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Facile Synthetic Route for Well-Defined Poly(3-hexylthiophene)-*block*-poly(methyl methacrylate) Copolymer by Anionic Coupling Reaction

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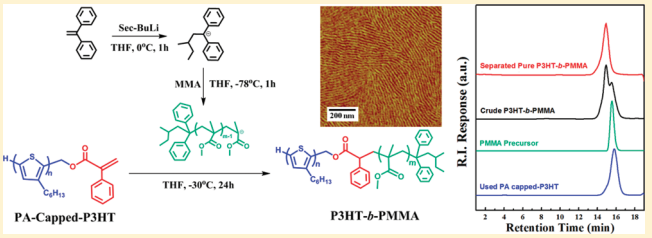
ABSTRACT: We have demonstrated a facile synthetic route for well-defined poly(3-hexylthiophene)-*block*-poly(methyl methacrylate) copolymer (P3HT-*b*-PMMA) by anionic coupling reaction. For successful coupling reaction, newly generated anions should be more stable (less reactive) than initial anions of reactants. In this study, we chose α-phenyl acrylate (PA)-capped P3HTs for successful coupling with living PMMA anions because the anions at PA group are more stable than living PMMA anions. We found that all of the PA groups located at the end of P3HT were completely coupled with living PMMA anions having slightly excess amount (1.5 equiv relative to PA-capped P3HT). The unreactive PMMA homopolymers in crude product were completely removed by using column chromatography, resulting in narrow molecular weight distribution of pure P3HT-*b*-PMMA. The optical property and thin film morphology of the P3HT-*b*-PMMA were investigated by using UV−vis spectra and atomic force microscopy, respectively.



1. INTRODUCTION

Because of high charge carrier mobility and good solubility in various organic solvents, regioregular poly(3-alkylthiophene) (P3AT) has been attracting great attention for organic field-effect transistors (OFET),[1,2] organic photovoltaics (OPV),[3,4] and chemical sensors.[5,6] Recently, many research groups synthesized rod−coil block copolymer composed of conductive poly(3-hexylthiophene) (P3HT) and nonconductive polymer to fabricate nanometer length scale of P3HT domains using block copolymer self-assembly, while the outstanding electronic property is maintained.[7] Such a nanoscale structure of P3HT would be ideal morphology for OPV with enhanced power conversion efficiency because of relatively short exciton diffusion length of 10−20 nm in OPV.[8−10] However, neat P3HT-containing rod−coil block copolymer itself has lower charge carrier mobility compared with pristine P3HT due to the existence of the insulating coil segment.[11] Thus, this insulating part should be removed so that n-type material is backfilled in the empty space with nanometer size.

For this purpose, poly(methyl methacrylate) (PMMA) or polylactide (PLA) would be good candidates as coil segments since both of PMMA and PLA are readily removable by UV irradiation followed by rinsing with acetic acid[12] and by etching with NaOH solution,[13−15] respectively. Boudouris et al.[15,16] synthesized rod−coil and coil−rod−coil block copolymers consisting of P3AT and PLA by ring-opening polymerization from hydroxyl group functionalized P3AT. Then, they obtained nanoporous P3AT thin films after selective removal of PLA. Botiz et al.[14] fabricated nanoporous P3HT from P3HT-*b*-poly(L-lactide) (PLLA) by removal of PLLA, and an electron-acceptor material of C_{60} was backfilled into nanoporous regions. Very recently, Grancharov et al.[17] prepared P3HT-*b*-PLA containing both of PLLA and poly(D-lactide) (PDLA) to control the supramolecular organization of P3HT chains. However, the molecular distribution of synthesized P3HT-*b*-PLA was relatively broad (polydispersity index (PDI) > 1.3). The synthesis of block copolymer containing P3HT block having narrow PDI is essential because the domain size of nanostructure relies on the molecular weight of a block copolymer.[18,19] On the other hand, there are a few papers for the synthesis of block copolymers containing both of P3HT and PMMA with narrow PDI. Higashihara et al.[20] reported the synthesis of PMMA-*b*-P3HT-*b*-PMMA triblock copolymers using anionic polymerization of MMA from 1,1-diphenylethylene (DPE) functionalized P3HT. The initiating sites for P3HT were formed at DPE groups by a reaction with excess quantity of *sec*-BuLi. Since PMMA homopolymer was not observed in the final block copolymer, the excessive *sec*-BuLi seemed to be completely inactivated in THF solution at room temperature. Then, MMA was initiated by P3HT

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anions at DPE moiety and polymerized at −78 °C. Although the crude product involved both PMMA-*b*-P3HT-*b*-PMMA triblock copolymer and unreacted P3HT arising from partially aggregated macroinitiator at −78 °C, they obtained final block copolymer having narrow molecular distribution after removing unreacted P3HT by fractionation.

