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Synthesis of Triphenylamine Copolymers and Effect of Their Chemical Structures on Physical Properties

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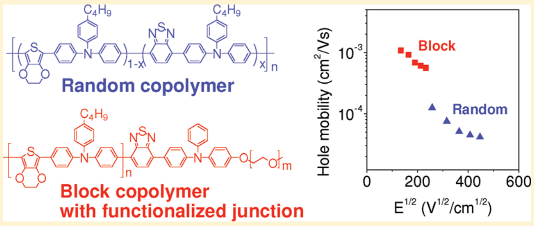
Supporting Information



ABSTRACT: A series of charge transporting triphenylamine (TPA) polymers containing 2,1,3-benzothiadiazole (BTH) and/or 3,4-ethylenedioxythiophene (EDOT) unit(s) in the backbone were synthesized via C−N coupling polymerization using a palladium catalyst system. The preparation of the diblock copolymers based on the TPA-polymers was achieved by introducing poly(ethylene oxide) (PEO) at the terminal. Furthermore, the block copolymers selectively functionalized by BTH at the junction point were also prepared. In order to investigate the structural and morphological effect on physical properties, the optical and electrical properties were measured and compared among the homopolymers, random copolymers, and block copolymers. The photoluminescent (PL) spectra of TPA-polymers containing BTH unit were tunable from blue to red-violet color by the amount of BTH unit. The EDOT-containing polymers showed high hole drift mobility up to 1×10^{-3} cm^2 V^{-1} s^{-1}. On the other hand, the mobility of the BTH-containing polymers was affected by the position of the BTH unit in the polymer structure. The polymers with BTH unit randomly involved in the backbone showed low mobility in the order of 10^{-6}−10^{-5}, whereas no decrease in the mobility was observed for the polymers modified by BTH unit at the junction point.

INTRODUCTION

Arylamine compounds have been widely synthesized and researched for various possible applications such as electroluminescent, photovoltaic, and magnetic devices because of their excellent electrical properties. There are also a large variety of polymers which contains an arylamine moiety as a backbone of main chain or a side group.[1−8] Poly(triphenylamine) (PTPA) is a class of such polymers which is conventionally prepared by oxidative polymerization from triphenylamine (TPA) derivatives as monomers.[9−11] PTPA was found to show high hole mobility and high photoconductivity among amorphous materials such as poly(9-vinylcarbazole), a well-known hole transporting polymer.[10] In our previous report, a novel synthetic route for the preparation of PTPA was developed by means of C−N coupling polymerization using a palladium-based catalytic system.[12] We demonstrated that the modification of each terminal of PTPA could be successfully achieved by adding terminal modifying derivatives during polymerization and that diblock copolymers consisting of PTPA and poly(ethylene oxide) (PEO) was prepared by our method. The diblock copolymer poly(4-butyltriphenylamine)-*block*-poly(ethylene oxide) (PTPA-*b*-PEO) exhibited microphase-separated structures in thin films, which offers a possibility of new application of PTPA in bulk.

Microphase separation behavior of block copolymers has been intensively studied in view of both academic and practical interests. Block copolymers provide a variety of microphase-separated structures such as lamellae and cylinder whose domain sizes ranging from several to tens of nanometers match the technological requirements for materials in future devices. Block copolymers containing arylamine have been prepared for application to organic light-emitting diode (OLED) or organic photovoltaic cell.[13−18] We previously prepared bipolar charge transporting block copolymers consisting of poly(3-vinyltriphenylamine)[19] or poly[2,7-dimethoxy-*N*-(4-vinylphenyl)carbazole][20,21] in order to compare the performance of OLED devices with corresponding random copolymers and polymer blends. It is revealed that the devices using block copolymers afforded higher external quantum efficiency compared with random copolymers or polymer blends. In such devices, the morphological effect on device performance must be of significant importance besides physical properties of the materials. Hence, sophisticated designs of block copolymers matching to desired functionality as well as evaluation on the synergistic performance attributed to the phase-separated structure created by these architectures are required for further improvement of the device performance. For example, we prepared the diblock copolymers consisting of regioregular poly(3-hexylthiophene) (P3HT) and PEO for a donor material in photovoltaic devices.[22] It was demonstrated that the introduction of PEO significantly changed the phase-separated morphology, where vertically aligned lamellar structures were observed, in the device using the block copolymer blended with a fullerene derivative. As a

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result, the device provided higher power conversion efficiency compared with the device based on P3HT homopolymer.

