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Well-Controlled Synthesis of Block Copolythiophenes

Kaoru Ohshimizu and Mitsuru Ueda*

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

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ABSTRACT: Well-controlled rod−rod block copolymers, poly(3-hexylthiophene)-*b*-poly(3-phenoxymethylthiophene)s, were successfully prepared by nickel-catalyzed coupling polymerization of 2-bromo-3-hexyl-5-iodothiophene followed by that of 2,5-dibromo-3-phenoxymethylthiophene. The homopolymerization of 2,5-dibromo-3-phenoxymethylthiophene was investigated in detail to determine the polymerization conditions. The structure of block copolymers was confirmed by FT-IR and ^{1}H NMR spectroscopies, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), ultraviolet−visible (UV−vis), and fluorescence spectroscopies. The thin film formed on a silicon wafer and annealed at 40 °C for 3 days was analyzed using atomic force microscopy (AFM), and the results indicated the existence of phase separation.

Introduction

Recently, a synthetic method applied to condensation polymers in order to control molecular weight (MW) and molecular weight distribution (MWD) has been developed.[1] It is called condensative chain polymerization, and many well-controlled polymers such as polyamides,[2] poly(ether ketone)s,[3] poly(ether sulfone)s,[4] polyethers,[5] polyesters,[6] polythiophenes,[7] polyphenylenes,[8] and polyfluorenes[9] have been successfully prepared. The MWs of these polymers can be controlled simply by changing the molar ratio of the initiator and a monomer.

Well-defined block copolymers can self-assemble into various types of well-ordered nanostructures on a variety of substrates after being cast from a number of solvents. Thus, the phase behavior of coil−coil and rod−coil block copolymers based on vinyl polymers has been widely investigated.[10] Recently, several reports on the synthesis and phase behavior of block condensation copolymers have been published.[11–15] Jenekhe et al. reported self-assembly from solutions, micelle-like aggregate morphologies, and aggregate supramolecular structures of a synthetic rod−coil diblock copolymer, poly(phenylquinoline)-*b*-polystyrene (PPQ-*b*-PS).[11,12] Poly(alkoxyphenylenevinylene-*b*-isoprene) rod−coil block copolymers have also been reported to self-assemble into lamellar microphases upon thermal annealing.[13–15] MWDs of these polymers, however, were not controlled.

Recently, two groups, McCullough et al. and Yokozawa et al., developed a simple method for the synthesis of end-functionalized regioregular poly(3-alkylthiophene)s independently,[16,17] and this method was used for the synthesis of rod−coil block copolymers, allowing for fine-tuning of the supramolecular architecture of the polymers.[18–21] On the other hand, reports on the synthesis of rod−rod block condensation copolymers are very few. A well-controlled diblock aramide with a molecular weight of 6200 was prepared from phenyl 4-(4-octyloxybenzylamino)benzoate and phenyl 4-(octylamino)benzoate, and the resulting block copolyamides produced supramolecular assemblies.[22] There has been no observation of any clear phase separation with ordered structures. We reported the synthesis of well-controlled block copolymers, poly(*N*-octyl-*p*-benzamide)-*b*-poly(*N*-fluoroalkyl-*p*-benzamide),[23] with a molecular weight of 20 600, and the AFM image of the resulting block copolyamides showed clear microphase separation.[24]

McCullough et al. reported that block copolythiophenes such as poly(3-dodecylthiophene)-*b*-poly(thiophene) had a MW of 6300 and a MWD of 1.33.[7] However, there is still no synthetic example of well-controlled block copolythiophenes with a much higher MW and a narrower MWD even at the present time.

In this paper we report the first synthesis of a well-controlled poly(3-hexylthiophene)-*b*-poly(3-phenoxymethylthiophene) (P3HT-*b*-P3PT) with a high MW of 34 800 and a MWD of 1.20 by nickel-catalyzed coupling polymerization of the corresponding 2,5-dihalogenated thiophene derivatives. The new combination of crystalline regioregular P3HT and amorphous P3PT, for which the corresponding monomer is specially designed, induced a microphase separation. In fact, the AFM image of P3HT-*b*-P3PT showed a clear microphase separation.

Experimental Section

Materials. Tetrahydrofuran (THF) was dried over sodium and distilled before use under nitrogen. 2-Bromo-3-hexyl-5-iodothiophene (B3HT) and 2,5-dibromo-3-bromomethylthiophene were prepared according to the literatures.[25,26] Lithium chloride was dried by a heat gun under reduced pressure and used under nitrogen. All other reagents and solvents were used without further purification.