Recently, we synthesized well-defined poly(2-vinylpyridine) (P2VP)-*b*-P3HT-*b*-P2VP and polyisoprene (PI)-*b*-P3HT-*b*-PI triblock copolymers by anionic coupling (or linking) reaction between aldehyde functionalized P3HT and living polymer anions.[21] The anionic coupling reaction is simple and efficient compared with anionic polymerization from P3HT macroinitiator. Furthermore, various kinds of coil blocks having both polar and nonpolar properties, for instance, P2VP,[21] PI,[21] and polystyrene (PS),[22,23] could be incorporated into block copolymers including P3HT block. However, these coil blocks are difficult to remove from P3HT-containing block copolymer.

We realize that once PMMA is employed as a coil block, it is easily removed by UV irradiation followed by rinsing with acetic acid. But, compared with living P2VP, PI, or PS anions, living PMMA anions have relatively weak reactivity, since the anion at the end of living PMMA is very stable due to strong electron-withdrawing effect of carbonyl group.[24] Lim et al.[23] reacted living PMMA anions with aldehyde-capped P3HT, but only half of living PMMA anions participated in the reaction to form PMMA-*b*-P3HT-*b*-PMMA triblock copolymers. This suggests that the aldehyde group might not be an appropriate functional group to couple with living PMMA anions.

Very recently, Sugiyama et al.[24] proposed the synthetic route for well-defined $(AB)_n$ multiblock copolymers using the reaction between living PMMA anion and α-phenyl acrylate (PA) functionalized polystyrene (PS). Although living PMMA anions have very low reactivity, they could react completely with PA groups at PS end, which supports that PA is a promising functional group for successful coupling with living PMMA anions.

In this study, we introduced a facile synthetic route for well-defined P3HT-*b*-PMMA via coupling reaction between mono-PA-capped P3HT with living PMMA anion. We first prepared mono-PA-capped P3HT by Steglich esterification reaction between mono-hydroxy-P3HT and PA. After successful coupling of PA-capped P3HT and living PMMA anion, unreacted PMMA homopolymers in crude product were completely removed by column chromatography with a mixed solvent of acetic acid and methanol as an eluent. As a result, we obtained very pure P3HT-*b*-PMMA without any homopolymer contamination. The optical property and thin film morphology of pure P3HT-*b*-PMMA having narrow molecular weight distribution were also investigated.

2. EXPERIMENTAL SECTION

Materials. All chemicals (>98% purities) were purchased from Sigma-Aldrich and used without further purification except a monomer and a solvent. Tetrahydrofuran (THF) and methyl methacrylate (MMA) were stirred with CaH_2 for 24 h. Then, MMA was vacuum-distilled and vigorously stirred with trioctylaluminum (TOA) at room temperature for 20 min, while THF was vacuum-distilled in sodium/benzophenone mixture and stirred until the solution became deep violet color, indicating oxygen and moisture-free state. Both of MMA and THF were distilled once again before use. Column chromatography was performed on silica gel (Merck silica gel 60, mesh size 0.2−0.5 μm).

The synthetic scheme for the PA-capped P3HT and P3HT-*b*-PMMA are shown in Scheme 1.

