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Facile Synthesis of Well-Defined Coil−Rod−Coil Block Copolymer Composed of Regioregular Poly(3-hexylthiophene) via Anionic Coupling Reaction

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ABSTRACT: We introduced a facile synthetic strategy of coil−rod−coil triblock copolymers containing regioregular poly(3-hexylthiophene) (P3HT) block via anionic coupling reaction. Two different coil blocks (poly(2-vinylpyridine) (P2VP) and polyisoprene (PI)) were selected. P2VP-*b*-P3HT-*b*-P2VP copolymer was synthesized in a polar solvent of tetrahydrofuran, whereas PI-*b*-P3HT-*b*-PI copolymer was synthesized in a nonpolar solvent of benzene. For the synthesis of both block copolymers, the chain ends of the P3HT were capped by the aldehyde group. Because of the higher electrophilicity of the carbon in the aldehyde group compared with that in allyl (or vinyl) group, the coupling reaction between living anions in the coil blocks and aldehyde-capped P3HT was carried out more effectively. When the excess amount of the living P2VP (or PI) anions was used, all of aldehyde-capped P3HT were completely reacted with P2VP (or PI) anions without leaving any P3HT homopolymer in the product. When the unreacted P2VP (or PI) was removed by column chromatography, two synthesized triblock copolymers had narrow molecular weight distributions.

1. Introduction

Regioregular poly(3-hexylthiophene) (P3HT) has been widely used for organic field-effect transistors (OFETs),[1,2] organic photovoltaics (OPV),[3,4] and chemical sensors[5] because of its high charge carrier mobility and good solubility in various organic solvents. However, it is expensive and has low environmental stability. To overcome these drawbacks, nonconductive commodity homopolymers are sometimes used as long as good electrical properties of P3HT are not sacrificed.[6,7] Although some research groups achieved this objective by physical blending of P3HT with nonconductive homopolymers,[6−8] block copolymers containing P3HT block would become more challenging materials because of their self-assembly on a nanometer length scale. For example, in OPVs, a careful control of the nanoscale phase separation of two components is necessary to increase the power conversion efficiency because typical exciton diffusion length is 10−20 nm.[9,10] In this situation, the synthesis of well-defined P3HT-containing block copolymer with narrow molecular weight distribution is needed because the size of the nanophase separation greatly depends on the molecular weight of a block copolymer.[11]

Several synthetic routes have been reported for the preparation of well-defined P3HT-containing block copolymers based on living anionic polymerization,[12−16] living radical polymerization,[17−19] ring-opening polymerization,[20] and click reaction[21] incorporated with quasi-living Grignard metathesis (GRIM) polymerization.[22,23] P3HT-containing block copolymers synthesized by living anionic polymerization have narrower polydispersity indices (PDIs) compared with those synthesized by living radical polymerization.

Dai et al. synthesized well-defined P3HT-*block*-poly(2-vinylpyridine) (P3HT-*b*-P2VP) copolymer with relatively low PDI (1.18 to 1.29).[13] They used P3HT with one chain end having a vinyl group and the other chain end with a phenyl group and an excess amount of *sec*-butyllithium (*sec*-BuLi) for activation of the double bond in the vinyl group of P3HT chains. However, because the deactivation of an excess *sec*-BuLi was achieved by the reaction with a polar solvent such as tetrahydrofuran (THF), only polar monomers (for instance, P2VP) should be used for a coil block.

Very recently, Higashihara et al. synthesized coil−rod−coil triblock copolymers containing P3HT block via the coupling reaction between living polystyrene (PS) (or living poly(4-vinyltriphenylamine) (PVTPA)) anion and P3HT with both chain ends of 1,1-diphenylethylene (DPE).[14,15] Although this method is versatile and simple compared with the previous method,[13] the final triblock copolymers contained a small amount (~5%) of unidentified high-molecular-weight byproduct.[14,15]

In this study, instead of anion generation at the end of vinyl-capped P3HT[13] or using DPE functionalized P3HT for the coupling reaction,[14,15] we employed aldehyde-capped P3HT for the coupling reaction with living anions in the coil blocks (Scheme 1). Because of the higher electrophilicity of the carbon in the aldehyde group compared with that in allyl (or vinyl) group, the coupling reaction between living anions of the coil blocks and aldehyde-capped P3HT was carried out more effectively. A similar coupling reaction was previously used for the synthesis of rod−coil diblock copolymer containing poly(alkoxyphenylene vinylene) block.[24,25]