Synthesis of 2,5-Dibromo-3-phenoxymethylthiophene (D3PT). 2,5-Dibromo-3-bromomethylthiophene (23.1 g, 69.0 mmol), K_2CO_3 (47.8 g, 346 mmol), and phenol (16.23 g, 172 mmol) were placed in a 500 mL round-bottomed flask, and acetone (300 mL) was added. Then, the reaction mixture was refluxed for 40 h, allowed to room temperature, and water was added. The mixture was extracted with $CHCl_3$. The organic layer was washed successively with 5% aqueous $NaHCO_3$ solution and water and dried over anhydrous $MgSO_4$. After the drying agent was removed by filtration, the solvent was removed by evaporation under reduced pressure. The residue was purified by silica gel column chromatography (eluent: CH_2Cl_2 and hexane) and distilled under reduced pressure to give D3PT as a clear oil (17.2 g, 72%), bp = 117 °C (0.01 Torr). IR (NaCl, cm^{-1}): 2919 ($-CH_2-$), 1596 (Ar−H). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, 25 °C): δ = 7.25 (m, ArH, 2H), 6.93 (m, ArH, 3H, thiophene, 1H). 4.86 (s, CH_2, 2H). ^{13}C NMR (300 MHz, $CDCl_3$, ppm, 25 °C): δ = 64.1, 109.8, 111.5, 114.6, 121.3, 129.5, 130.5, 137.9, and 158.1. Anal. Calcd for $C_{11}H_8Br_2OS$: C, 37.96; H, 2.32; Br, 45.91; S, 9.21. Found: C, 37.96; H, 2.42.

Synthesis of Poly(3-phenoxymethylthiophene) (P3PT). A round-bottomed flask equipped with a three-way stopcock was charged with lithium chloride (180 mg, 4.24 mmol) and was heated by a heat gun under reduced pressure. After the flask was cooled to room temperature under a nitrogen stream, a solution of D3PT (264 mg, 0.759 mmol) in dry THF (20.0 mL) was added via a

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* Corresponding author: Tel +81-3-57342127; fax +81-3-57342127; e-mail ueda.m.ad@m.titech.ac.jp.

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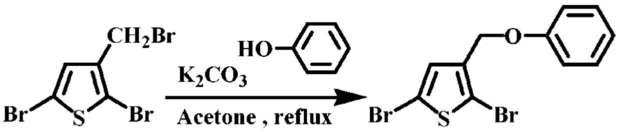
Scheme 1. Synthesis of D3PT



syringe, and the mixture was stirred at 0 °C for 30 min. To the mixture was added isopropylmagnesium chloride (2.0 M solution in THF, 0.390 mL, 0.780 mmol) via a syringe, and the mixture was stirred for 30 min. Then, a suspension of 1,3-bis(diphenylphosphino)propane]nickel(II) dichloride (Ni(dppp)Cl$_2$) (10.0 mg, 0.0185 mmol) in dry THF (5.0 mL) was added to the mixture via a syringe, and then the mixture was stirred for 1 h (conversion = 97%). The polymerization was quenched by the addition of 5 M HCl solution. The polymer solution was poured into a mixture solution of methanol (200 mL) and water (100 mL), and the residue was filtered and dried overnight under reduced pressure to give P3PT (M_n = 8800, MWD = 1.33) as a purple solid (0.125 g, 88%). T_g = 38 °C. IR (KBr, cm^{-1}): 2923 (−CH$_2$−), 1596 (Ar−H). ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, ppm, 25 °C): δ = 7.25 (m, ArH, 2H), 6.90 (m, ArH, 3H, thiophene, 1H), 5.07−4.93 (m, CH$_2$, 2H).

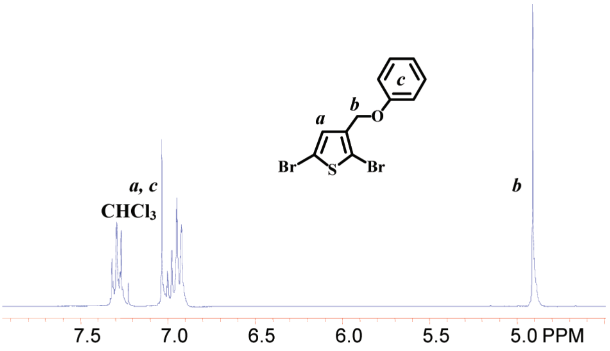


Figure 1. ^{1}H NMR spectrum of D3PT.

