Facile Syntheses, Morphologies, and Optical Absorptions of P3HT Coil-Rod-Coil Triblock Copolymers

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ABSTRACT: Here we report syntheses, photophysical properties, and morphologies of a series of coil-rod-coil ABA triblock copolymers containing highly regioregular poly(3-hexylthiophene) (P3HT) as the central rod block. A new methodology, based on the coupling reaction between living polymeric anions [polystyrene, polyisoprene, and poly(methyl methacrylate)] and aldehyde terminated P3HT, was successfully developed to synthesize the triblock copolymers with low polydispersities. This coupling reaction was effective for building blocks with a variety of molecular weights; therefore, a good variation in compositions of the triblock copolymers could be feasibly achieved. The non-P3HT coil segments and the solvents were found to exhibit noticeable effects on morphologies of the spin-coated thin films. Attachment of the coil segments to P3HT did not change the optical absorption of the P3HT segment as the block copolymers were dissolved in solution regardless the chemical structure and the molecular weight of the coil segment. Interestingly, different UV–vis absorption behaviors were observed for the spin-coated thin films of the block copolymers, which closely related to their morphologies. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 3311–3322, 2010

KEYWORDS: anionic polymerization; block copolymer; conducting polymers; self-assembly; UV–vis spectroscopy

INTRODUCTION Recently, poly(3-hexylthiophene) (P3HT) has been intensively studied for their applications in flexible electronic devices, such as field effective transistors (FETs) and photovoltaics owing to its good processability and high charge carrier mobility.[1] A good variety of novel thiophene-based materials had also been synthesized and characterized to enhance the device performances.[2–6] For a polymer solar cell, the power conversion efficiency is significantly affected by exciton dissociation and charge transportation within the photoactive layer. To improve the device performance, large interfacial areas between electron donors and acceptors for exciton dissociation, as well as continuous pathways for effective charge transportation are desired.[7] Block copolymers are well-known for their microphase separation behavior to facilitate well-organized, self-assembled nanostructures, such as lamellar and cylindrical morphologies, which could provide large interfacial areas between domains consisted of different blocks and continuity of domains consisted of the same segment.[8] Therefore, the use of P3HT block copolymers is expected to improve the device performance through the possibility of morphology optimization within the photoactive layer. Moreover, the incorporation of coil segment may further improve solubility and mechanical properties of P3HT.[9]

Syntheses of regioregular P3HT (rr-P3HT) block copolymers can be generally categorized into macroinitiator methods and coupling methods. In the former approach, one or both terminal(s) of P3HT were modified to possess initiating species to generate P3HT macroinitiator for the following living polymerizations, such as atom transfer radical polymerization (ATRP),[9–11] nitroxide mediated polymerization (NMP), reversible addition fragmentation chain transfer (RAFT) polymerization,[12] ring-opening polymerization (ROMP),[13] and anionic polymerization.[14] When ATRP, NMP, RAFT, or ROMP was employed, the molecular weight of the subsequently grown non-P3HT segment, such as polystyrene (PS), polyisoprene (PI), and poly(methyl methacrylate) (PMMA), was usually small due to the slow kinetics and the polydispersities (PDI) became broader with increasing molecular weight. Although a good variety of P3HT block copolymers have been synthesized, the requisites of suitable matches between initiating species and monomers for highly efficient initiation would limit the selection of monomers for a specific P3HT macroinitiator. For the later approach, the non-P3HT segment having an active chain end was synthesized separately and this segment was then attached to end-functionalized P3HT through the coupling reaction between the active chain end of the non-P3HT segment and the terminal groups of P3HT.[15–17] Two advantages of this method are: first, each building block can be well defined and characterized before coupling; and second, a wide variety of chemical structures and molecular weights of the non-P3HT segment could be introduced to the resulted block copolymers using
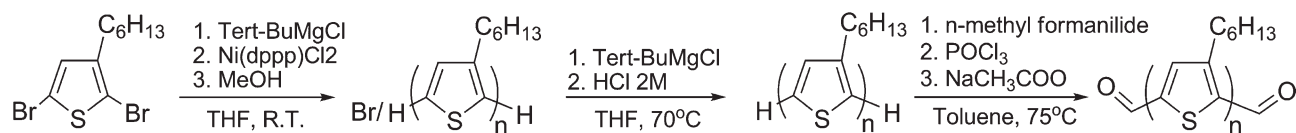
SCHEME 1 End functionalization of regioregular P3HT.

the same P3HT segment. Nevertheless, the efficiency of the coupling reaction was the key to successful syntheses of block copolymers.

It has been observed that the chemical structures and the molecular weights of the non-P3HT segments affected the morphologies, the optical absorptions, and the electronic properties of P3HT block copolymers in solid state, which were critical to the performance of the corresponding photovoltaic devices. Most of the studies concerned samples prepared from solvent casting; therefore, the molecular arrangements observed were mainly governed by thermodynamic equilibrium. Except the copolymers in strong segregation regimes, nanofibrils were generally found as a result of strong π–π stacking of P3HT segment.[12,15,18] Nevertheless,

fast-evaporation spin-coating process, the mostly used method for solar cell fabrication, might lead to different morphologies and optical properties of the thin films since kinetic features should play important roles. However, very limited works regarding the effect of non-P3HT segment on the spin-coated thin films of the P3HT block copolymers have been reported; and systematic studies were lacking.