In this paper, a novel series of charge transporting polymers containing TPA moiety were designed and synthesized by C−N coupling polymerization explained above. To the PTPA backbone, 2,1,3-benzothiadiazole (BTH) and 3,4-ethylenedioxythiophene (EDOT) were introduced for modifying optical and electrical properties. Diblock copolymers consisting of TPA-polymers and PEO were also prepared by terminal modification during polymerization using PEO derivatives. The optical and electrical properties were thoroughly examined for these TPA-polymers. So far, although numerous works on charge transporting property have been done on not only arylamine polymers but also molecular-doped polymer blend systems,[23,24] the charge drift mobility in the block copolymer films and its dependence on the morphology have not been profoundly concerned. We demonstrated in this work that the hole drift mobility was compared among TPA-containing homopolymer, random copolymer, and block copolymer in order to investigate structural and morphological effects on hole-transporting ability of the TPA-polymers.

EXPERIMENTAL SECTION

Materials. Toluene was distilled over CaH_2 and stored under nitrogen. Tetrahydrofuran (THF) was used as distilled over sodium and benzophenone. 4,7-Dibromo-2,1,3-benzothiadiazole (**1**),[25] 4,7-bis-(4′-bromophenyl)-2,1,3-benzothiadiazole (**3**),[26] and 2,5-dibromo-3,4-ethylenedioxythiophene (**5**)[27] were prepared by reported procedures. For the preparations of 4,7-diphenyl-2,1,3-benzothiadiazole (**2**) and 2,5-diphenyl-3,4-ethylenedioxythiophene (**6**), the modified procedure reported by Fang et al. was applied.[28] A monomer for poly(4-butyltriphenylamine), 4-(4′-bromophenyl)-4″-butyldiphenylamine (**9**), and poly(ethylene oxide) with a 4-bromophenyl terminal (PEO-Br) were prepared according to previous report.[12] All the other reagents were used as purchased without any further purification.

Synthesis of 4,7-Diphenyl-2,1,3-benzothiadiazole (2). To a two-necked flask equipped with a stopcock and a condenser were added **1** (10.0 g, 34.0 mmol), phenylboronic acid (9.12 g, 74.8 mmol), tetrakis-(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) (0.078 g, 0.068 mmol), and distilled THF (50 mL) under nitrogen. After 2 M K_2CO_3(aq) (50 mL, purged by nitrogen for 1 h) was added, the mixture was vigorously stirred at reflux for 24 h. Chloroform was added after cooling down to room temperature, and the mixture was washed with water. The organic layer was dried with $MgSO_4$ and concentrated by a rotary evaporator. The crude product was recrystallized from hexane to give a yellow needle crystal. Yield was 7.31 g (75%). ^{1}H NMR ($CDCl_3$): δ 7.97 (d, J = 7.2 Hz, 4H), 7.80 (s, 2H), 7.56 (t, J = 7.2 Hz, 4H), 7.47 (t, J = 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 154.11, 137.42, 133.37, 129.24, 128.62, 128.36, 128.12. Anal. Calcd for $C_{18}H_{12}N_2S$: C, 74.97; H, 4.19; N, 9.71. Found: C, 75.01; H, 4.29; N, 9.96.

Synthesis of 4-(4′-Bromophenyl)-7-[4″-(4‴-butylphenylamino)phenyl]-2,1,3-benzothiadiazole (4). To a two-necked flask equipped with a stopcock and a condenser were added **3** (8.00 g, 17.9 mmol), 4-butylaniline (2.83 mL, 17.9 mmol), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($Pd(dppf)Cl_2$) (0.14 g, 0.18 mmol), sodium *tert*-butoxide (2.41 g, 25.1 mmol), and dry toluene (50 mL) under nitrogen. The mixture was stirred at reflux for 12 h. After cooling down to room temperature, the mixture was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated by a rotary evaporator. The crude product was purified by column chromatography eluted with toluene/hexane (4/1 in volume ratio) to give an orange crystal. The yield was 2.50 g (27%). ^{1}H NMR ($CDCl_3$): δ 7.89 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.72 (s, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.18−7.08 (m, 6H), 5.82 (s, 1H), 2.59 (t, J = 7.5 Hz, 2H), 1.60 (quint, J = 7.5 Hz, 2H), 1.37 (sex, J = 7.5 Hz, 2H), 0.94 (t, J = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 154.09, 153.88, 144.51, 139.56, 136.87, 136.39, 133.54, 131.72, 130.86, 130.68, 130.26, 129.29, 128.61, 128.19, 126.62, 122.41, 119.61, 116.08, 34.98, 33.79, 22.35, 13.99. Anal. Calcd for $C_{28}H_{24}BrN_3S$: C, 65.37; H, 4.70; N, 8.17. Found: C, 65.08; H, 4.62; N, 8.17.