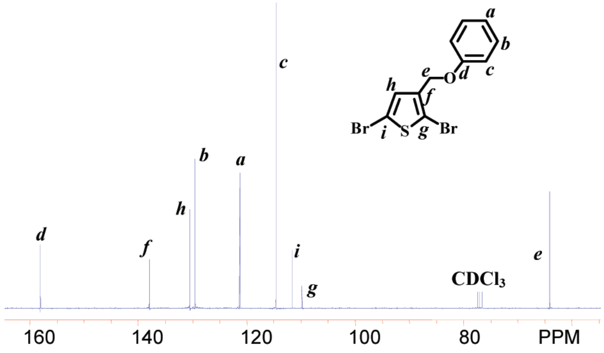
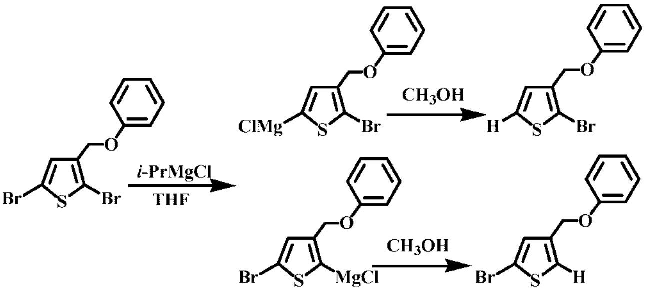


Figure 2. ^{13}C NMR spectrum of D3PT.

Scheme 2. Reaction of *i*-PrMgCl with D3PT



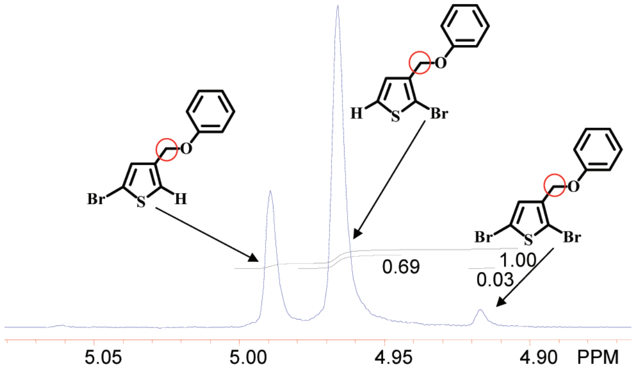
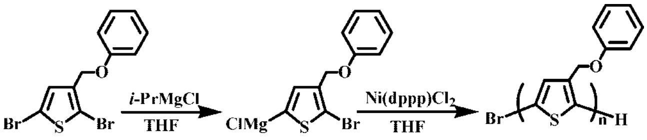


Figure 3. ^{1}H NMR spectrum of protonated monomer’s phenoxymethylene proton.

Scheme 3. Synthesis of P3PT



Synthesis of Poly(3-hexylthiophene)-*b*-poly(3-phenoxymethylthiophene) (P3HT-*b*-P3PT). A round-bottomed flask equipped with a three-way stopcock was charged with lithium chloride (0.18 g, 4.24 mmol) and was heated by a heat gun under reduced pressure. After the flask was cooled to room temperature under a nitrogen stream, a solution of B3HT (178 mg, 0.477 mmol) in dry THF (15.0 mL) was added via a syringe, and the mixture was stirred at 0 °C for 30 min. To the mixture was added isopropylmagnesium chloride (2.0 M solution in THF, 0.250 mL, 0.500 mmol) via a syringe, and the mixture was stirred for 30 min at 0 °C. Then, a suspension of Ni(dppp)Cl$_2$ (7.0 mg, 0.0129 mmol) in dry THF (5.0 mL) was added to the mixture via a syringe. The polymerization continued for 9 min at room temperature (M_n = 7500, MWD = 1.09), and then a solution of 2-bromo-5-chloromagnesium-3-phenoxymethylthiophene in dry THF (5 mL) was added to the mixture. This 2-bromo-5-chloromagnesium-3-phenoxymethylthiophene solution was prepared as follows.

A round-bottomed flask equipped with a three-way stopcock was charged with lithium chloride (0.19 g, 4.48 mmol) and heated by a heat gun under reduced pressure. The flask was cooled to room temperature under a nitrogen atmosphere. A solution of D3PT (213 mg, 0.611 mmol) in dry THF (10.0 mL) was added via a syringe, and the mixture was stirred at room temperature. To the mixture was added isopropylmagnesium chloride (2.0 M solution in THF, 0.310 mL, 0.620 mmol) via a syringe, and the mixture was stirred for 30 min at room temperature.

The polymerization of the second monomer was continued for 9 min at room temperature and quenched by addition of 5 M HCl solution. Then, the polymer solution was poured into a mixture solution of methanol (330 mL) and water (170 mL), and the residue was filtered and purified via a Soxhlet extraction with methanol and then with acetone. The residue was extracted again with chloroform using a Soxhlet. The chloroform was removed by

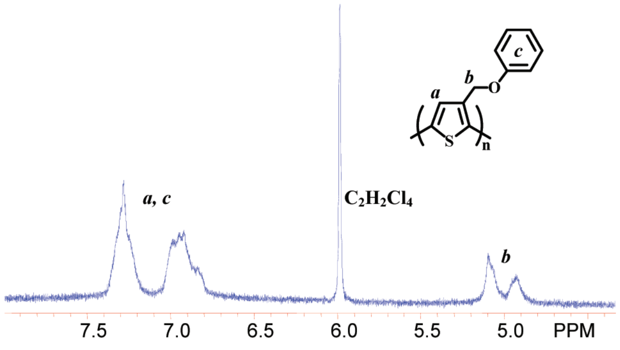


Figure 4. ^{1}H NMR spectrum of P3PT.