In this article, we report the syntheses of highly regioregular P3HT ABA triblock copolymers with P3HT as the center block based on the coupling reaction between living polymeric anions and a regioregular P3HT bi-end functionalized with aldehydes (denoted as P3HT-CHO/CHO). The non-P3HT segments, including PS, PI, and PMMA, with accurate controlled molecular weights and narrow polydispersities were
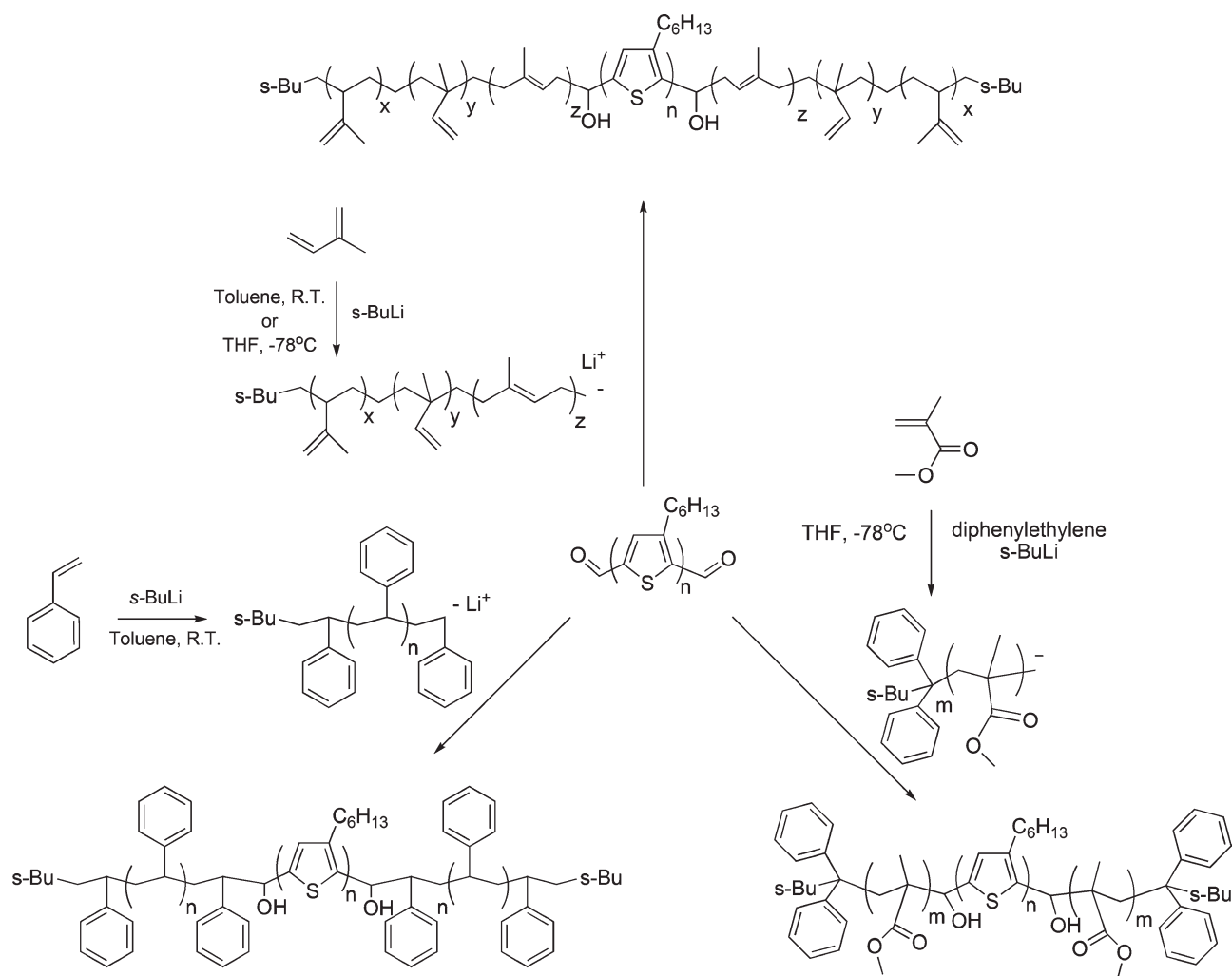
SCHEME 2 Synthesis of P3HT triblock copolymers through coupling reaction.
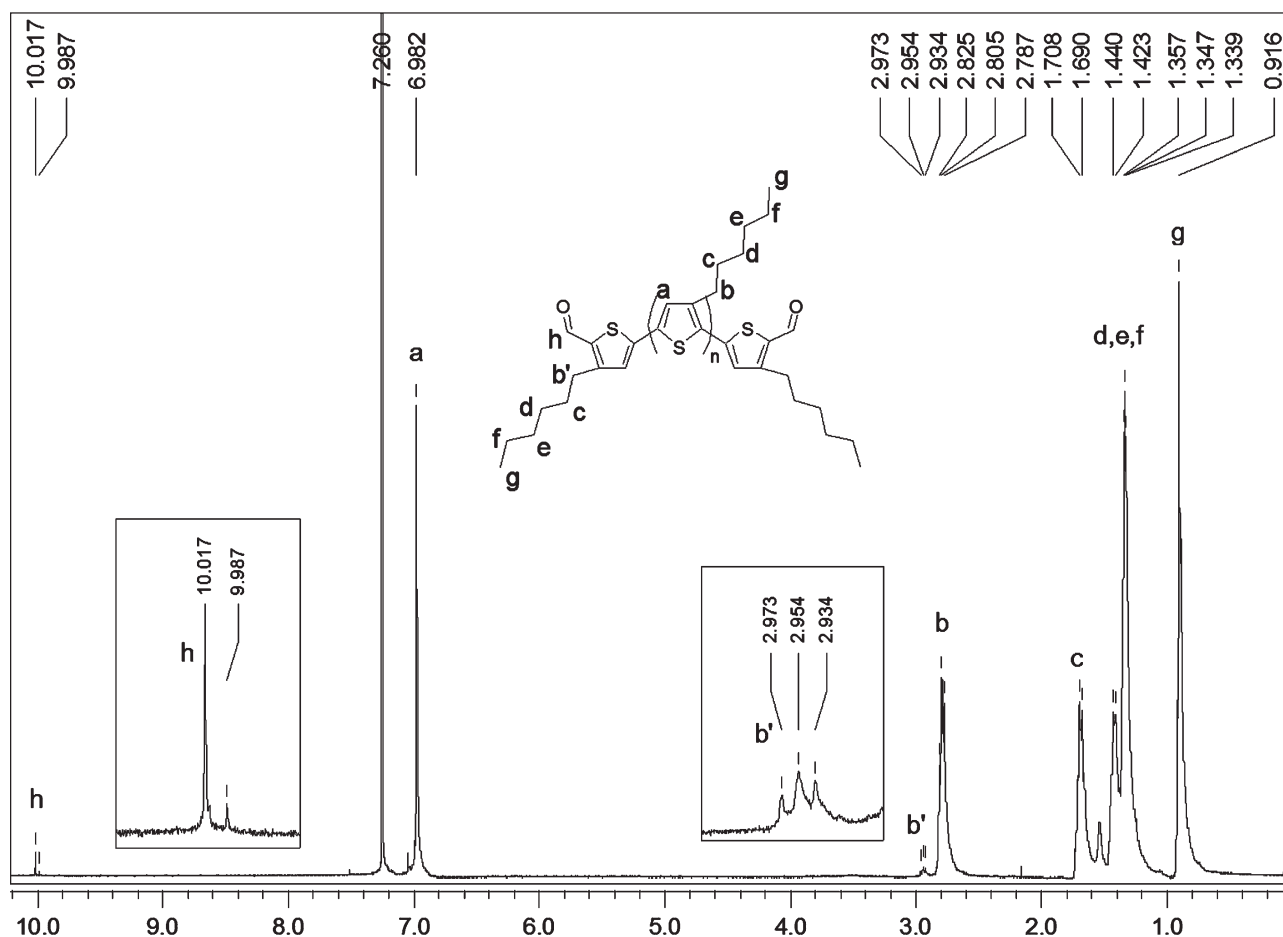
FIGURE 1 ^{1}H NMR Spectra of P3HT-CHO/CHO in d-chloroform.

synthesized from anionic polymerization. Grignard Metathesis polymerization (GRIM) was empolyed to synthesis the regioregular P3HT with a H at one terminal thophene and a Br at the other terminal thiophene, denoted as P3HT-H/Br, which was then converted to the P3HT-CHO/CHO by postpolymerization formylation (Scheme 1). The aldehyde groups were found to be very reactive toward various polymeric anions to allow a wide range of chemical structures and molecular weights in the non-P3HT segments (Scheme 2). The morphologies and the photophysical properties of the spin-coated thin films of the resulted block copolymers were found to be affected by the chemical structure of the non-P3HT segment as well as the spin-coating condition.

RESULTS AND DISCUSSIONS

Synthesis of P3HT-CHO/CHO

Several methods for end-group functionalization of P3HT to facilitate the syntheses of P3HT-based diblock or triblock copolymers[19,20] showing new microstructures have been reported. As the reaction of aldehyde group toward living polymeric anions is highly effective[21,22]; the coupling method employing aldehyde-terminated P3HT and polymeric anions in this article could open a new route for the synthesis of P3HT diblock and triblock copolymers in high yield. In addi-

tion, anionic polymerization could produce polymers with accurate controlled molecular weights and narrow polydispersities so that the resulting block copolymers with well-defined compositions could be feasibly synthesized to achieve order microstructure.