*H/Br-Capped Poly(3-hexyl)thiophene (**1**).* 2-Bromo-3-hexyl-5-iodothiophene (5.14 g, 13.8 mmol) prepared according to the literature[25] was dissolved in THF (20 mL) at 0 °C, and then *iso*-PrMgCl (2.0 M solution in THF 6.90 mL, 13.8 mmol) was added and reacted for 1 h at 0 °C. Ni(dppp)Cl_2 (0.190 g, 0.351 mmol) was added, and polymerization was conducted for 15 min at room temperature after dried THF (40 mL) was additionally injected. To quench the reaction, 10 mL of 5 N HCl was quickly injected, and the solution was stirred for 0.5 h followed by precipitation into methanol. This synthetic route has been well-known for the preparation of fully H/Br functionalized P3HT.[26] The product was fractionated by sequential Soxhlet extraction by using methanol, hexane, dichloromethane (DCM), and THF. We employed DCM fractionated part in this study, which was precipitated into methanol, filtered, and dried under vacuum. **1** (1.19 g, yield 51.9%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (s, 1H), 2.80 (t, 2H), 1.71 (m, 2H), 1.43 (m, 2H), 1.34 (m, 4H), 0.91 (t, 3H). M_n: 9800 (SEC), 4800 (MALDI-TOF); PDI: 1.12. The molecular weight of P3HT measured by SEC calibrated with PS standards is overestimated compared with that determined by MALDI-TOF.[27]

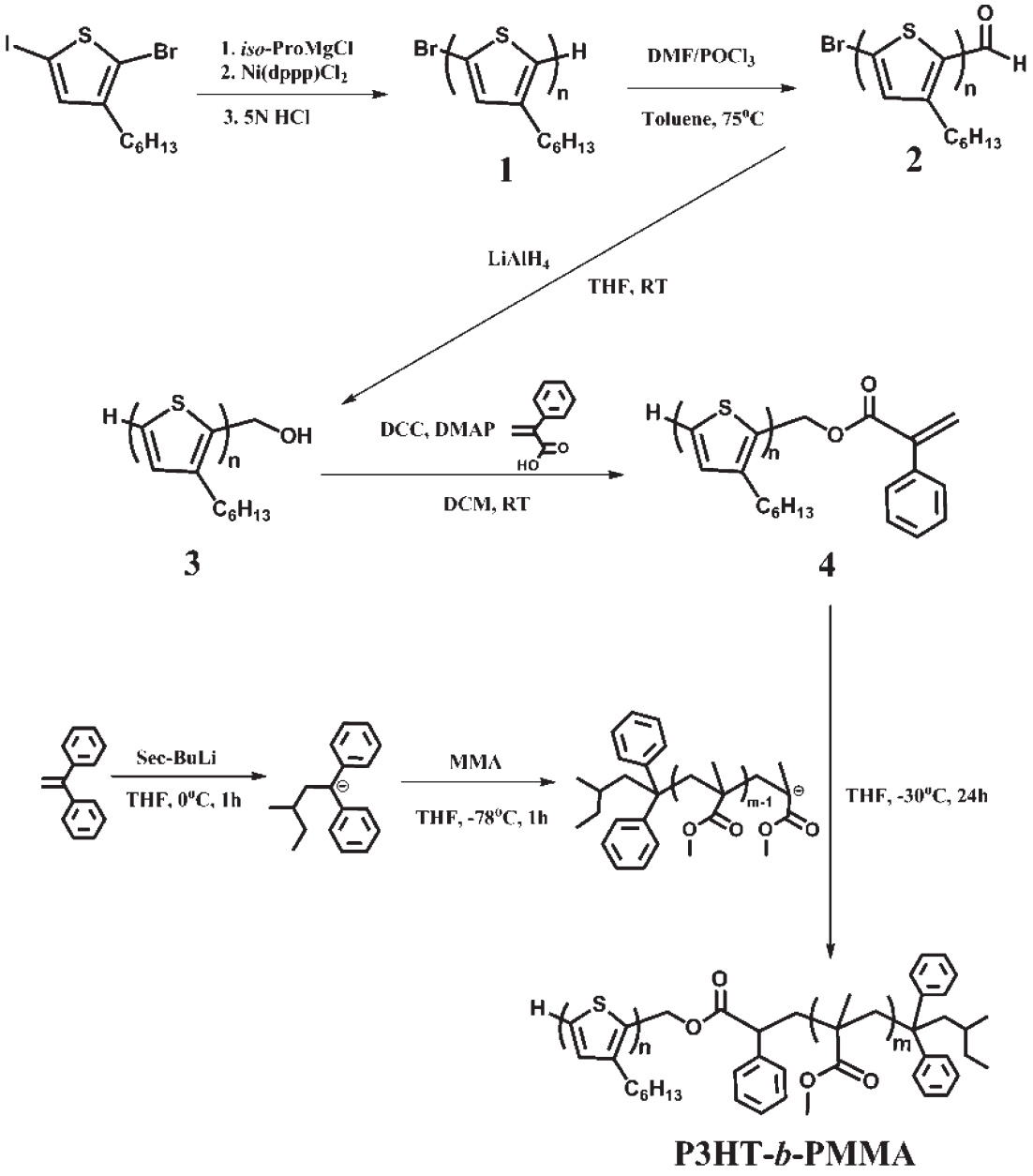
*Mono-Aldehyde-Capped Poly(3-hexyl)thiophene (**2**).* First, we prepared the Vilsmeier reagent as follows. DMF (1.90 mL, 24.5 mmol) was reacted with phosphorus oxychloride ($POCl_3$) (2.00 mL, 21.5 mmol) at 0 °C, and anhydrous toluene solution (90 mL) of **1** (0.600 g, 0.125 mmol) was injected and stirred at 75 °C. After 24 h, the solution was neutralized at room temperature with 70 mL of DI water solution of sodium acetate (2.50 g, 30.5 mmol). Crude product was extracted with chloroform several times, and all of the organic fractions were collected, precipitated into methanol, and dried under vacuum. Pure product was obtained by Soxhlet extraction with methanol and DCM and then dried under reduced pressure. **2** (0.540 g, yield: 90%) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.01 (s, 1H), 6.98 (s, 1H), 2.80 (t, 2H), 1.70 (m, 2H), 1.43 (m, 2H), 1.34 (m, 4H), 0.91 (t, 3H). M_n: 4800 (MALDI-TOF); PDI: 1.12.