Scheme 4. Synthesis of P3HT-*b*-P3PT

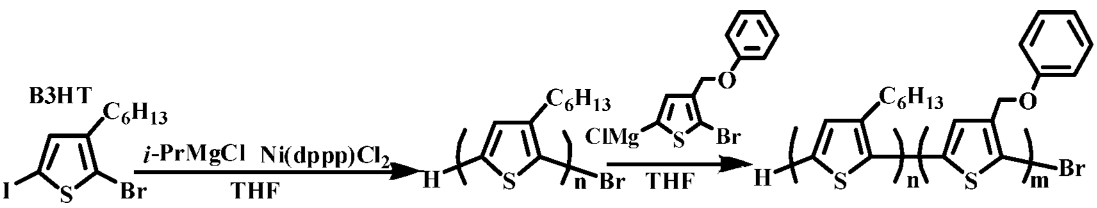


Table 1. Synthesis of P3HT-*b*-P3PT[a]

run	M_n[b]	MWD[b]	molar ratio (%)[c]	*n*/*m* (%)[d]	yield (%)
1	11 600	1.13	50/50	55/45	82
2	34 800	1.20	72/28	74/26	80
P3PT	8 800	1.33	0/100	0/100	88
P3HT	7 500	1.09	100/0	100/0	87

[a] [LiCl]/[M] = 5, THF = 25 mL. [*i*-PrMgCl]/[M] = 1.0, [Ni(dppp)Cl$_2$] = 3.68−5.16 mmol/L. [b] Determined by GPC (CHCl$_3$, PSt standard). [c] B3HT/D3PT [d] Determined by ^{1}H NMR.

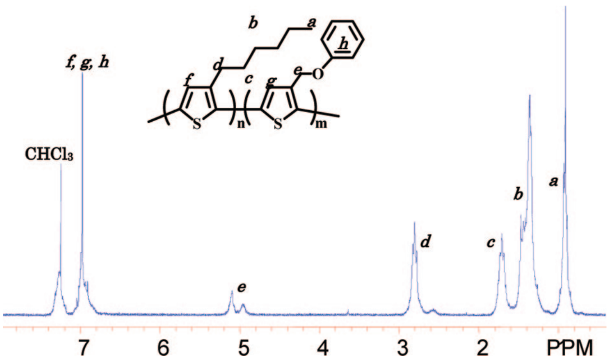


Figure 5. ^{1}H NMR spectrum of P3HT-*b*-P3PT.

evaporation under reduced pressure, and the polymer was dried overnight under reduced pressure to give P3HT-*b*-P3PT (M_n = 11 600, MWD = 1.13) as a purple solid (0.111 g, 82%). IR (KBr, cm^{-1}): 2854, 2923 ($-CH_2-$), 1596 (Ar−H). ^{1}H NMR (300 MHz, CDCl$_3$, ppm, 25 °C): $\delta = 7.24, 6.94$ (m, ArH, 5H, thiophene, 2H), 5.04−4.89 (m, $-CH_2O$, 2H), 2.74 (s, $-CH_2$, 2H), 1.63 (s, CH_2-CH_2, 2H), 1.29 (s, $CH_2-(CH_2)_3$, 6H), 0.85 (s, CH_2-CH_3, 3H).

Measurements. The FT-IR spectra were measured on a Horiba FT-720 spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DPX300S spectrometer. Number- and weight-average molecular weights (M_n and M_w) were measured by gel permeation chromatography (GPC) on a Jasco GULLIVER 1500 system equipped with a polystyrene gel column (Plgel 5 μm MIXED-C) eluted with CHCl$_3$ at a flow rate of 1.0 mL min^{-1} calibrated by standard polystyrene samples. Thermal analysis was performed on a Seiko EXSTAR 6000 DSC 6200 at a heating rate of 20 °C/min for differential scanning calorimetry (DSC) under nitrogen. Ultraviolet−visible (UV−vis) absorption spectra of polymer thin films and solution in CHCl$_3$ were taken on a Jasco V-560 UV/vis spectrophotometer over a wavelength range of 250−800 nm. Fluorescence spectra of polymer solution in CHCl$_3$ were taken on a Jasco FP-750 spectrofluorometer over a wavelength range of 400−700 nm. Atomic force microscopy (AFM) images were taken with a SII-NT SPA 400 operating in tapping mode.