GRIM method was employed to synthesize highly regioregular P3HT with narrow polydispersity.[23,24] In general, two different forms of the P3HT were obtained as categorized by the structure of the terminal thiophenes: the majority has a hydrogen at 2- or 5-positions of one terminal thiophene and a bromine at the other, denoted as P3HT-H/Br; while the minority has hydrogens at both terminal thiophenes, denoted as P3HT-H/H. Conversion of P3HT-H/Br to P3HT-H/H is critical for the synthesis of pure triblock copolymers since the formylation can only be performed on the hydrogen at the terminal thiophene. The conversion was done through a magnesium halogen exchange reaction between *tert*-butyl magnesium chloride and the Br at the terminal thiophene of P3HT, which was confirmed by ^{1}H NMR and MALDI-TOF spectra (Supporting Information Figs. S1 and S2). The Vilsmeier formylation of P3HT-H/H was then carried out to afford bi-end functionalized, aldehyde-terminated P3HT-CHO/CHO,[20] whose ^{1}H NMR spectrum was illustrated in Figure 1 showing two sharp peaks at 10.02 and 9.99 ppm corresponding to CHO at 2- and
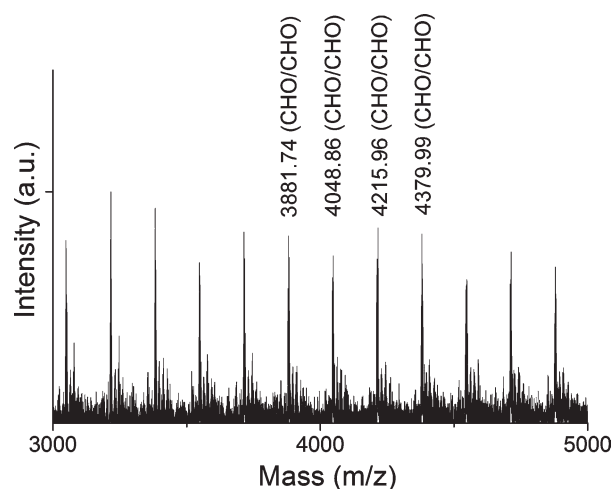
FIGURE 2 MALDI-TOF spectra of P3HT-CHO/CHO.

5-positions of the terminal thiophene, respectively.[20,25] The chemical shift of the CH_2 in the hexyl side chain attached to the terminal thiophenes moves from 2.62 ppm in the P3HT-H/H to 2.95 ppm in the P3HT-CHO/CHO. In the MALDI-TOF spectra as illustrated in Figure 2, the mass (m/z) representing a certain P3HT chain was close to the theoretical formula weight of a P3HT-CHO/CHO; for example, $m/z = 4048.86$ is close to $(166.3 \times n) + 29 + 29$ as $n = 24$. The above results suggested the completion of the formylation of P3HT-H/H to P3HT-CHO/CHO with a yield of 95%.

Synthesis of Block Copolymers via Coupling Reaction

Triblock copolymers with various compositions and molecular weights were obtained through coupling different non-P3HT blocks with P3HT-CHO/CHO. Characterization of the building blocks could be done separately in prior to the coupling reaction, which is beneficial to the control of compositions and molecular weights of desired copolymers. Table 1 summarized the triblock copolymers synthesized in this work. PS, PI, and PMMA anions were synthesized from anionic polymerization with predictable molecular weights and narrow polydispersity. To ensure the achievement of complete coupling reaction to obtain pure triblock copolymers without contamination from diblock copolymers, excess amount of polymeric anions (the molar ratio of P3HT to PS
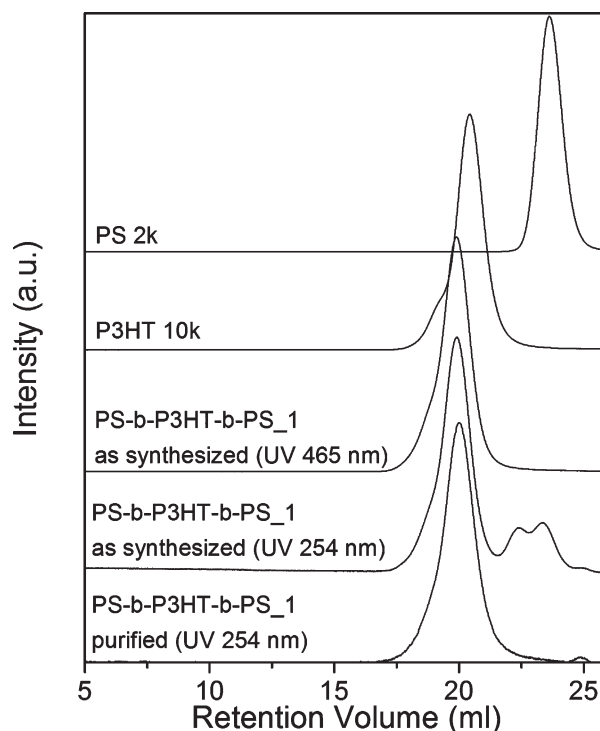

FIGURE 3 Normalized GPC traces of triblock copolymer PS-b-P3HT-b-PS_1 (as synthesized and after purification) and corresponding building polystyrene and P3HT.

(or PI or PMMA) = 1:5) was intentionally added. This strategy could also simplify purification steps since P3HT homopolymers should be completely reacted and only excess non-P3HT homopolymers need to be removed.

Figure 3 shows the gel permeation chromatography (GPC) traces of PS-b-P3HT-b-PS_1 and the corresponding homopolymers. The crude product before purification showed the existence of excess PS and coupled PS homopolymers indicated by two small peaks presented in UV 254 nm signal but absent in UV 465 nm signal. The PS homopolymers were then easily removed by reprecipitation of the crude products in acetone. The M_n (15,053, PDI = 1.21) of PS-b-P3HT-b-PS_1, obtained from GPC measurement, was reasonably close to the sum of the M_n of P3HT (10,855, PDI = 1.21) and twice the M_n of PS

TABLE 1 Compositions and Molecular Weight Distributions of P3HT Triblock Copolymers

Polymer	P3HT M_n (PDI)	Non-P3HT M_n (PDI)	Copolymer M_n (PDI)	Expected M_n[a]
PS-b-P3HT-b-PS_1	10,855 (1.21)	1772 (1.12)	15,053 (1.21)	14,399
PS-b-P3HT-b-PS_2	10,320 (1.23)	4257 (1.05)	19,453 (1.25)	18,834
PS-b-P3HT-b-PS_3	10,855 (1.21)	9533 (1.05)	26,676 (1.35)	29,921
PI-b-P3HT-b-PI_1[b]	10,855 (1.21)	6980 (1.05)	24,206 (1.23)	24,815
PI-b-P3HT-b-PI_2[b]	19,578 (1.4)	7942 (1.04)	34,288 (1.29)	35,462
PI-b-P3HT-b-PI_3[c]	10,855 (1.21)	6876 (1.09)	22,710 (1.34)	24,607
PMMA-b-P3HT-b-PMMA	12,762 (1.20)	4287 (1.05)	18,855 (1.15)	21,336

[a] Expected $M_n = M_n$ of P3HT block + 2 × M_n of non-P3HT block.
[b] PI contains the adducts from 1,4- and 3,4-additions.
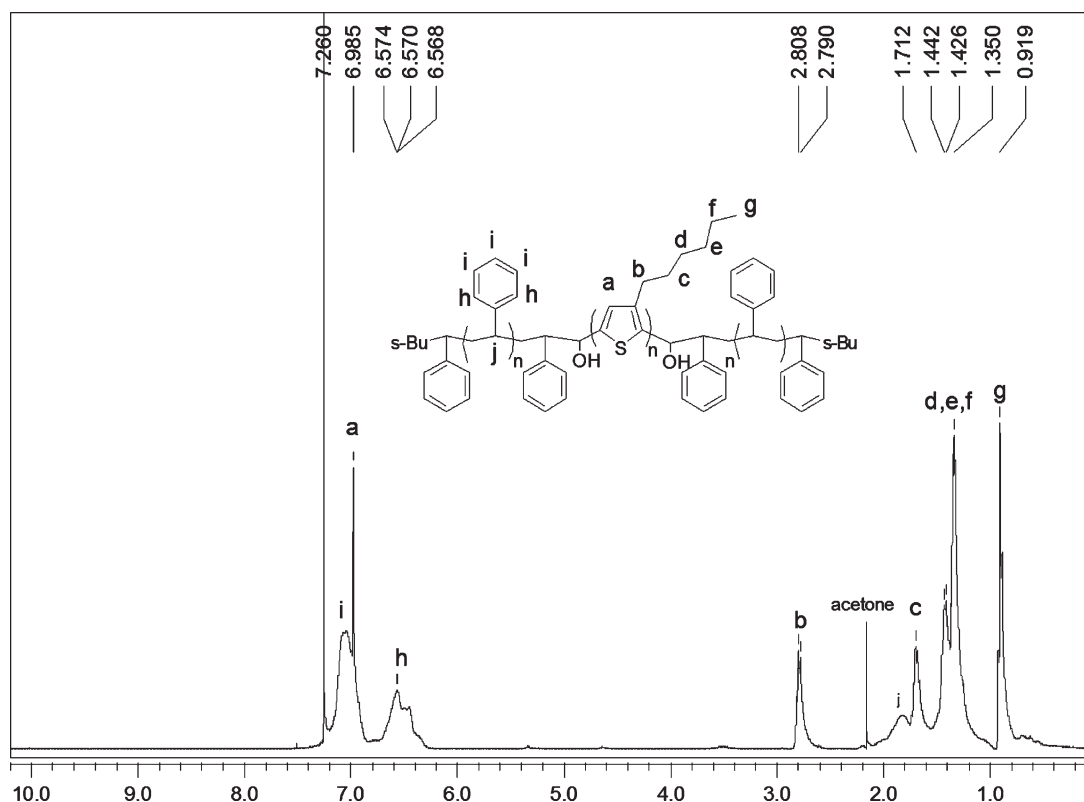[c] The majority of PI is from 1,2/3,4 addition.