*Mono-Hydroxy-Capped P3HT (**3**).* Polymer **2** (0.520 g, 0.108 mmol) was dissolved in 60 mL of anhydrous THF with nitrogen purging. Lithium aluminum hydride ($LiAlH_4$) (1.0 M solution in THF 3.30 mL, 3.30 mmol) was injected dropwise via a syringe and reacted at room temperature for 1 h, and then 3 mL of HCl solution (1.2 M) was added for quenching. The insoluble part was filtered and the filtrate was concentrated, precipitated, and dried under reduced pressure followed by Soxhlet extraction using methanol and DCM. **3** (0.491 g, yield: 94.2%) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.98 (s, 1H), 4.78 (d, 2H), 2.80 (t, 2H), 1.70 (m, 2H), 1.43 (m, 2H), 1.34 (m, 4H), 0.91 (t, 3H). M_n: 4800 (MALDI-TOF); PDI: 1.12.

*Mono-Phenyl Acrylate (PA)-Capped P3HT (**4**).* At first, α-phenylacrylic acid was prepared according to the reference.[24] α-Phenylacrylic acid (0.650 g, 4.39 mmol), 4-(dimethylamino)pyridine (DMAP) (0.129 g, 1.06 mmol), and *N,N′*-dicyclohexylcarbodiimide (DCC) (1.09 g, 5.28 mmol) dissolved in 5 mL of DCM were sequentially injected to anhydrous DCM solution (60 mL) of **3** (0.440 g, 0.0917 mmol), and the reaction was performed at room temperature for 12 h. After the reaction, the white insoluble part was separated by filtration, and the filtrate was concentrated and precipitated into an excess amount of methanol. The reprecipitation with methanol was conducted twice for further purification. **4** (0.381 g, yield: 86.4%) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34−7.44 (m, 5H), 6.98 (s, 1H), 6.39 (s, 1H), 5.94 (s, 1H), 5.37 (s, 2H), 2.80 (t, 2H), 1.70 (m, 2H), 1.43 (m, 2H), 1.34 (m, 4H), 0.91 (t, 3H). M_n: 4800 (MALDI-TOF); PDI: 1.15.