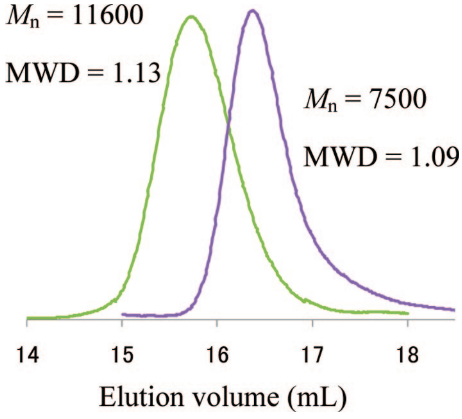


Figure 6. GPC profiles of P3HT and P3HT-*b*-P3PT.

Results and Discussion

Diblock copolymers can exhibit spherical, cylindrical, or lamellar morphologies in the microphase-separated state. This behavior of copolymers in bulk has provided important insights into the interactions occurring between the two different block

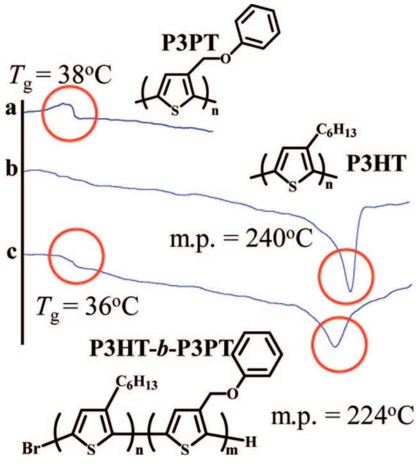


Figure 7. DSC profiles of P3PT (a), P3HT (b), and P3HT-*b*-P3PT (c).

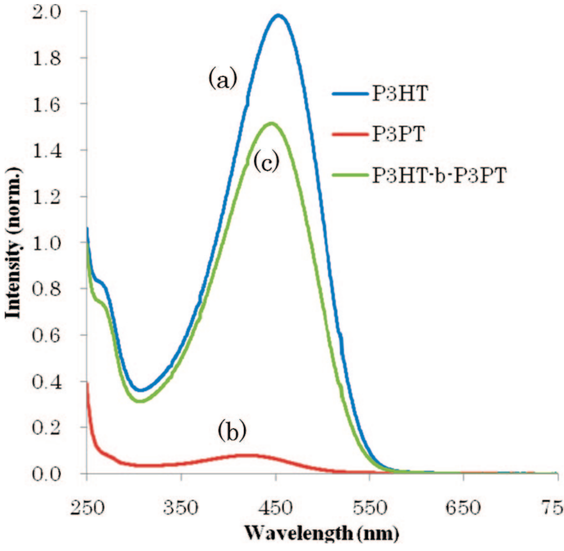


Figure 8. UV−vis spectra of P3HT (a), P3PT (b), and P3HT-*b*-P3PT (c) in CHCl$_3$.

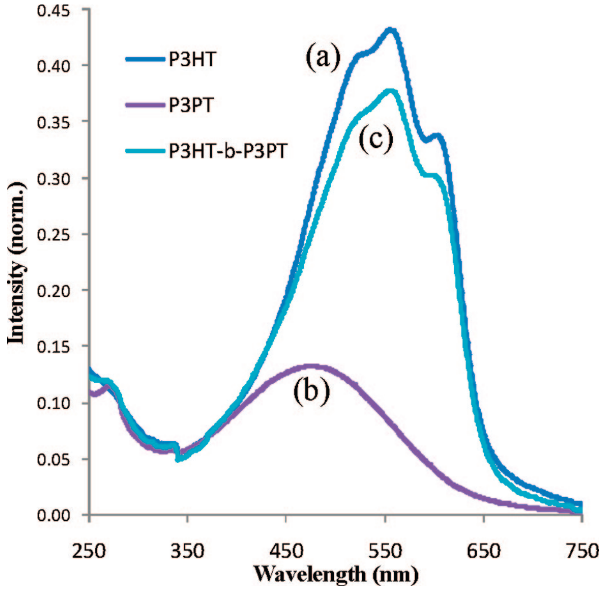


Figure 9. UV−vis spectra of P3HT film (a), P3PT film (b), and P3HT-*b*-P3PT film (c).

