cantilever oscillation amplitude was equal to ~1 to 2 V and the images were acquired at 0.5 Hz scan frequency in 5x5 μm scan areas. The samples were prepared by drop casting a solution of polymer in toluene (1mg/mL) on to mica substrates. The polymer thin films were annealed at 120°C prior to AFM measurements.

X-ray diffraction studies

X-Ray diffraction patterns were obtained on a RIGAKU Ultima III diffractometer. Samples were subjected to Cu K α radiation ($\lambda \sim 1.5406 \text{ \AA}$) and scanned from 1 to 40 degrees (2θ) at 0.04 degree intervals at a rate of 1 degree/min. A microscope cover glass was used as the sample substrate. The copolymer film obtained from chloroform was deposited in air by drop casting a 15.0 mg/mL polymer solution and allowed to dry in a Petri dish saturated with chloroform.

Electrical conductivity measurements

Conductivity of triblock copolymer was measured on thin polymer film by the standard four-point probe method at ambient conditions. The polymer solution in anhydrous chloroform was drop casted onto a clean cover glass slips. The solvent was evaporated in an open atmosphere. The film was oxidized by exposure to iodine vapors for 12 hrs. A minimum of five readings were taken for the selected uniform film area. The film thickness was measured using an Ambios Technology XP-1 Stylus Profiler.

The conductivity σ [S cm^{-1}] was calculated according to the following equation:

$$\sigma = 1 \div (4.53 * R * l)$$

where R is the resistance ($R=V/I$) [Ω] and l is the film thickness [cm].

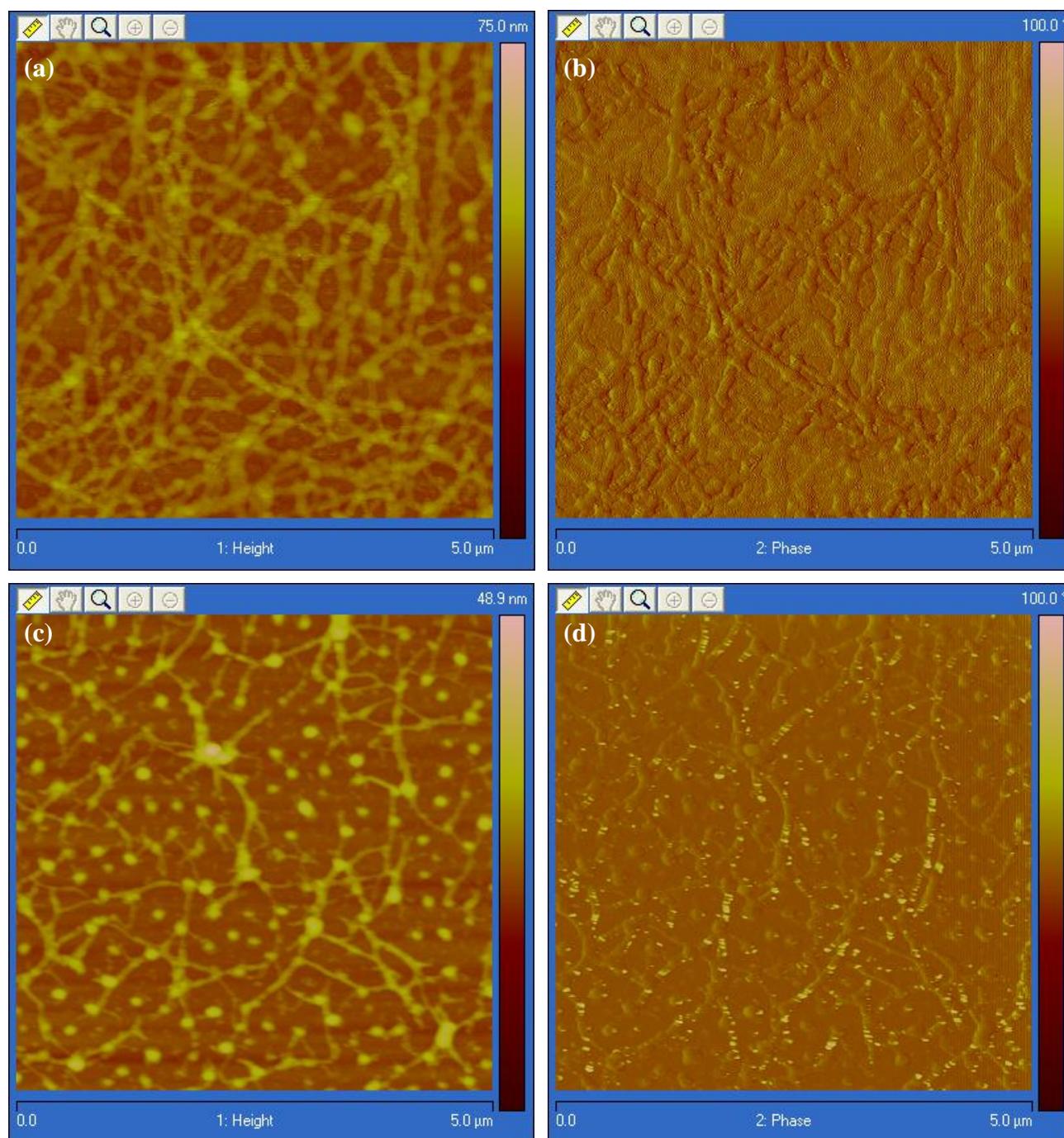


Figure S2. Height and phase TMAFM (a, b) of PI-PS-P3HT (non-annealed); height and phase TMAFM (c,d) of PI-PS-P3HT (annealed)