*P3HT-b-PMMA (**5**).* To make an initiator for polymerization of MMA, diphenylethylene (DPE) (1 mL, 5.66 mmol) was reacted with *sec*-BuLi (1.3 M solution in cyclohexane, 3.80 mL, 4.94 mmol) with 30 mL of vigorously purified THF at 0 °C for 1 h. Lithium chloride (LiCl) (30.0 mg, 0.708 mmol) was dried at 170 °C for 24 h under vacuum, and 20 mL of purified THF was distilled. After fully dissolving LiCl in THF, temperature was decreased to −78 °C followed by injection in drops of the initiator (220 μL, 31.2 μmol). MMA (0.340 g, 3.40 mmol) was added and

Scheme 1. Synthetic Scheme for the PA-Capped P3HT and P3HT-*b*-PMMA by Coupling of Living PMMA Anion and PA-Capped P3HT



polymerized for 1 h, and a small quantity of aliquot was extracted. The molecular weight of PMMA precursor was measured by SEC calibrated with PMMA standards. THF solution (10 mL) of dried PA-capped P3HT **4** (0.101 g, 0.0210 mmol) was carefully injected at −78 °C and allowed to stir for 1 h, and then solution temperature was increased up to −30 °C. After 24 h, reaction was terminated by adding 1 mL of anhydrous methanol. The unreacted PMMA homopolymer in the crude product was removed by column chromatography using 20/80 (v/v) acetic acid/methanol mixture as an eluent. Yield: 0.202 g (63.3%); PDI: 1.16; weight fraction of P3HT (^{1}H NMR) in the block copolymer: 0.294.

Characterization. Molecular weight and polydispersity index (PDI) of all the polymers were measured by size exclusion chromatography (SEC: Waters 2414 refractive index detector) with two 300 mm (length) × 7.5 mm (inner diameter) columns including particle size of 5 μm (PLgel 5 μm MIXED-C: Polymer Laboratories) with THF as an eluent and a flow rate of 1 mL/min at 30 °C. 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). It was recorded by linear mode with a nitrogen laser (337 nm), and the accelerating potential was 20 kV. Dithranol was employed as a matrix without adding any salts. Sample was prepared by mixing of 1 mL of polymer solution (0.5 mg/mL) in THF and 2 mL of matrix solution (20 mg/mL) in THF, and the 1 μL of final solution was spotted on the plate. The standards kit (calibration mixture 2: Applied Biosystems) was used for the calibration. ^{1}H NMR spectra were recorded on Bruker digital Avance III 400. The solvent used in ^{1}H NMR for all samples was chloroform-*d* ($CDCl_3$).

The UV−vis absorption spectra of thin film and solution state in chloroform for pure P3HT-*b*-PMMA were recorded on the UV−vis spectrometer (Varian Cary-5000). Thin film of the block copolymer was prepared by spin-coating of chloroform solution (0.9 wt %) on a silicon

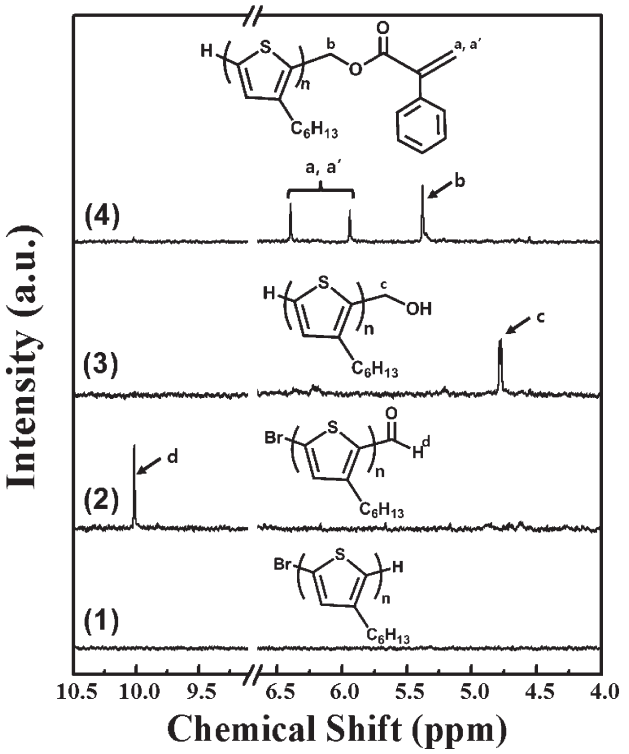


Figure 1. ^{1}H NMR spectra for P3HTs with various functional groups at the chain end: (1) H/Br-capped P3HT **1**, (2) mono-aldehyde-capped P3HT **2**, (3) mono-hydroxy-capped P3HT **3**, and (4) mono-α-phenyl acrylate (PA)-capped P3HT **4**.