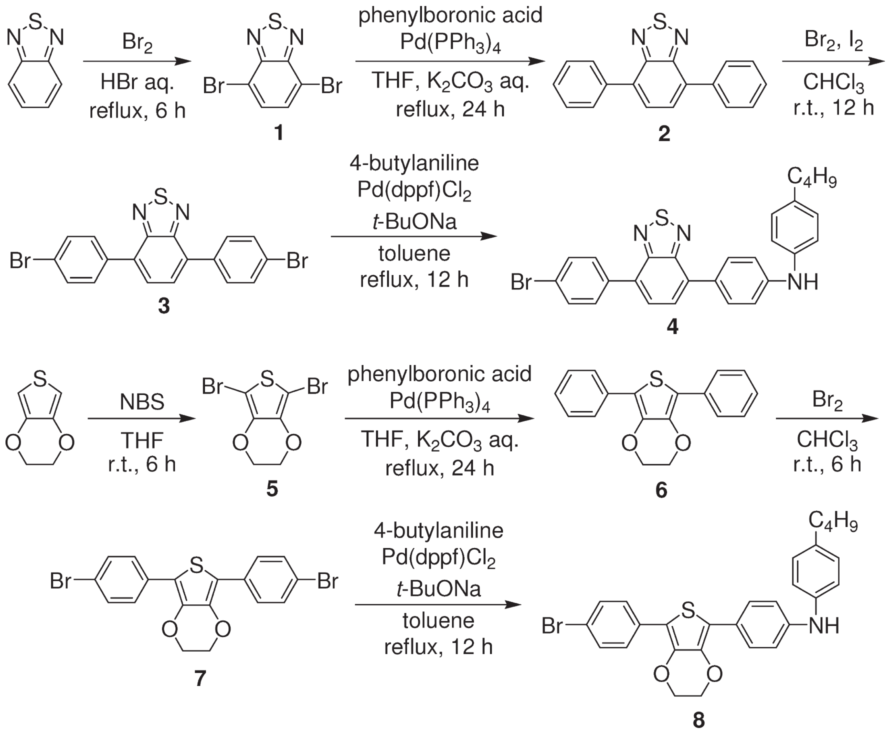
Synthesis of 2,5-Diphenyl-3,4-ethylenedioxythiophene (6). To a two-necked flask equipped with a stopcock and a condenser were added **5** (12.7 g, 42.4 mmol), phenylboronic acid (11.4 g, 93.2 mmol), $Pd(PPh_3)_4$ (0.392 g, 0.339 mmol), and distilled THF (50 mL) under nitrogen. After 2 M K_2CO_3(aq) (50 mL, purged by nitrogen for 1 h) was added, the mixture was vigorously stirred at reflux for 24 h. Chloroform was added after cooling down to room temperature, and the mixture was washed with water. The organic layer was dried with $MgSO_4$ and concentrated by a rotary evaporator. The crude product was recrystallized from methanol to give a yellow needle crystal. The yield was 7.91 g (63%). ^{1}H NMR ($CDCl_3$): δ 7.79 (d, J = 7.2 Hz, 4H), 7.41 (t, J = 7.2 Hz, 4H), 7.26 (t, J = 7.2 Hz, 2H), 4.36 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 138.56, 132.92, 128.61, 126.58, 126.07, 115.36, 64.56. Anal. Calcd for $C_{18}H_{14}O_2S$: C, 73.44; H, 4.79. Found: C, 73.62; H, 4.93.