We found that the coupling reaction introduced in this study is facile and efficient for the synthesis of well-defined coil−rod−coil triblock copolymers containing regioregular P3HT block. Furthermore, because both nonpolar and polar solvents could be used, various coil blocks would be employed, although we demonstrated two coil blocks (P2VP and PI). When an excess amount of the living P2VP (or PI) anions was used, all of the aldehyde-capped P3HT was completely reacted with P2VP (or PI) anions without leaving any P3HT homopolymer in the product. When the unreacted P2VP (or PI) was removed by

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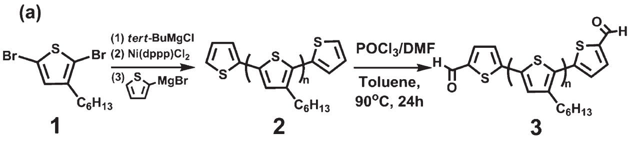
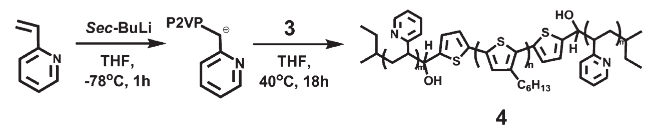
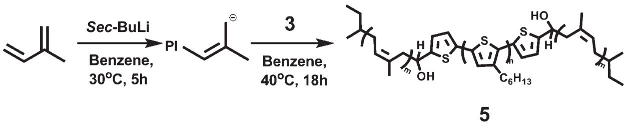
Scheme 1. Synthetic Routes of (a) Thienyl- and Aldehyde-Capped Poly(3-hexylthiophene) (P3HT), (b) Poly(2-vinylpyridine)-*b*-poly-(3-hexylthiophene)-*b*-poly(2-vinylpyridine) Copolymer (P2VP-*b*-P3HT-*b*-P2VP), and (c) Polyisoprene-*b*-poly(3-hexylthiophene)-*b*-polyisoprene Copolymer (PI-*b*-P3HT-*b*-PI)



(b) 2-Vinyl pyridine for polar case



(c) Isoprene for non-polar case



column chromatography, synthesized poly(2-vinylpyridine)-*b*-poly(3-hexylthiophene)-*b*-poly(2-vinylpyridine) (P2VP-*b*-P3HT-*b*-P2VP) and polyisoprene-*b*-poly(3-hexylthiophene)-*b*-polyisoprene (PI-*b*-P3HT-*b*-PI) copolymers had narrow molecular weight distributions (< 1.18).

2. Experimental Section

Materials. All chemicals (> 98% purities) were purchased from Sigma Aldrich and used without further purification except monomers and solvents. THF and benzene as well as 2-vinylpyridine (2VP) and isoprene were first purified with CaH_2 for 24 h. Then, THF was vacuum-distilled in the sodium/benzophenone mixture and stirred until the solution became a deep-violet color, whereas benzene was vacuum-distilled in *n*-butyl lithium (*n*-BuLi). 2VP and isoprene were vacuum-distilled and vigorously stirred with trioctyl aluminum (TOA) at room temperature for 20 min and *n*-BuLi at 0 °C for 1 h, respectively. Before polymerization, the monomers were distilled once again. Column chromatography was performed on silica gel (Merck silica gel 60 (0.063−0.200 mm)).

Characterization. Molecular weight and PDI of all samples were measured by size exclusion chromatography (SEC: Waters 2414 refractive index detector) with two columns including particle size of 5 μm (PLgel 5 μm MIXED-C: Polymer Laboratories) using PS standards with THF as an eluent and a flow rate of 1 mL/min at 30 °C. The chemical structure of all samples was determined by ^{1}H nuclear magnetic resonance spectra (^{1}H NMR: Bruker DPX300). The solvent used in ^{1}H NMR for all samples except aldehyde-capped P3HT was chloroform-*d* ($CDCl_3$) (δ = 7.26), whereas dichloromethane-*d* (CD_2Cl_2) (δ = 5.30) was selected for aldehyde-capped P3HT. This is because one of the resonance peaks of aldehyde-capped P3HT was overlapped with the peak of $CDCl_3$. The absolute molecular weight of the samples was measured by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometer (Bruker REFLEX III). All MALDI-TOF spectra were recorded by linear mode with the accelerating potential of 20 kV. Dithranol was employed as a matrix without adding any salt, and the standards kit (calibration mixture 2: Applied Biosystems) was used for the calibration. The UV−vis absorption spectra of solutions in chloroform and thin films for pristine aldehyde-capped P3HT and synthesized triblock copolymers were recorded on a UV−vis spectrometer (Varian Cary-5000). Thin film samples for UV−vis spectrometer were prepared by drop casting of chloroform solution (0.5 mg/mL), and the solvent was removed very slowly under saturated chloroform vapor. It was found that without using slow evaporation of solvent, P3HT chains do not crystallize enough.[26] Finally, the surface morphology of thin films of two synthesized block copolymers was investigated by atomic force microscopy (AFM: Digital Instrument, Multimode Nanoscope III) with tapping mode.