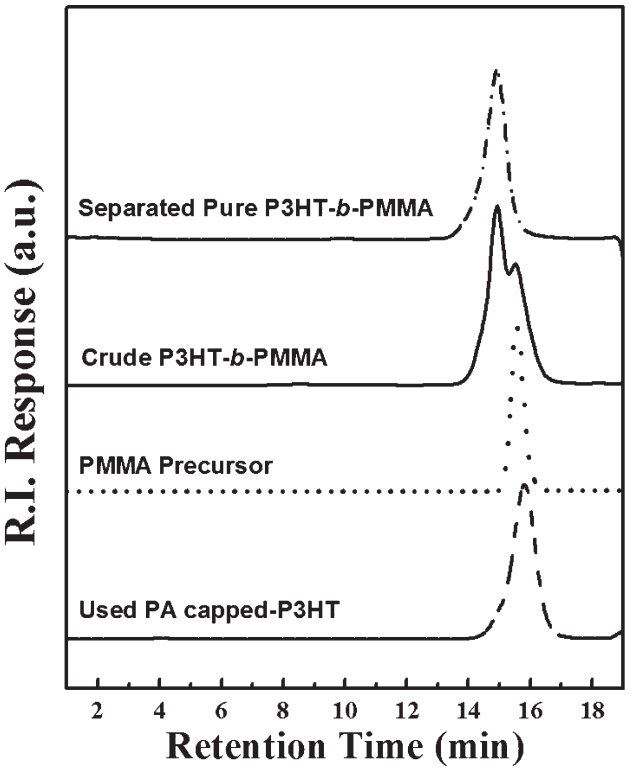


Figure 2. SEC traces for PA-capped P3HT (dashed line), extracted PMMA precursor (dotted line), crude product (solid line), and pure P3HT-*b*-PMMA (dash-dotted line) after the removal of unreacted PMMA.

substrate at a rotating speed of 2000 rpm for 5 s. Then, it was placed into a Petri dish under saturated chloroform vapor and covered. Chloroform vapor was slowly removed at room temperature for 12 h. The surface morphology of the thin film was investigated by tapping mode atomic force microscopy (AFM: Digital Instrument, Multimode Nanoscope III). Grazing incidence wide-angle X-ray scattering (GIWAXS) was conducted at the 4C2 beamline of the Pohang Light Source (PLS). A sample-to-detector distance was 119.5 mm. The wavelength of the X-ray beam was 0.138 nm, and 2D GIWAXS patterns were recorded on a CCD detector (Princeton Instrument). The employed incidence angle and exposure time were 0.16° and 60 s, respectively.

3. RESULTS AND DISCUSSION

Figure 1 shows ^{1}H NMR spectra of P3HTs with various functional groups at the chain end (**1**−**4**). After the Vilsmeier reaction, a new singlet peak of $\delta \sim 10.01$ ppm appeared, indicating the successful introduction of aldehyde group. The reduction of this aldehyde group was completely performed by use of excess reducing agent, $LiAlH_4$. A new doublet of $\delta \sim 4.78$ ppm appeared while the peak at $\delta \sim 10.01$ ppm was not observed. Finally, mono-PA-capped P3HT **4** was prepared via Steglich esterification between mono-hydroxy-capped P3HT **3** and α-phenylacrylic acid. The complete conversion of the functional group was confirmed by ^{1}H NMR spectra change that the peak of $\delta \sim 4.78$ ppm (peak c) was shifted to $\delta \sim 5.37$ ppm (peak b), and two new singlets (peak a and a′) arising from the hydrogen at the double bond of PA moiety were observed at $\delta \sim 5.94$ and ∼6.39 ppm.

The mono-PA-capped P3HT **4** was coupled with living PMMA anions to form P3HT-*b*-PMMA. SEC traces of mono-PA-capped P3HT, PMMA precursor, crude product, and pure P3HT-*b*-PMMA after the removal of unreacted PMMA homopolymers are shown in Figure 2. The mono-PA-capped P3HT and extracted PMMA precursor (M_n = 11 000) had narrow molecular weight distribution of PDI = 1.15 and 1.04, respectively. We used slightly excess quantity of living PMMA anion (1.5 equiv relative to PA-capped P3HT) to ensure complete coupling of PA-capped P3HT. Thus, the crude product exhibited a shoulder corresponding to PMMA precursor, but this unreacted PMMA was successfully removed by column chromatography with mixed solvents of acetic acid/methanol (20/80, volume ratio) as an eluent. The SEC peak for pure P3HT-*b*-PMMA was clearly shifted to higher molecular weight region compared with employed PMMA precursor and mono-PA-capped P3HT and had narrow molecular distribution (PDI = 1.16) without any byproducts.