FIGURE 4 ^{1}H NMR spectra of PS-b-P3HT-b-PS_2 in d-chloroform.

(1772, PDI = 1.12). The narrow polydispersity of the resulting block copolymers suggested that the completion of the coupling reaction without the existence of diblock copolymers. The absence of aldehyde peaks (10.02 and 9.99 ppm) and the presence of broad PS peaks (peaks h and i in ^{1}H NMR spectrum of the triblock copolymer in *d*-chloroform (Fig. 4) further confirmed the success of the coupling reaction.

PI consisted of the adducts of both 1,4-addition and 3,4-addition, denoted as PI(1,4/3,4), was also successfully coupled with P3HT-CHO/CHO to afford PI-b-P3HT-b-PI_1 and PI-b-P3HT-b-PI_2. Trace amount of tetrahydrofuran (THF; as polar additive) was intentionally added to promote the adducts from 3,4-addition in the resulted PI to ~50%mol. The pendant double bonds from 3,4-addition would be useful for further postpolymerization chemistry to functionalize the non-P3HT block. Figure 5 shows the GPC traces of PI-b-P3HT-b-PI_1 and the corresponding homopolymers P3HT (M_n = 10,855, PDI = 1.21) and PI (M_n = 6980, PDI = 1.05). M_n of the triblock copolymer was 24,206, reasonably close to the sum of the M_n of P3HT and twice the M_n of PI. The ^{1}H NMR spectrum of PI-b-P3HT-b-PI_1 in *d*-chloroform (Fig. 6) showing the absence of aldehyde peaks (10.02 and 9.99 ppm) and the presence of PI peaks (**h** associated with PI from 1,4-addition and **j** for PI from 3,4-addition) further confirmed the success of the coupling reaction.

To evaluate the commonness of this coupling method, a batch of anionic polymerization of isoprene was carried out at −78 °C in THF to afford a PI anion consisted of the
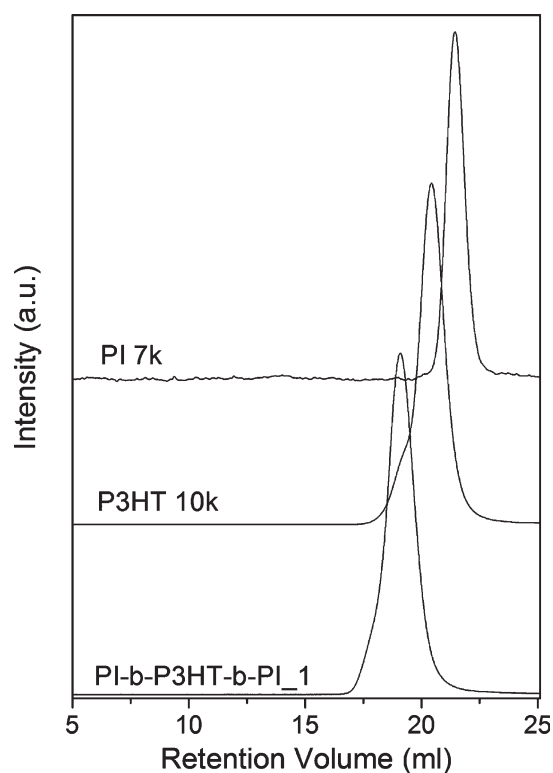

FIGURE 5 Normalized GPC traces of triblock copolymer PI-b-P3HT-b-PI_1 after purification (M_n = 24,202, PDI = 1.25) and the corresponding polyisoprene (1,4/3,4 addition) (M_n = 6980, PDI = 1.05) and P3HT (M_n = 10,855, PDI = 1.21).
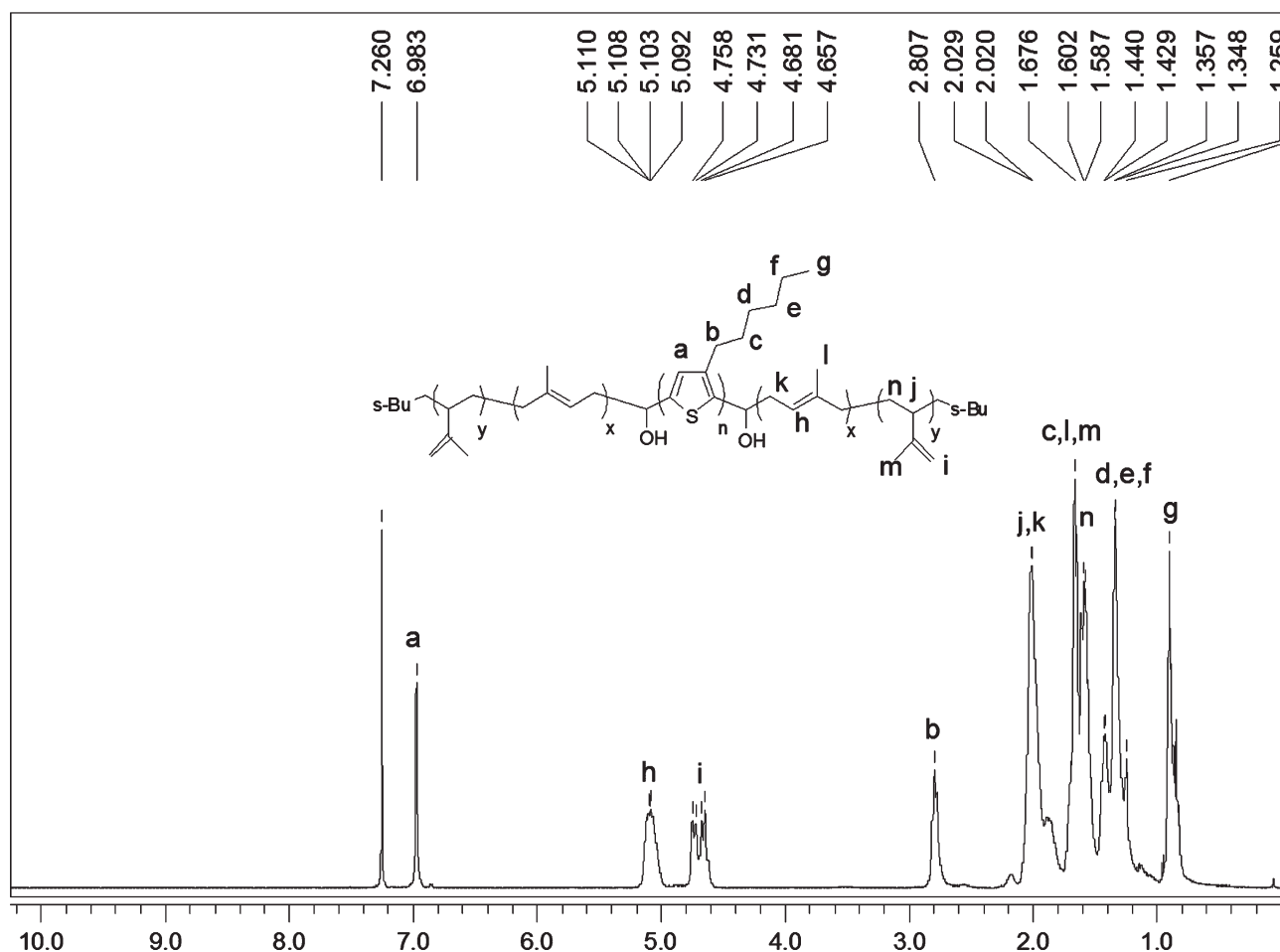
FIGURE 6 ^{1}H NMR Spectra of PI-b-P3HT-b-PI_1 in d-chloroform.