Synthesis of Thienyl-Capped Poly(3-hexyl)thiophene (2). 2,5-Dibromo-3-hexyl thiophene **1** (10.0 g, 30.7 mmol) synthesized according to the literature[27] was dissolved in THF (20 mL), and *tert*-BuMgCl (1.0 M solution in THF 30.7 mL, 30.7 mmol) was injected and reacted during 2 h. After this solution was diluted with the addition of dried THF (30 mL), Ni(dppp)Cl_2 (0.45 g, 0.83 mmol) was added and polymerized for 15 min, followed by injection of 2-thienylmagnesium bromide solution (1.0 M solution in THF 9 mL, 9 mmol) and stirred for 5 min. Then, the solution was poured into 700 mL of methanol and filtered and dried (4.1 g). Finally, it was fractionated by sequential Soxhlet extractions by using methanol, hexane, dichloromethane (DCM), and THF. We used the DCM fractionated part, which is precipitated in methanol. **2** (2.1 g, yield 51.2%): ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.32 (d, 2H), 7.16 (d, 2H), 7.08 (t, 2H), 6.98 (s, 1H), 2.80 (t, 2H), 1.71 (m, 2H), 1.49 (m, 2H), 1.36 (m, 4H), 0.91 (t, 3H). M_n (SEC): 6900. PDI: 1.15.

Synthesis of Aldehyde-Capped Poly(3-hexyl)thiophene (3). Although two step reactions ((1) debromination of bromine/proton terminated P3HT to proton/proton terminated P3HT and (2) the Vilsmeier reaction for the introduction of aldehyde group) were usually used for the synthesis of aldehyde-capped P3HT,[28,29] we carried out the Vilsmeier reaction directly on thienyl-capped P3HT (**2**) without performing the debromination step. First, DMF (3.24 mL, 41.8 mmol) was reacted with phosphorus oxychloride ($POCl_3$) (3.4 mL, 36.5 mmol) at 0 °C to form the Vilsmeier reagent, and toluene solution (100 mL) of **2** (0.73 g, 0.106 mmol) was injected. After stirring this solution for 24 h at 90 °C, it was cooled to room temperature, followed by neutralization with 100 mL of DI water solution of sodium acetate (3.5 g, 42.7 mmol). The toluene layer was separated and washed out with DI water several times. The product was purified by Soxhlet extraction with methanol and DCM and then dried under reduced pressure. **3** (0.65 g, yield: 89%): ^{1}H NMR (CD_2Cl_2, 300 MHz, δ): 9.87 (s, 2H), 7.72 (d, 2H), 7.26 (d, 2H), 6.98 (s, 1H), 2.81 (t, 2H), 1.72 (m, 2H), 1.49 (m, 2H), 1.36 (m, 4H), 0.92 (t, 3H). M_n (SEC): 6900. PDI: 1.15.

Synthesis of P2VP-*b*-P3HT-*b*-P2VP Copolymer (4). *sec*-BuLi (1.4 M solution in cyclohexane 0.050 mL, 0.070 mmol) initiated 2VP (0.23 g) at −78 °C in THF (10 mL). After 1 h of reaction, P2VP precursor was extracted for the molecular characterization. The solution of poly(2-vinylpyridyl) lithium was slowly heated to room temperature because of the relatively poor solubility of P3HT in THF at −78 °C. As the solution temperature increased, the solution maintained a red-wine color, a characteristic of living P2VP anion. Then, THF solution (8 mL) of dried **3** (0.128 g, 0.019 mmol) was carefully injected and reacted with poly(2-vinylpyridyl) lithium for 18 h at 40 °C. This solution was precipitated in *n*-hexane. Unreacted P2VP homopolymer in the product was completely removed by column chromatography with methanol as an eluent. A deep-purple solution including only neat P2VP-*b*-P3HT-*b*-P2VP copolymer **4** was collected, precipitated, and dried. Yield: 0.190 g (77%). M_n (SEC): 13 500, PDI: 1.18. Weight fraction of P3HT (^{1}H NMR): 0.43.