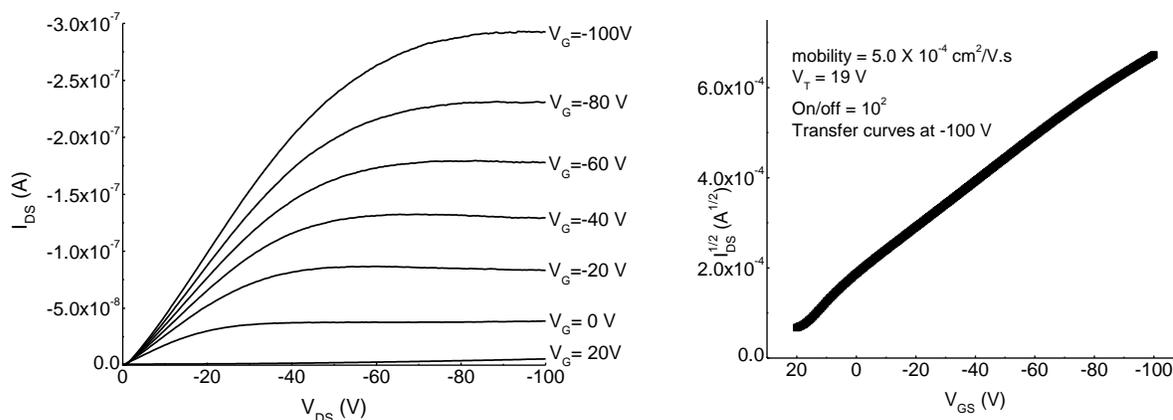


Figure S3. Current-voltage characteristics of polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) (PI-PS-P3HT) on untreated OFET device; left: output curves at different gate voltages; right: transfer curves at $V_{DS} = -100$ V ($\mu = 5.0 \times 10^{-4}$ cm²/V s, $V_T = 19.0$ V, on/off ratio = 10^2 , $W = 475$ μ m, $L = 20$ μ m)

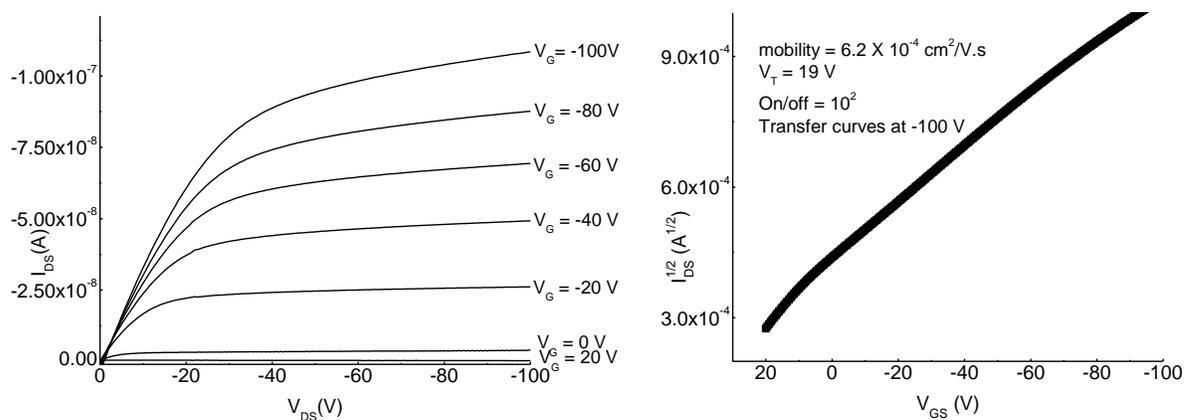


Figure S4. Current-voltage characteristics of polyisoprene-*b*-polystyrene-*b*-poly(3-hexylthiophene) (PI-PS-P3HT) on OFET device treated with octyl trichlorosilane (OTS); left: output curves at different gate voltages; right: transfer curves at $V_{DS} = -100$ V ($\mu = 6.2 \times 10^{-4}$ cm²/V s, $V_T = 19.0$ V, on/off ratio = 10^2 , $W = 475$ μ m, $L = 20$ μ m)

References:

- 1) Iovu, Mihaela C.; Jeffries-EL, M.; Zhang, R.; Kowalewski, T.; McCullough, R. D., *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, **2006**, *43*, 1991-2000.
- 2) (a) Iovu, Mihaela C.; Buzdugan, E.; Teodorescu, M.; Britchi, A. G.; Hubca, G.; Iovu, H., *Angewandte Makromolekulare Chemie* **1999**, *271*, 18; (b) Schue, F., Worsfold, D. J., Bywater, S., *Macromolecules*, **1970**, *3*, 509.