adducts of 1,2-addition and 3,4-addition, denoted as PI(1,2/3,4), and the coupling reaction was then performed at low temperatures (<-30 °C). The GPC traces of the resulting block copolymer PI-b-P3HT-b-PI_3 and the corresponding homopolymers are shown in Figure 7. The measured M_n (22,710, PDI = 1.34) of PI-b-P3HT-b-PI_3 was quite close to the predicted M_n, indicating the success of coupling reaction of PI anions and aldehydes at low temperature in THF. ^{1}H NMR spectra of the block copolymer (Supporting Information Fig. S3) suggested that the PI segment consisted approximately of the adducts from 1,2-addition (44 mol %) and from 3,4-addition (56 mol %).

The reactivity of a polymeric anion is known to strongly depend on the chemical structure of the monomer. To further investigate the effectiveness of the coupling reaction between a less-reactive polymeric anion and aldehydes, a PMMA anion was synthesized via anionic polymerization at -78 °C in THF and the coupling reaction was then carried out in the same environment. The GPC trace of the resulting copolymer (Fig. 8) obviously shifts to the range of higher molecular weight in comparison with that of the corresponding P3HT-CHO/CHO. Unlike the triblock copolymers containing PS or PI, the M_n (18,855, PDI = 1.15) of the resulted co-

polymer measured from GPC is smaller than the predicted M_n (21,336). Figure 9(a,b) show the ^{1}H NMR spectra of the P3HT-CHO/CHO and the block copolymer PMMA-b-P3HT-b-PMMA. The presence of the signal corresponding to methyl methacrylate [proton h in Fig. 9(b)] provides a further evidence for the occurrence of the coupling reaction. By comparing the integral area of the aldehyhde peak in Figure 9(a) and in Figure 9(b), about 51% of the aldehyde end-groups were estimated to couple with the PMMA anions. Hence, both diblock and triblock copolymers should present in the product. The coupling reaction is suggested to be less effective toward less-reactive PMMA anion when compared with PI or PS anion.

Morphologies and Photophysical Properties of Spin-Coated Thin Films

To investigate the morphologies and photophysical properties of P3HT triblock copolymer thin films resembling the photoactive layer in the photovoltaic cell, the copolymers were spin coated onto PEDOT:PSS coated glass substrates. Figure 10 are the atomic force microscopy (AFM) images of the spin-coated films of pristine P3HT and the P3HT triblock copolymers without annealing. Regarding the pristine P3HT, fibrils were observed for all the thin films with different explicitness. The fribils were not clearly depicted when the
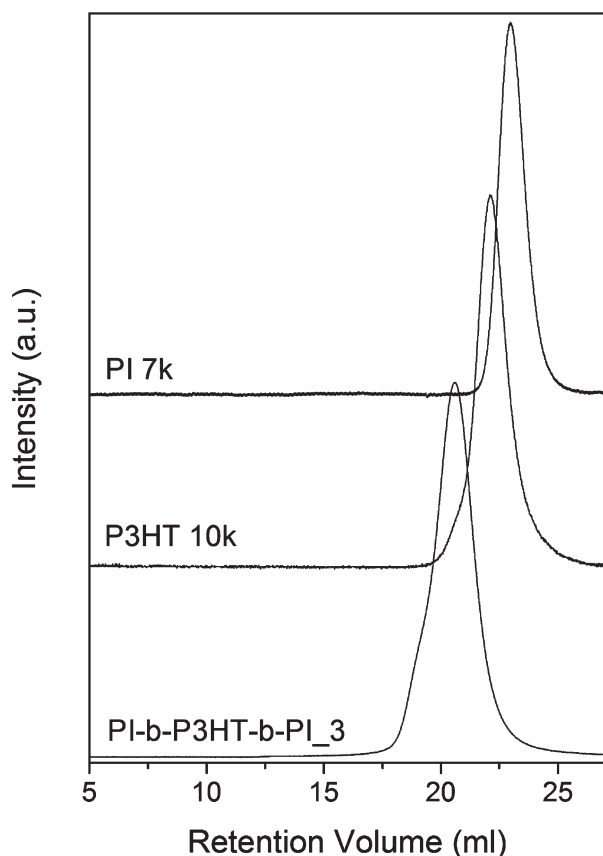
FIGURE 7 Normalized GPC traces of triblock copolymer PI-b-P3HT-b-PI_3 after purification (M_n = 22,710, PDI = 1.34) and the corresponding polyisoprene (1,2/3,4 addition) (M_n = 6876, PDI = 1.09) and P3HT (M_n = 10,855, PDI = 1.21).

nization were found for the thin film spin coated from the toluene solution [Fig. 10(k)]. When casted from the dicholorobenzene solution [Fig. 10(k)], the thin film revealed wide fibrils packing in a high density.

Based on the compatibility between P3HT and non-P3HT segment, the Flory-Huggins parameter χ for the combination of PMMA and P3HT was estimated to be the highest, followed by the combination of PI and P3HT, while the combination of PS and P3HT would offer the smallest χ. Although the combination of PI and P3HT possesses a moderate χ, the spin-coated thin film of the triblock copolymer exhibited long fibrils arranging in an ordered lamellar fashion as PMMA-b-P3HT-b-PMMA did. This better-than-expected self-assembly might associate with the much lower glass transition temperature of PI when compared with PMMA and PS. The highly flexible PI may enhance the mobility of P3HT segment to facilitate the formation of long fibrils and enhance the stacking of P3HT. Meanwhile, the combination of PS and P3HT was classified as weak segregation, in which some degree of mixing of PS and P3HT could hinder the formation of long fibrils with order arrangement.
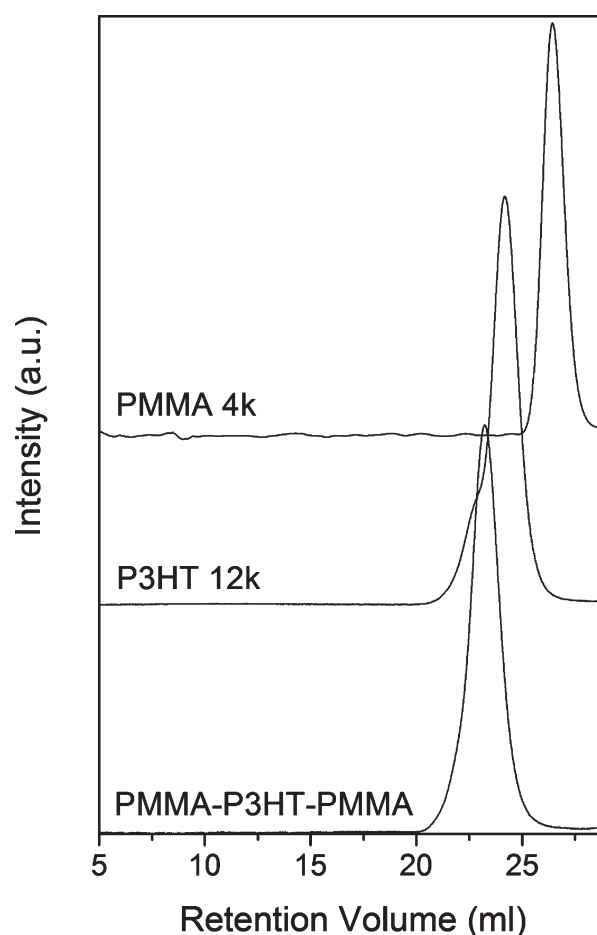
thin film was spin coated from the chloroform solution [Fig. 10(a)]. However, the fibrils appeared more obviously for the thin film spin coated from the toluene solution [Fig. 10(b)], and became more pronounced (with the length up to 100 nm) for the thin film spin coated from the dichlorobenzene solution [Fig. 10(c)]. For PS-b-P3HT-b-PS_2, all the thin films spin coated from the chloroform solution [Fig. 10(d)], the toluene solution [Fig. 10(e)] and the dicholorobenzene solution [Fig. 10(f)] showed less-organized morphologies with P3HT assembled as short worms. For PI-b-P3HT-b-PI_1, the thin film spin coated from the CHCl₃ solution [Fig. 10(g)] exhibited long fibrils with the length over 100 nm and the diameter about 10 nm. Both the thin films spin coated from the toluene solution [Fig. 10(h)] and the dicholorobenzene solution [Fig. 10(i)] depicted similar morphologies showing longer fibrils arranged in a parallel fashion, resembling a lamellar morphology, although the thin film from the dichlorobenzene solution was expected to show a more well-organized morphologies for the higher boiling point of dichlorobenzene. For PMMA-b-P3HT-b-PMMA, short fibrils arranging in a parallel fashion within small areas were observed for the thin film spin coated from the CHCl₃ solution [Fig. 10(j)], resembling a lamellar morphology with a short range order. Longer fibrils with a higher ordered orga-