Synthesis of PI-*b*-P3HT-*b*-PI Copolymer (5). *sec*-BuLi (1.4 M solution in cyclohexane 0.040 mL, 0.056 mmol) initiated isoprene monomer (0.60 g) at 30 °C in benzene (10 mL). After 5 h of reaction, PI aliquot was extracted for the molecular characterization. Then, benzene solution (8 mL) of dried **3** (0.104 g, 0.015 mmol) was carefully injected and reacted with polyisoprenyl lithium during 18 h at 40 °C. This solution was precipitated in methanol. Unreacted PI homopolymer in the product

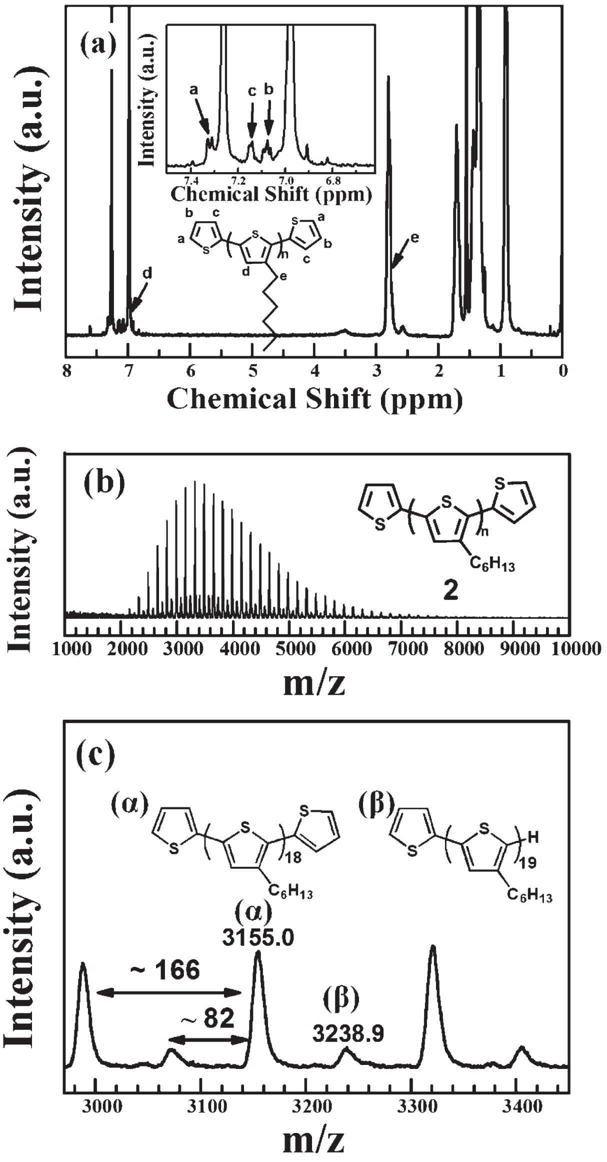


Figure 1. (a) ^{1}H NMR spectra of thienyl-capped poly(3-hexylthiophene) (P3HT) in $CDCl_3$. The inset is the expanded spectra at $\delta \approx 7$. (b) Full and (c) enlarged matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectra of thienyl-capped poly(3-hexylthiophene) (P3HT). The molecular structures in Figure 1c correspond to peaks α and *β*, respectively.