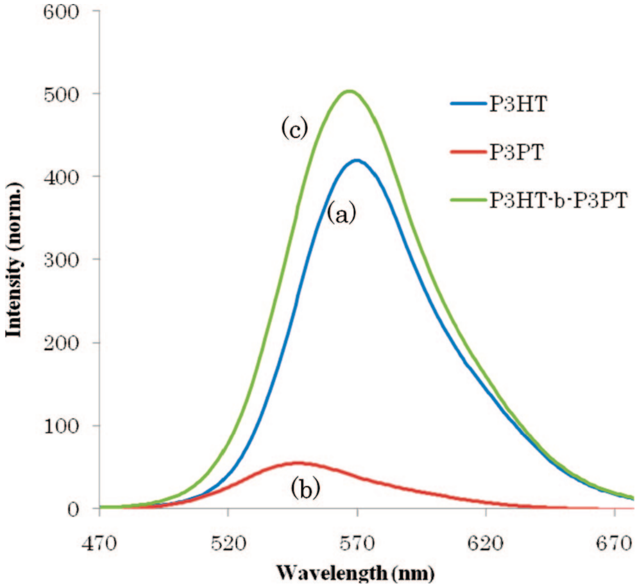


Figure 10. Fluorescence spectra of P3HT (a), P3PT (b), and P3HT-*b*-P3PT (c) in $CHCl_3$.

constituents. To get well-ordered nanostructures from rod−rod block condensation copolymers, some different properties of each segment are required, such as hydrophilic and hydrophobic and crystalline and amorphous properties.

Synthesis of Monomer. To prepare a well-controlled block copolythiophene, which will exhibit a microphase-separation structure, we selected P3HT-*b*-P3PT. Because P3HT is a crystalline polymer and P3PT is an amorphous polymer due to the bulky phenoxymethylene groups as substituents, D3PT as a monomer was chosen to prepare a regiorandom P3PT. D3PT was prepared via three steps from 3-methylthiophene, as shown in Scheme 1. The structure of D3PT was identified by FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopies and elemental analysis. The FT-IR spectrum of D3PT showed characteristic absorptions at 2919 and 1596 cm^{-1} due to the aliphatic C−H and the aromatic C═C stretching vibration, respectively.

Figure 1 shows the ^{1}H NMR spectrum with assignments of all peaks, where the characteristic signal due to the CH_2 proton appears at 4.86 ppm. Furthermore, signals assignable to the methylene (e) and the aromatic (d) carbons appear at 64.1 and 158.1 ppm, respectively, in the ^{13}C NMR spectrum (Figure 2). The elemental analysis also supported the formation of D3PT.

Synthesis of P3PT. To check the nature of condensative chain polymerization in D3PT, we first examined the reaction of D3PT with a Grignard reagent, followed by quenching with methanol (Scheme 2) under various conditions. The complete exchange reaction is critical for condensative chain polymerization, and a random exchange is also important for the synthesis of an amorphous P3PT. D3PT was reacted with an equivalent of isopropylmagnesium chloride in THF, and the reaction was quenched with methanol. Isopropylmagnesium chloride was added at −20 °C, 0 °C, and room temperature for 30 min. The molar ratio of 2-bromo-3-phenoxymethylthiophene and 5-bromo-3-phenoxymethylthiophene was determined by using the methylene protons in the ^{1}H NMR spectra of each compound (Figure 3). The Grignard exchange reaction and the head-to-tail content of D3PT reach 97% and 69%, respectively, under the optimal condition (room temperature).

On the basis of these findings, nickel-catalyzed coupling polymerization of D3PT was carried out at room temperature in THF (Scheme 3). However, the MWs and MWDs of the resulting polymers were low and in a broad range of 1.5−1.8, respectively. Thus, lithium chloride was added to the polymerization solution according to Yokozawa's paper.[17] The MWD was improved to around 1.3, but the MW was still low at around 3000 because of the low solubility of P3PT in THF. When the monomer concentration in the polycondensation decreased from 0.20 to 0.030 mol/L, polymerization yielded P3PT with a relatively high MW of 9000 and a MWD of 1.3. The structure of P3PT obtained was characterized by FT-IR and ^{1}H NMR spectroscopies. The FT-IR spectrum showed the characteristic C−H and C═C stretchings due to the methylene and aromatic groups at 2923 and 1596 cm^{-1}, respectively. Figure 4 shows the ^{1}H NMR spectrum of P3PT, where the characteristic signals due to the methylene protons appear at 4.86 and 5.07 ppm. As expected from the model reaction described above, P3PT is a regiorandom polymer.

The thermal properties of P3PT were evaluated by TGA and DSC. P3PT exhibited a high degradation temperature (5% weight loss) of around 300 °C in both air and nitrogen, while its glass transition temperature (T_g) was 38 °C and no melting point was observed. It indicates that P3PT is an amorphous polymer because the bulky substituent and regiorandom sequence prevent the chains from ordered packing.