FIGURE 8 Normalized GPC traces of triblock copolymer PMMA-b-P3HT-b-PMMA after purification (M_n = 18,855, PDI = 1.15) and the corresponding PMMA (M_n = 4287 PDI = 1.05) and P3HT (M_n = 12,762, PDI = 1.20).
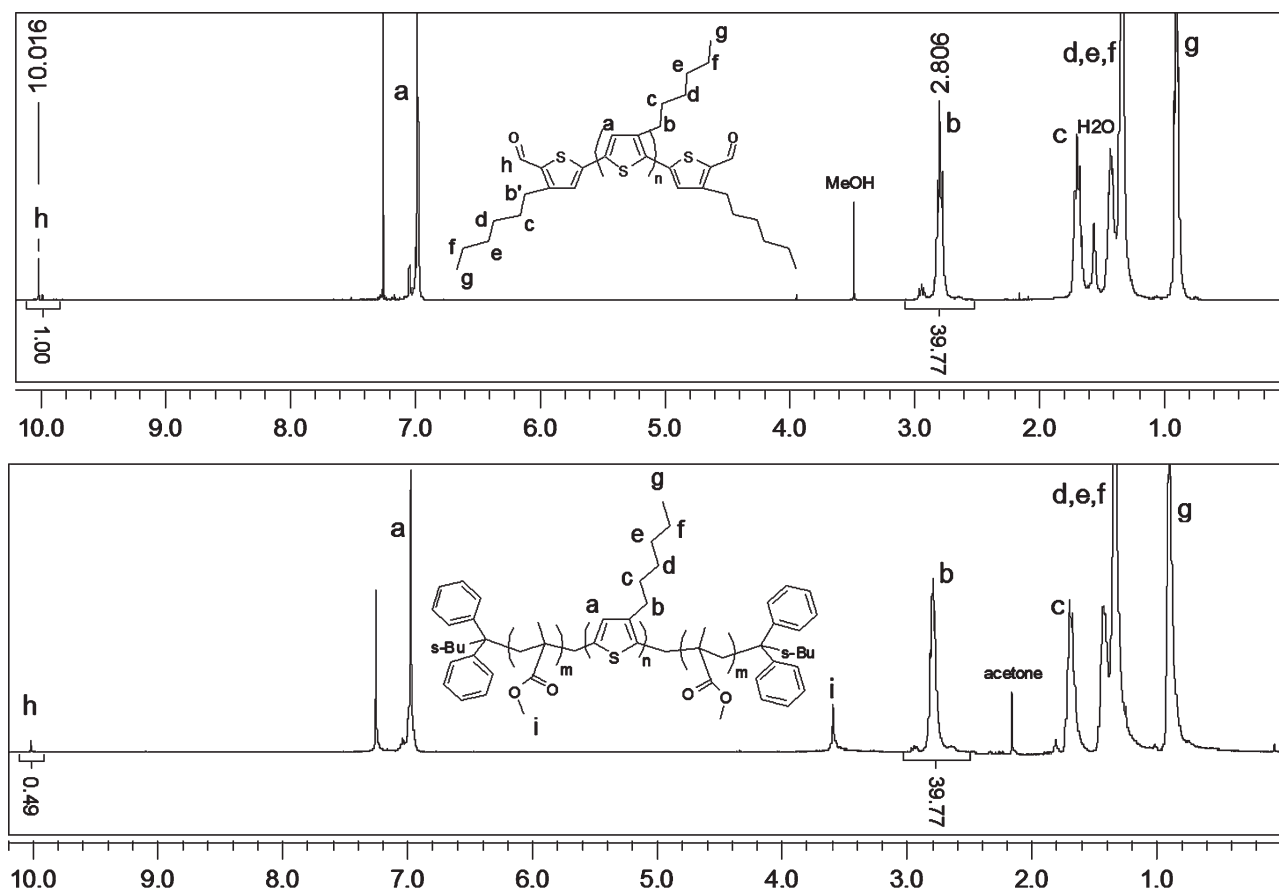
FIGURE 9 ^{1}H NMR spectra of (a) P3HT-CHO/CHO and (b) PMMA-b-P3HT-b-PMMA in d-chloroform.

Figure 11 shows UV–vis absorption spectra of PS-b-P3HT-b-PS_2, PI-b-P3HT-b-PI_1, and PMMA-b-P3HT-b-PMMA dissolved in chloroform in a very diluted concentration (less than 10^{-2} mg/mL) to avoid aggregation. The P3HT segments of these three block copolymers were identical while the non-P3HT segments have similar molecular weights. The UV–vis absorptions of these copolymers were very similar to that of the pristine P3HT, indicating the presence of coil PS, PI, or PMMA segment has very little effect on the optical properties of P3HT as isolated molecules. For UV–vis spectra of the spin-coated thin films of these triblock copolymers, differences were observed depending on the non-P3HT segment as well as the solvent used for spin coating (Fig. 12). Generally, all thin films showed similar absorption pattern with three maxima located at 525, 555, and 603 nm but with different intensity ratios. When chloroform was used as the solvent for spin coating, the intensity ratios of these three block copolymers were very similar except a slightly higher absorption at 555 nm for PI-b-P3HT-b-PI_1 [Fig. 12(a)]. Thin films spin coated from the toluene and the dicholorobenzene solutions showed more pronounced absorptions at 555 nm and 603 nm for P3HT with either PI or PMMA attachment [Fig. 12(b,c)]. The increased absorptions at longer wavelengths should be attributed to a more enhanced π–π stacking of P3HT segment.[2] This result was in accordance with longer fibrils and more ordered morphologies observed from AFM for PI-b-P3HT-b-PI and PMMA-b-P3HT-b-PMMA.

The above observations regarding the morphologies and UV–vis absorptions inferred that a solvent possessing a higher boiling point, such as toluene and dicholorobenzene, could allow more time for the P3HT block copolymers to undergo self-assembly during a spin coating process. In this study, we found that attaching suitable coil segments (such as PI and PMMA) to P3HT might enhance the solubility of P3HT in common organic solvents leading to thin films with better flatness, as well as improve the packing of P3HT with the assistance of microphase separation. As dicholorobenzene, a commonly used solvent for the spin coating process of the photoactive layer during the fabrication of a polymer photovoltaic device, is carcinogenic, which could lead to a serious environmental issue for mass production, the less toxic solvents, such as toluene, could be possibly used for the spin coating process if P3HT block copolymers with suitable structures would be adopted instead of P3HT.