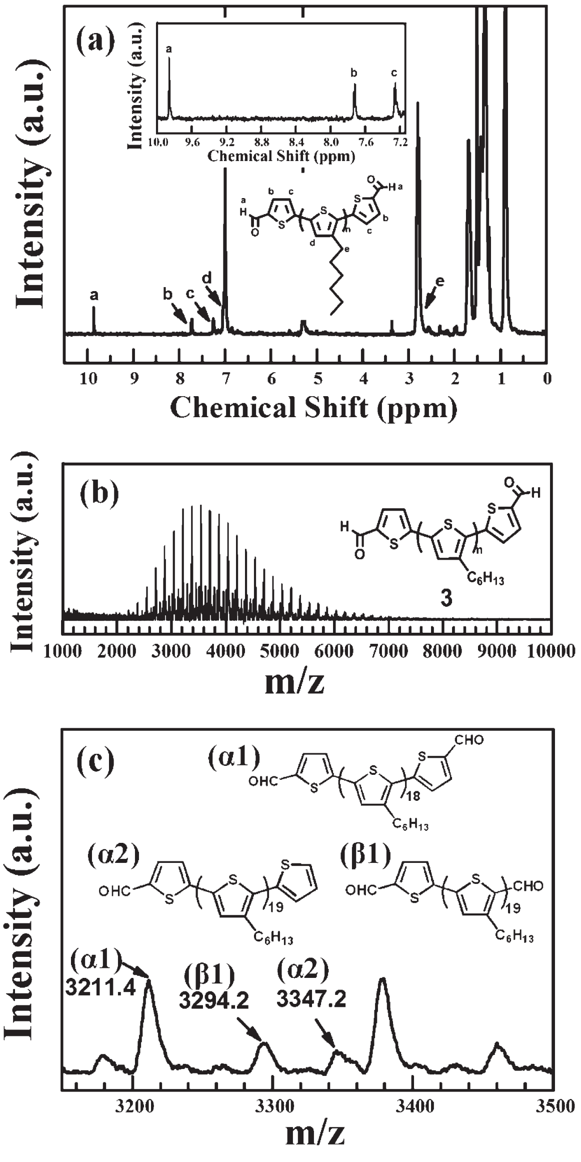


Figure 2. (a) ^{1}H NMR spectra of aldehyde-capped poly(3-hexylthiophene) (P3HT) in CD_2Cl_2. The inset is the enlarged spectra from 7.15 to 10 ppm. (b) Full and (c) extended matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectra of aldehyde-capped poly(3-hexylthiophene) (P3HT).

was removed by column chromatography with (60/40 vt/vt) acetonitrile (ACN) and DCM mixture as an eluent, followed by 20/80 (vt/vt) of ACN/DCM to obtain pure PI-*b*-P3HT-*b*-PI copolymer **5**. Yield: 0.38 g (76%). M_n (SEC): 33 400. PDI: 1.17. Weight fraction of P3HT (^{1}H NMR): 0.16.

3. Results and Discussion

Figure 1a shows ^{1}H NMR spectra of thienyl-capped P3HT (**2**). The thienyl end group was successfully attached to P3HT, confirmed by three peaks of δ at 7.32, 7.16, and 7.08 ppm. To check whether this thienyl-capped P3HT was dicapped or monocapped, we characterized **2** by MALDI-TOF. Figure 1b,c gives MALDI-TOF spectra of **2** in the entire and expanded range of molecular weights, respectively. As shown in Figure 1b, the molecular distribution of **2** was quite narrow, but two kinds of peaks (one major and the other minor) were detected. In Figure 1c, peak (α) at $m/z \approx 3155.0$ corresponds to 18 P3HT repeating units ($m/z \approx 2988$) plus two thienyl ends ($m/z \approx 166$), whereas peak (*β*) at $m/z = 3238.9$ corresponds to 19 P3HT repeating units ($m/z \approx 3154$) plus one thienyl ($m/z \approx 83$) and one proton ($m/z \approx 1$) end. Because peak (α) is much more intense than peak (*β*), the major portion of **2** is thienyl/thienyl dicapped P3HT, although small amounts of proton/thienyl monocapped P3HT exist. This result is consistent with previous results.[30,31] Namely, when Grignard reagents having unsaturated alkenyl or alkynyl group were used, monocapped P3HT was dominantly formed through the formation of the stable π-complex resulting from the reaction of Grignard reagent with Ni(0).[30−32] But, because Grignard reagents employed in this study did not have any alkenyl or alkynyl group, a majority of P3HT would have dicapped ends. However, both thienyl/thienyl- and proton/thienyl-capped P3HTs could be converted to dialdehyde-capped P3HT by the Vilsmeier reaction.