Synthesis of P3HT-*b*-P3PT. Block copolythiophenes were synthesized by the sequential monomer addition of D3PT after the quantitative conversion of B3HT (Scheme 4). The polymerization was initiated by Ni(dppp)Cl_2 in the presence of lithium chloride. Table 1 summarizes the results of the synthesis of the block copolymers from B3HT and D3PT. The block copolymers with narrow MWDs were obtained in 80−82% yields. Changing the feed ratio of the two monomers and the initiator can easily control the MWs of the block copolymers. Furthermore, the feed molar ratios of two monomers are almost the same as the molar ratio of those in the block copolymers. The structure of P3HT-*b*-P3PT was characterized by FT-IR and ^{1}H NMR spectroscopies. The IR spectrum showed the characteristic C−H and C═C stretchings due to the methylene and aromatic groups at 2923 and 1596 cm^{-1}, respectively. Figure 5 shows the ^{1}H NMR spectrum of P3HT-*b*-P3PT, in which a triplet signal due to methylene protons (d) next to the thiophene ring of P3HT and two signals (e) assignable to the methylene protons of P3PT were observed at 2.74, 4.89, and 5.04 ppm, respectively.

Figure 6 shows the GPC profiles of the prepolymer obtained by the condensative chain polymerization of B3HT and the

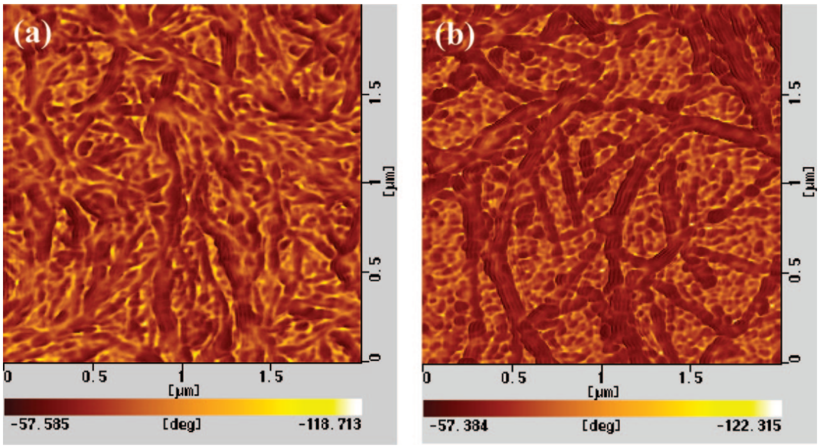


Figure 11. AFM images of P3HT-*b*-P3PT casting films from THF (a) and dichlorobenzene (b).

postpolymer after the second-stage polymerization of D3PT before Soxhlet extractions. The peak of the profile shifted to a high-MW region, and the postpolymer maintained a narrow MWD of 1.13, indicating the formation of the block copolymer.

The DSC profiles of P3PT, P3HT, and P3HT-*b*-P3PT are shown in Figure 7. The T_g value of P3PT is 38 °C (Figure 7a), and the melting point of P3HT obtained from P3HT is 240 °C (Figure 7b). On the other hand, P3HT-*b*-P3PT shows the melting point at 224 °C and the glass transition temperature at 36 °C corresponding to each unit, clearly indicating the formation of the block copolymer (Figure 7c).

UV−vis and Fluorescence Spectra of P3HT-*b*-P3PT. The optical properties of P3HT-*b*-P3PT (Table 1, run 2) were investigated with UV−vis and fluorescence spectroscopy. The solution-state UV−vis spectra of P3HT, P3PH, and P3HT-*b*-P3PT show the maximum absorptions ($\lambda_{\max}$) for the $\pi-\pi^*$ transition at 455, 420, and 445 nm (Figure 8). The $\lambda_{\max}$ of regiorandom P3PT is 35 nm shorter than that of regioregular P3HT, and its absorption is very weak, which suggests that the P3HT chain has a more rodlike conformation with a longer conjugation length and regiorandom P3PT has a more coillike conformation with a shorter conjugation length.[27] On the other hand, P3HT-*b*-P3PT has middle $\lambda_{\max}$, between those of P3HT and P3PT, reflecting the molar ratio of each unit. In a film state, the $\lambda_{\max}$ values of the three polymers are bathochromically shifted to 475−555 nm compared with those in a solution state due to a higher degree of ordering in all polymers (Figure 9). The shoulder at ∼625 nm is related to vibronic absorption and is an indicator that there is a high degree of ordering in both P3HT and P3HT-*b*-P3PT despite the presence of the amorphous P3PT. The chloroform solution of P3HT gives a bright-yellow fluorescence with a maximum emission wavelength of 570 nm, corresponding to the onset of the $\pi-\pi^*$ transition of the electronic absorption spectrum (Figure 10). The solution of regiorandom P3PT shows a greenish-yellow fluorescence with a maximum emission wavelength of 546 nm, which is a 24 nm blue shift from the 570 nm of P3HT. The maximum fluorescence wavelength (567 nm) of P3HT-*b*-P3PT is also a middle one, between those of P3HT and P3PT. These results suggest the formation of a block copolymer.