EXPERIMENTAL

Materials

THF and toluene were freshly distilled from CaH$_2$ and sodium/benzophenone under nitrogen. Solvents for anionic polymerization (toluene and THF) were further distilled from
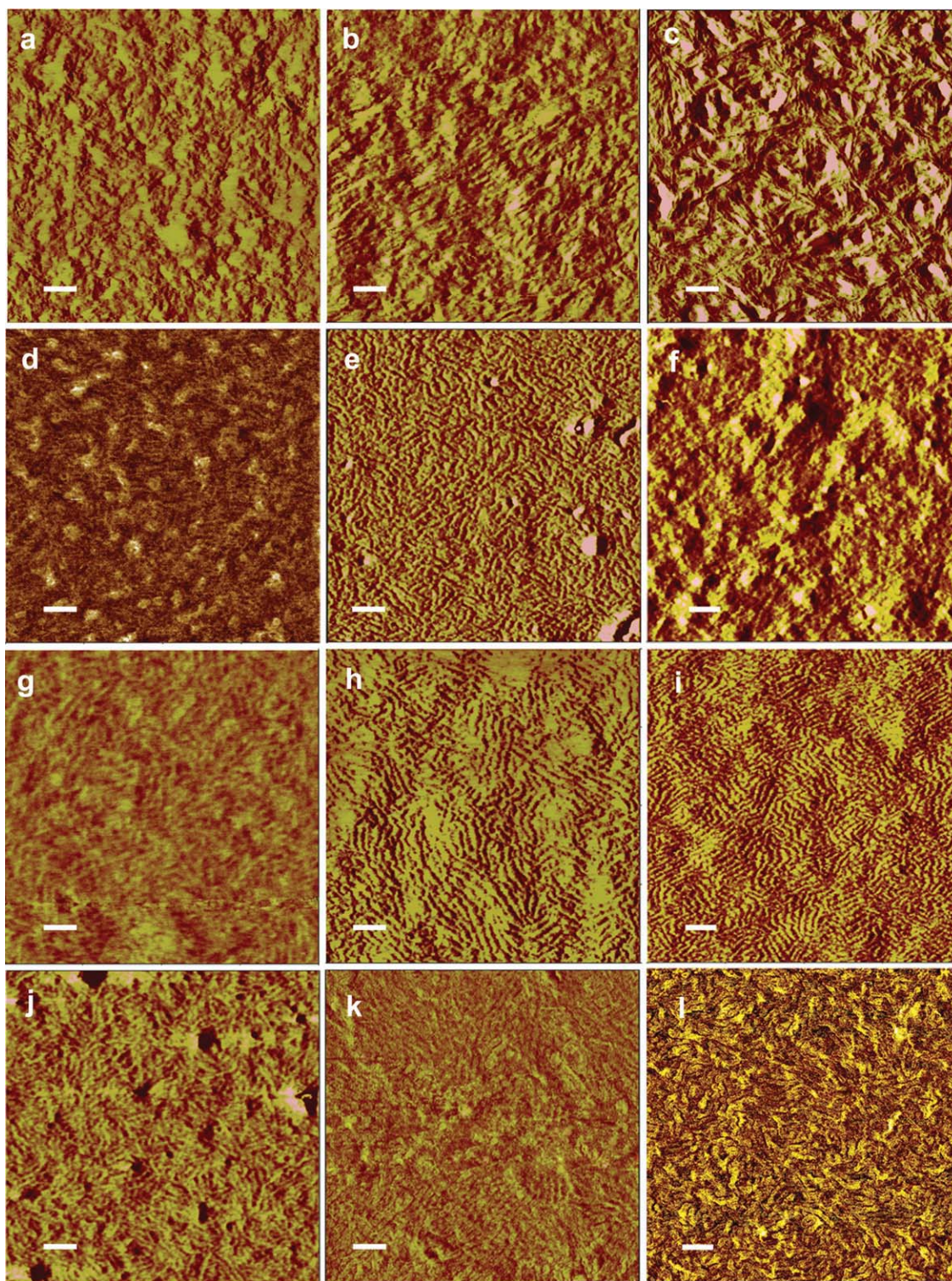
FIGURE 10 AFM phase images of spin-coated thin films from (a) CHCl3 solution, (b) toluene solution and (c) dichlorobenzene solution of P3HT; from (d) CHCl3 solution, (e) toluene solution, and (f) dichlorobenzene solution of PS-b-P3HT-b-PS_2; from (g) CHCl3 solution, (h) toluene solution, and (i) dichlorobenzene solution of PI-b-P3HT-b-PI_1; as well as from (j) CHCl3 solution, (k) toluene solution, and (l) dichlorobenzene solution of PMMA-b-P3HT-b-PMMA. The scale bar represents 100 nm.
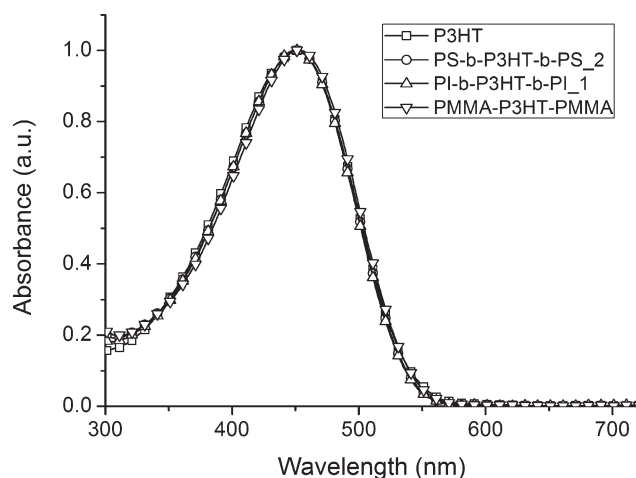
FIGURE 11 UV–Vis absorption spectra of P3HT triblock copolymers dissolved in chloroform.

PS solution. Styrene and isoprene were degassed and distilled from dibutylmagnesium (Aldrich, 1.0 M solution in heptane) prior to use. Methylmethacrylate was dried from trioctyl alumina (sigma Aldrich) and distilled prior to use. *tert*-Butyl magnesium chloride (2.0 M in diethyl ether), *N*-methylformanilide, $POCl_3$, $Ni(dppp)Cl_2$, and 1,1-diphenylethylene were purchased from Aldrich and used as received.

Synthesis of Aldehyde-Terminated Bi-End–Functionalized P3HT (P3HT-CHO/CHO)

3-Hexylthiophene (3HT) was synthesized according to literature.[26] Bromination of 3HT was carried out using *N*-bromosuccinimide in THF at room temperature for 3 h and then purified by column chromatography and vacuum distillation to afford 2,5-dibromo-3-hexylthiophene in high purity. P3HT was synthesized by Grignard methathesis (GRIM) method ($M_n = 10,855$, PDI = 1.21). The crude product was washed using Soxhlet extraction with methanol and acetone to remove remaining monomer and oligomers and then extracted with chloroform. Br/H terminated P3HT (P3HT-Br/H), the majority of the product from GRIM, was then converted to H/H terminated P3HT (P3HT-H/H) by refluxing in THF with *tert*-butyl magnesium chloride (2.0 M) for 3 h. End-group functionalization of P3HT-H/H to introduce aldehyde end-group was carried out using $POCl_3$ and *n*-methylformanilide at 75 °C for 24 h to obtain P3HT-CHO/CHO.[27] The reaction mixture was precipitated in methanol, followed by Soxhlet extraction with methanol, acetone, and then extracted with chloroform. The purified products were characterized by MALDI-TOF analysis and ^{1}H NMR (see Supporting Information).