Figure 2a shows ^{1}H NMR, and Figure 2b,c gives MALDI-TOF spectra of the aldehyde-capped P3HT (**3**). After the Vilsmeier reaction, peak *a* ($\delta = 7.32$ ppm) in Figure 1a became a new peak at $\delta = 9.87$ in Figure 2a, whereas peaks *b* ($\delta = 7.08$) and

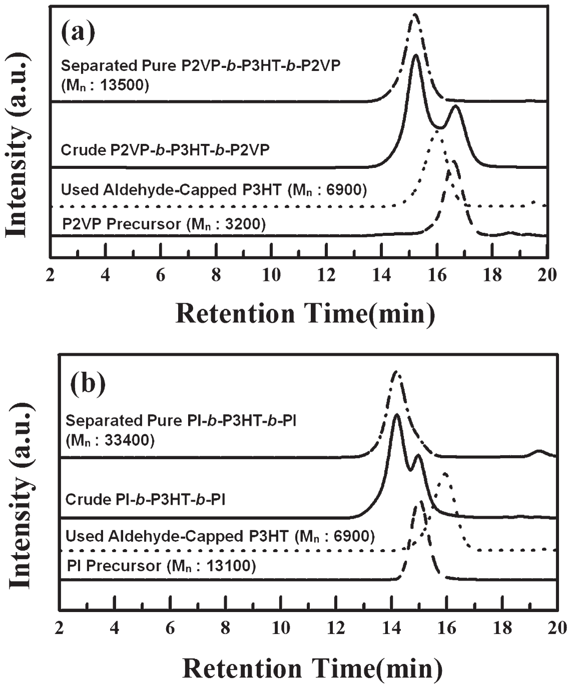


Figure 3. SEC traces for aldehyde-capped poly(3-hexylthiophene) (dotted line), extracted precursor of the coil living anion (dashed line), crude product (solid line), and neat block copolymer (dashed-dotted line) after the removal of unreacted anion: (a) poly(2-vinylpyridine)-*b*-poly(3-hexylthiophene)-*b*-poly(2-vinylpyridine) copolymer (P2VP-*b*-P3HT-*b*-P2VP) and (b) polyisoprene-*b*-poly(3-hexylthiophene)-*b*-polyisoprene copolymer (PI-*b*-P3HT-*b*-PI).

c (δ = 7.16) in Figure 1a were shifted to downfield, δ = 7.72 and δ = 7.26, respectively. This indicates that the aldehyde group, an electron withdrawing group, is successfully introduced. The peak of the hydrogen in the aldehyde groups of **3** was observed at δ = 9.87, which was different from those of directly attached to the two-position (δ = 10.00) or five-position (δ = 9.96) of P3HT.[28,29] From Figure 2b,c, all peaks of **3** were shifted to higher mass compared with those of **2**, and the molecular weight distribution of **3** was quite narrow, too. Three different peaks (one intense peak and two minor peaks) were observed for **3** different from **2**. It is seen in Figure 2c that the peaks (α) and (β) in Figure 1c were shifted to higher *m*/*z* of 56.4 and 55.3, respectively. These values are almost the same as m/z = 56, corresponding to two newly formed −CHO groups ($m/z \approx 58$) minus two protons ($m/z \approx 2$). This result implies that the Vilsmeier reaction was successfully done irrespective of thienyl/thienyl-capped or proton/thienyl-capped P3HT, and both generated coil−rod−coil triblock copolymers. Although mono-aldehyde-capped P3HT was also observed (the peak (α2) in Figure 2c), the amount of dialdehyde-capped P3HT (peaks (α1) plus (β1)) was >90%.

Figures 3a,b gives two sets of SEC traces for living anions of P2VP and PI, aldehyde-capped P3HT (**3**), P2VP-*b*-P3HT-*b*-P2VP (**4**), and PI-*b*-P3HT-*b*-PI (**5**) before and after complete removal of unreacted P2VP (or PI) homopolymers. After the coupling reaction between **3** and each of living anions, the peak was shifted to higher molecular weight, as expected. For example, when the P2VP living anion with the number-average molecular weight (M_n) = 3200 and PDI = 1.06 was reacted with **3** (M_n = 6900 and PDI = 1.15), the M_n and PDI of P2VP-*b*-P3HT-*b*-P2VP copolymer (**4**) was 13 500 and 1.18, respectively. It is noted that M_n of **3** measured by SEC (6900) is larger than that determined by MALDI-TOF (3900) (Figure 2b), which is well known for P3HT.[33] Even though a longer molecular weight of PI living anion (M_n = 13 100 and PDI = 1.04) and a nonpolar solvent of benzene were used, a well-defined PI-*b*-P3HT-*b*-PI copolymer (**4**) was synthesized (M_n = 33400) with narrow molecular distribution (PDI = 1.17). This indicates that the complete coupling reaction between **3** and living anions was successfully carried out irrespective of M_n and the types of the living anions.