Figure 3 shows ^{1}H NMR spectra of P3HT-*b*-PMMA after removal of unreacted excess PMMA. While the peak ∼5.37 ppm remained, the peaks of ∼5.94 and ∼6.39 ppm corresponding to a and a′ in PA moiety (see Figure 1) disappeared completely after the coupling reaction. This result supports that all the PA functional groups in P3HT were reacted fully. The weight fraction of P3HT in the block copolymer was calculated to be 0.294 from the ratio of peak d and peak a in Figure 3a. This value is consistent with the expected one (0.304) when we consider the molecular weights of PA-capped P3HT (M_n = 4800) and PMMA precursor (M_n = 11 000).

UV−vis absorption spectra of chloroform solution and thin film of P3HT-*b*-PMMA are shown in Figure 4. Both solution and solid state of P3HT-*b*-PMMA indicated very similar spectra to pristine P3HT or other P3HT-containing block copolymers.[14−17,20−23]

The maximum absorption for solution state was ~448 nm, while the absorption for thin film was red-shifted compared with that of solution state. The thin film exhibited two strong absorption peaks at ~522 and ~553 nm related to $\pi-\pi^*$ transition and one weak absorption at ~603 nm originating from P3HT interchain interactions.[28] This means that electronic structure of P3HT was preserved, even though insulating PMMA exists in the block copolymer.

Figure 5 gives phase contrast AFM images and 2D GIWAXS pattern of P3HT-*b*-PMMA thin film. The nanofibril structure was clearly found. Also, two distinct bright and dark regions were shown, which correspond to P3HT and PMMA phase, respectively. The inset image in Figure 5a indicates the fast Fourier transform (FFT) of the AFM image, from which a ring pattern having two arcs with strong intensity was observed.

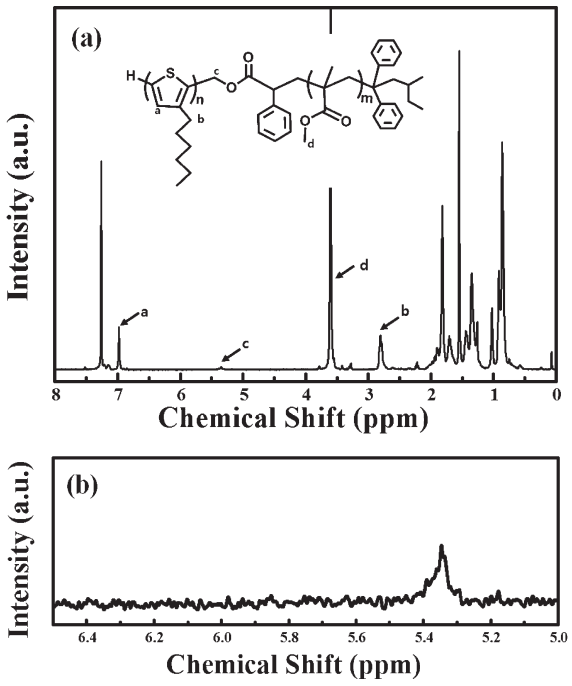


Figure 3. (a) Full and (b) expanded from 5.0 to 6.5 ppm ^{1}H NMR spectra of pure P3HT-*b*-PMMA.

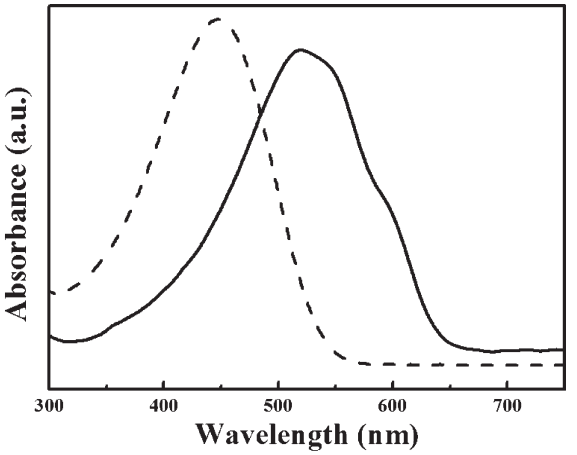


Figure 4. UV—vis absorption spectra for chloroform solution (dashed line) and thin film (solid line) prepared by spin-coating of neat P3HT-*b*-PMMA.