General Procedure for Synthesis of PS-b-P3HT-b-PS Triblock Copolymer

All the following procedures were carried out under moisture-free and oxygen-free environments. The P3HT-CHO/CHO was charged into a Rotaflo flask and dried by applying vacuum at 40 °C overnight. Dry toluene was transferred using a double-tip needle into the flask under nitrogen to dissolve the P3HT-CHO/CHO. Anionic polymerization of styrene was
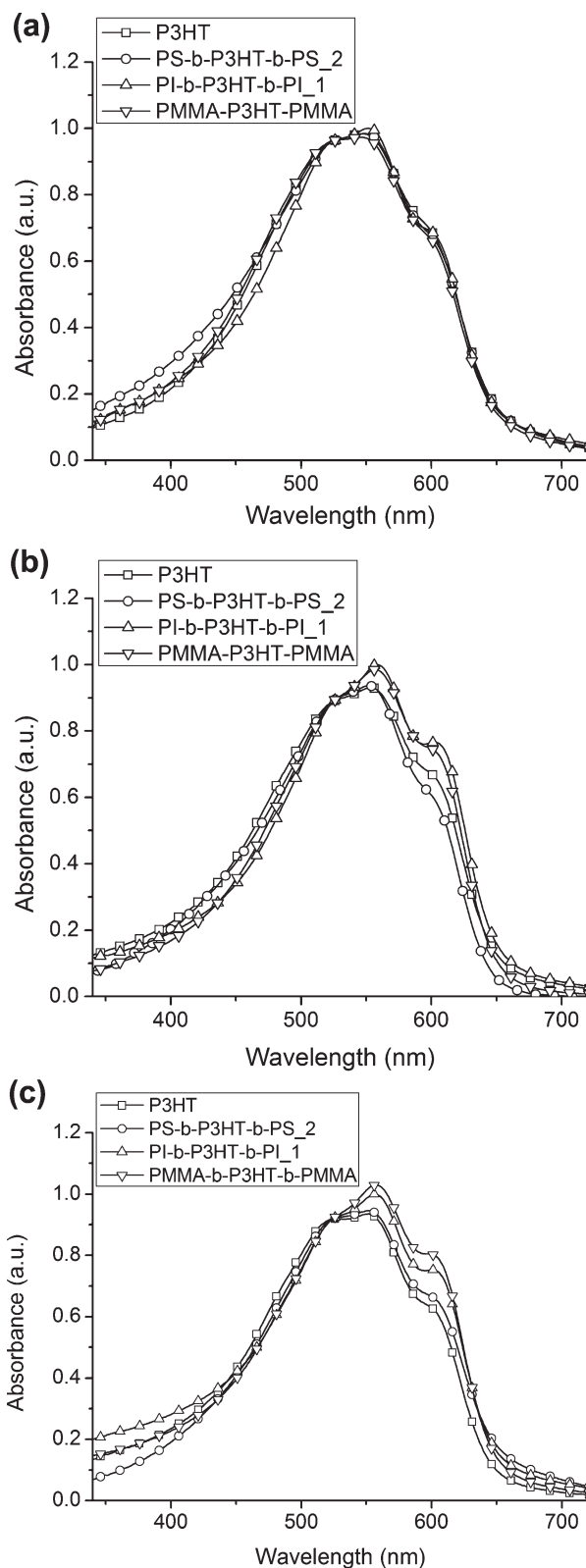

FIGURE 12 UV–Vis absorption spectra of the spin-coated thin films of P3HT triblock copolymers from (a) CHCl3 solution, (b) toluene solution, and (c) dichlorobenzene solution.

carried out in dry toluene using *sec*-BuLi (115.4 μL, 0.15 mmol) as initiator for 1 h at room temperature. A small portion of PS homopolymer solution was taken and terminated for GPC analysis. Living polystyryl-lithium was then transferred into the P3HT-CHO/CHO solution at room temperature under nitrogen. The mixture was then allowed to react for 2 h at room temperature before termination with anhydrous methanol. The reaction mixture was then poured into methanol and the precipitate was the crude product. Purified PS-b-P3HT-b-PS was obtained after reprecipitate crude product in acetone (yield = 91%).

General Procedure for Synthesis of PI-b-P3HT-b-PI

P3HT-CHO/CHO was prepared as described in the previous paragraph. PI anions consisted of the adducts of both 1,4-addition and 3,4-addition, denoted as PI(1,4/3,4), were synthesized from anionic polymerization at room temperature in toluene with a trace amount of THF. The coupling reaction between the PI-1,4/3,4 anions and the P3HT-CHO/CHO was carried out following the similar procedure as described in the synthesis of PS-b-P3HT-b-PS. Crude products were obtained by evaporating off the solvent. Excess PI homopolymers were then removed by column chromatography with ethyl acetate as the eluent to afford purified products (yield = 87%). PI anions consisted of the adducts of 1,2-addition and 3,4-addition, denoted as PI(1,2/3,4), were synthesized from anionic polymerization with *sec*-BuLi as the initiator at −78 °C in anhydrous THF for 2 days. P3HT-CHO/CHO dissolved in anhydrous toluene was then transferred to the living PI solution at −78 °C under nitrogen. The resulted mixture was then slowly warmed to −30 °C and allowed to react for 2 h. Anhydrous methanol was injected to terminate the excess PI anions. Similar workout procedures were performed to obtain purified PI-b-P3HT-b-PI(1,2/3,4) (yield = 89%).

Synthesis of PMMA-b-P3HT-b-PMMA

P3HT-CHO/CHO was prepared as described before. PMMA anions were synthesized from anionic polymerization with *sec*-BuLi activated diphenylethilene as the initiator at −78 °C in anhydrous THF containing LiCl (1.25 mmol/mL THF) for 30 min. The P3HT-CHO/CHO was dissolved in anhydrous toluene and then was transferred to the living PMMA anion solution at −78 °C under nitrogen. The resulted mixture was then slowly warmed to −30 °C and allowed to react for 2 h at −30 °C. The crude product was obtained by precipitating the reaction mixture in methanol. Excess PMMA was removed by reprecipitation of the crude product in acetone (yield = 45%).

Characterization of the Block Copolymers and Their Thin Films

GPC was performed on a Viscotech HTGPC module 350 equipped with RI and UV detectors and THF was used as the eluent at 1 mL/min flow rate running at room temperature. Calibration was performed using PS standards from Viscotech. ^{1}H-NMR spectra were obtained using Bruker Avance 400 MHz spectrometer with *d*-chloroform as solvent. MALDI-TOF MS spectra were obtained using Voyager DE-PRO MALDI-TOF MS (Applied Biosystems, Texas) equipped with a N_2 laser (337 nm). UV–Vis spectra were recorded using JASCO V-570 UV/Vis Spectrometer. PEDOT:PSS was spin coated onto a glass substrate at 5000 rpm for 60 s and then dried under vacuum at 150 °C for 30 min. P3HT block copolymers solution was then spin coated onto this substrate at 1000 rpm for 60 s and allowed to dry at room temperature. The UV–vis spectra of the spin coated thin films were obtained by subtracting the absorption of the PEDOT:PSS coated glass substrate. The phase images of thin film were taken by AFM (Digital Instruments, Nanoscope III).

CONCLUSIONS

A series of P3HT ABA triblock copolymers containing highly regioregular P3HT as the center block have been synthesized based on coupling reaction between aldehyde-terminated bi-end–functionalized P3HT and designated polymeric anions. High yield of coupling reactions were achieved for PS anion at room temperature and for PI anion at either room temperature or −78 °C. Poly(methylmethacrylate) anion with less reactivity was coupled to P3HT with a moderate yield. Attachment of non-P3HT coil segment did not alter the optical absorption of P3HT in solution while affected the absorption of P3HT in spin-coated thin films. The flexibility of the non-P3HT segment and the χ value between the non-P3HT segment and the P3HT are the key factors to determine the morphologies of the spin-coated thin films and the photophysical properties of the block copolymers.

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