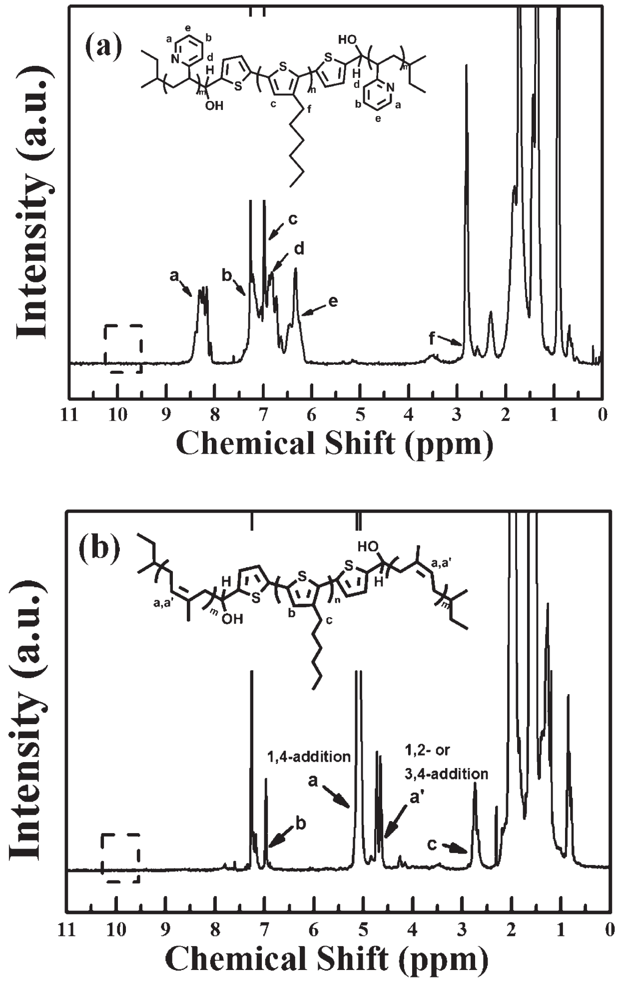


Figure 4. ^{1}H NMR spectra of neat (a) poly(2-vinylpyridine)-*b*-poly(3-hexylthiophene)-*b*-poly(2-vinylpyridine) copolymer (P2VP-*b*-P3HT-*b*-P2VP) and (b) polyisoprene-*b*-poly(3-hexylthiophene)-*b*-polyisoprene copolymer (PI-*b*-P3HT-*b*-PI). The complete disappearance of the aldehyde peak (δ = 9.87) (see the dotted square region), indicating that all of aldehyde-capped poly(3-hexylthiophene) was completely reacted with excess living anions.

Figure 4a,b shows ^{1}H NMR spectra of P2VP-*b*-P3HT-*b*-P2VP and PI-*b*-P3HT-*b*-PI copolymers, respectively, after unreacted P2VP and PI homopolymers are completely removed. The peak at δ = 9.87 ppm was not detected for both block copolymers, suggesting that all of the aldehyde-capped P3HT **3** was completely reacted with the excess of the P2VP (or PI) anions. The microstructure of PI block had dominant 1,4-addition (peak *a* in Figure 4b) over 1,2- (or 3,4-) addition (peak *a*′ in Figure 4b), which was expected for PI synthesized anionically in a nonpolar solvent.[34]

The UV−vis absorption spectra of thin film and solution state for pristine aldehyde-capped P3HT (**3**), P2VP-*b*-P3HT-*b*-P2VP (**4**), and PI-*b*-P3HT-*b*-PI (**5**) were given in Figure 5. The aldehyde-capped P3HT (**3**) in chloroform exhibited a maximum absorption (λ_{max}) at ~450 nm, and those of two block copolymers showed identical λ_{max}. All samples in thin film showed two absorption peaks at ~522 and ~553 nm corresponding to the $\pi-\pi^*$ transition and one shoulder at ~603 nm arising from the