AFM Images of P3HT-*b*-P3PT. To observe a phase separation, the solutions of P3HT-*b*-P3PT dissolved in THF and dichlorobenzene were cast on silicon wafer substrates. The solution was slowly evaporated to promote the phase separation, and the resulting film was annealed at 40 °C for 3 days under reduced pressure. The surface profile of the specimen was investigated using AFM. Figure 11 shows an AFM tapping-mode phase contrast image, where the bright and dark parts represent the P3HT and P3PT domains, respectively, and a clear contrast elastic modulus between the two segments with disordered nanofiber structures can be observed in both specimens. Phase separation may be induced by the crystallization of P3HT, and then amorphous P3PT fills the space not occupied by the crystalline domains of P3HT.

Conclusion

We have demonstrated the synthesis of P3HT-*b*-P3PTs with high MWs and narrow MWDs by nickel-catalyzed coupling polymerization of B3HT followed by that of D3PT. The IR and ^{1}H NMR spectroscopies, GPC, DSC profiles, UV−vis, and fluorescence spectroscopies indicated the formation of the corresponding block copolymers. The AMF profile showed microphase separation in the block copolymers.

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References and Notes

(1) Yokozawa, T.; Yokoyama, A. *Prog. Polym. Sci.* **2007**, *32*, 147–172.
(2) Shibasaki, Y.; Araki, T.; Okazaki, M.; Ueda, M. *Polym. J.* **2002**, *4*, 261–266.
(3) Shibasaki, Y.; Araki, T.; Nagahata, R.; Ueda, M. *Eur. Polym. J.* **2005**, *41*, 2428–2433.
(4) Yokozawa, T.; Taniguchi, T.; Suzuki, Y.; Yokoyama, A. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3460–3464.
(5) Suzuki, Y.; Hiraoka, S.; Yokoyama, A.; Yokozawa, T. *Macromolecules* **2003**, *36*, 4756–4765.
(6) Yokoyama, A.; Iwashita, K.; Hirabayashi, K.; Aiyama, K.; Yokozawa, T. *Macromolecules* **2003**, *36*, 4328–4336.
(7) Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, *38*, 8649–8656.
(8) Miyakoshi, R.; Shimono, K.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2006**, *128*, 16012–16013.
(9) Yokoyama, A.; Suzuki, H.; Kubota, Y.; Ohuchi, K.; Higashimura, H.; Yokozawa, T. *J. Am. Chem. Soc.* **2007**, *129*, 7236–7237.
(10) Myongsoo, L.; Byoung-Ki, C.; Wang-Cheol, Z. *Chem. Rev.* **2001**, *101*, 3869–3892.
(11) Jenekhe, S. A.; Chen, X. L. *Science* **1999**, *283*, 372–375.
(12) Jenekhe, S. A.; Chen, X. L. *J. Phys. Chem. B* **2000**, *104*, 6332–6335.
(13) Olsen, B. D.; Segalman, R. A. *Macromolecules* **2005**, *38*, 10127–10137.
(14) Olsen, B. D.; Segalman, R. A. *Macromolecules* **2006**, *39*, 7078–7083.
(15) Olsen, B. D.; Li, X.; Wang, J.; Segalman, R. A. *Macromolecules* **2007**, *40*, 3287–3295.
(16) Jeffries-EL, M.; Sauve, G.; McCullough, R. D. *Macromolecules* **2005**, *38*, 10346–10352.
(17) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542–17547.
(18) Dai, C.; Yen, W.; Lee, Y.; Ho, C.; Su, W. *J. Am. Chem. Soc.* **2007**, *129*, 11036–11038.

(19) Iovu, M. C.; Cralry, R.; Jeffries-EL, M.; Krankowski, A. B.; Zhang, R.; Kowalewski, T.; McCullough, R. D. *Macromolecules* **2007**, *40*, 4733–4735.

(20) Sauve, G.; McCullough, R. D. *Adv. Mater.* **2007**, *19*, 1822–1825.

(21) Boudouris, B. W.; Frisbie, C. D.; Hillmyer, M. A. *Macromolecules* **2008**, *41*, 67–75.

(22) Yokozawa, T.; Ogawa, M.; Sekino, A.; Sugi, R.; Yokoyama, A. *J. Am. Chem. Soc.* **2002**, *124*, 15158–15159.

(23) Ohshimizu, K.; Shibasaki, Y.; Ueda, M. *Polym. J.* **2007**, *8*, 777–782.

(24) Ohshimizu, K.; Shibasaki, Y.; Kokura, M.; Nakajima, K.; Ueda, M. *Chem. Lett.* **2007**, *6*, 742–743.

(25) Rughooputh, S. D.; Hotta, S.; Heeger, A. J.; Wudl, F. J. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 1071–1078.

(26) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169–1171.

(27) Hou, J.; Yang, C.; He, C.; Li, Y. *Chem. Commun.* **2006**, *8*, 871–873.

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