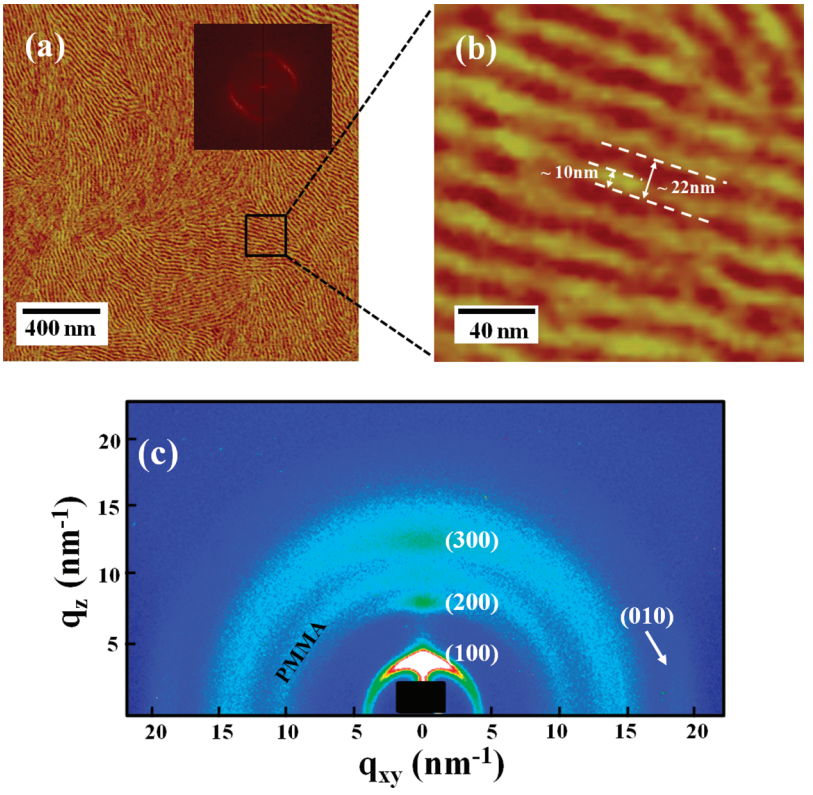


Figure 5. Phase contrast AFM images (a) 2 μm × 2 μm scale with inset of FFT image for acquired phase image, (b) enlarged (0.2 μm × 0.2 μm scale) image of (a), and (c) 2D GIWAXS pattern of P3HT-*b*-PMMA thin film.

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The total domain spacing was determined as ~22 nm from FFT image as well as enlarged image (Figure 5b). The bright P3HT microdomain was ~10 nm in width, which is quite close to the P3HT fibril width for P3HT homopolymer with the similar molecular weight (M_n = 4800) in P3HT-*b*-PMMA.[29] GIWAXS patterns were obtained to investigate the orientation of P3HT backbones in P3HT-*b*-PMMA thin film. As shown in Figure 5c, we observed the GIWAXS patterns arising from both of PMMA and P3HT blocks. While the isotropic ring was originated from the amorphous PMMA chains, three distinct spots along the q_z, which correspond to (100), (200), and (300) diffractions, respectively, and (010) diffraction along the in-plane direction (q_{xy}) indicated that the P3HT lamellae were stacked as the edge-on structure.

4. CONCLUSIONS

We have synthesized P3HT-*b*-PMMA by coupling reaction between PA-capped P3HT and living PMMA anion. The PA-capped P3HT was completely coupled with the PMMA anion, so that synthesized P3HT-*b*-PMMA exhibited very narrow molecular weight distribution, when we removed completely unreacted PMMA homopolymer. The coupling reaction employed in this study is simple and efficient. Moreover, it could be applicable to synthesis for P3HT-containing block copolymer with various kinds of coil segments. Because PMMA chains in the block copolymer are easily removable by UV irradiation followed by rinsing with acetic acid, we expected that this well-defined P3HT-*b*-PMMA could be used as P3HT nanopatterns with 10−20 nm length scale, which would be applied to organic electronic devices such as OPV.

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