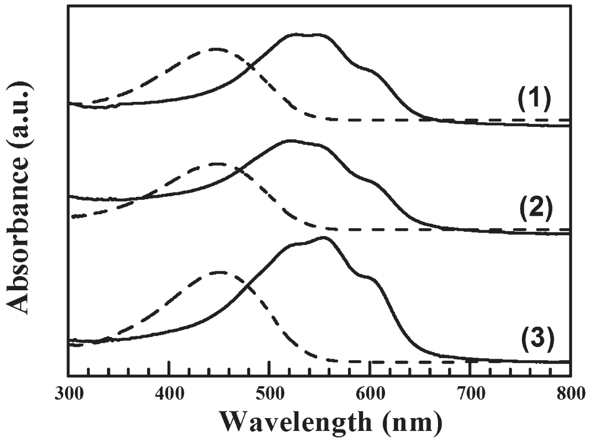


Figure 5. UV−vis absorbance spectra of solution state (dashed line) and thin film (solid line): (1) aldehyde-capped poly(3-hexylthiophene) (P3HT), (2) neat poly(2-vinylpyridine)-*b*-poly(3-hexylthiophene)-*b*-poly(2-vinylpyridine) copolymer (P2VP-*b*-P3HT-*b*-P2VP), and (3) neat polyisoprene-*b*-poly(3-hexylthiophene)-*b*-polyisoprene copolymer (PI-*b*-P3HT-*b*-PI).

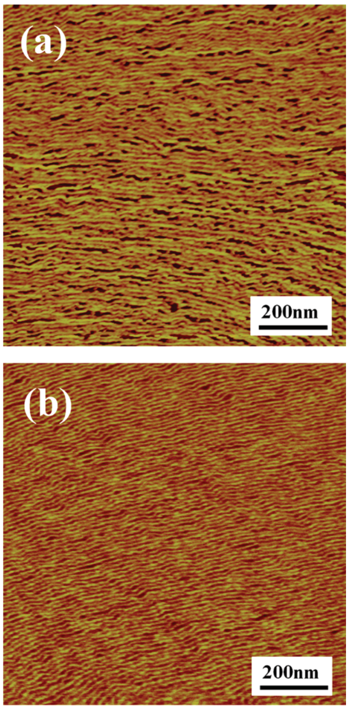


Figure 6. Phase contrast AFM images of thin films of (a) poly(2-vinylpyridine)-*b*-poly(3-hexylthiophene)-*b*-poly(2-vinylpyridine) copolymer (P2VP-*b*-P3HT-*b*-P2VP) and (b) polyisoprene-*b*-poly(3-hexylthiophene)-*b*-polyisoprene copolymer (PI-*b*-P3HT-*b*-PI).

interchain interactions.[35] The existence of shoulder at ∼603 nm implied that structural ordering of P3HT were maintained even in the block copolymers containing P2VP (or PI) blocks.

Figure 6 gives the phase contrast AFM images of P2VP-*b*-P3HT-*b*-P2VP (**4**) and PI-*b*-P3HT-*b*-PI (**5**) thin films. It was shown that well-ordered nanofibril structures of P3HT were clearly shown regardless of weight fractions of the coil blocks. Similar nanofibril structures were observed for PS-*b*-P3HT-*b*-PS,[14] PVTPA-*b*-P3HT-*b*-PS,[15] and PMMA-*b*-P3HT-*b*-PMMA[16] copolymers.

In summary, we have shown that the coupling reaction of aldehyde-capped P3HT with living anions was effectively employed in synthesizing well-defined and narrow molecular weight distribution of P3HT-containing coil−rod−coil triblock copolymers with various coil blocks. The synthesized P2VP-*b*-P3HT-*b*-P2VP and PI-*b*-P3HT-*b*-PI could be used for various applications. For instance, because PI is selectively removed by ozone treatment,[36] nanoscale pattern of P3HT could be generated. Also, metal precursors are easily incorporated into the P2VP block.[37] Once nanoparticles with electron-accepting properties are sequestered into the P2VP block, P2VP-*b*-P3HT-*b*-P2VP could be used for an organic−inorganic hybrid solar cell with higher power conversion efficiency.

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Note Added after ASAP Publication. This article posted ASAP on January 25, 2010. The last sentence in the Results and Discussion section has been revised. The correct version posted on January 28, 2010.

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