Synthesis of 2,5-Bis(4′-bromophenyl)-3,4-ethylenedioxythiophene (7). To a mixture of **6** (9.50 g, 32.3 mmol) and chloroform (200 mL) were added bromine (3.31 mL, 64.6 mmol) and chloroform (100 mL) dropwise at 0 °C, and the resulting mixture was stirred for 30 min. Additional stirring were carried out for 6 h at room temperature. The mixture was successively washed with 3% NaOH(aq), saturated $NaHSO_3$(aq), and water. The organic layer was dried with $MgSO_4$ and concentrated by a rotary evaporator. The crude product was recrystallized from hexane to give a white needle crystal. The yield was 14.1 g (97%). ^{1}H NMR ($CDCl_3$): δ 7.61 (d, J = 8.4 Hz, 4H), 7.48 (d, J = 8.4 Hz, 4H), 4.37 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 139.19, 132.00, 131.92, 127.75, 120.59, 114.86, 64.79. Anal. Calcd for $C_{18}H_{12}Br_2O_2S$: C, 47.81; H, 2.68. Found: C, 47.87; H, 2.58.

Synthesis of 2-(4′-Bromophenyl)-5-[4″-(4‴-butylphenylamino)phenyl]-3,4-ethylenedioxythiophene (8). To a two-necked flask equipped with a stopcock and a condenser were added **7** (4.78 g, 10.6 mmol), 4-butylaniline (1.67 mL, 10.6 mmol), $Pd(dppf)Cl_2$ (0.086 g, 0.106 mmol), sodium *tert*-butoxide (1.42 g, 14.8 mmol), and dry toluene (75 mL) under nitrogen. The mixture was stirred at reflux for 12 h. After cooling down to room temperature, the mixture was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated by a rotary evaporator. The crude product was purified by column chromatography eluted with toluene/hexane (2/1 in volume ratio) to give a yellow powder. The yield was 2.34 g (43%). ^{1}H NMR (acetone-d_6): δ 7.69−7.58 (m, 4H), 7.51 (d, J = 8.7 Hz, 2H), 7.27 (s, 1H), 7.14−7.05 (m, 6H), 4.38 (s, 4H), 2.57 (t, J = 7.5 Hz, 2H), 1.59 (quint, J = 7.5 Hz, 2H), 1.37 (sex, J = 7.5 Hz, 2H), 0.93 (t, J = 7.5 Hz, 3H). ^{13}C NMR (acetone-d_6): δ 144.70, 141.67, 140.75, 138.77, 136.40, 133.64, 132.52, 129.98, 128.12, 127.98, 125.07, 120.06, 119.56, 117.30, 117.08, 112.29, 65.74, 65.45, 35.61, 34.67, 23.01, 14.25. Anal. Calcd for $C_{28}H_{26}BrNO_2S$: C, 64.61; H, 5.04; N, 2.69. Found: C, 64.82; H, 5.09; N, 2.42.

Synthesis of Poly(ethylene oxide) with a Diphenylamine Terminal (PEO-DPA). To a two-necked flask equipped with a stopcock and a condenser were added PEO-Br (M_n = 2000, 4.30 g, 2.15 mmol), aniline (0.39 mL, 4.30 mmol), sodium *tert*-butoxide (0.413 g, 4.30 mmol), $Pd(OAc)_2$ (0.0097 g, 0.043 mmol), tri-*tert*-butylphosphine (41.7 μL, 0.172 mmol), and dry THF (10 mL) under nitrogen. The mixture was stirred at reflux for 24 h. After cooling to room temperature chloroform was added, and the mixture was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated by a rotary evaporator. The crude product was washed with diethyl ether and dried. The yield was 3.55 g (83%). ^{1}H NMR ($CDCl_3$): δ 7.20

Scheme 1. Synthesis of BTH- and EDOT-Containing Monomers



(t, J = 8.1 Hz, 2H), 7.05 (d, J = 8.1 Hz, 2H), 6.93–6.72 (m, 5H), 5.62 (s, 1H), 4.10 (t, J = 4.5 Hz, 2H), 3.89–3.51 (m, 200H), 3.37 (s, 3H).

Synthesis of Poly(ethylene oxide) with a BTH Terminal (PEO-BTH). To a two-necked flask equipped with a stopcock and a condenser were added PEO-DPA (3.50 g, 1.75 mmol), **3** (1.17 g, 2.63 mmol), sodium *tert*-butoxide (0.185 g, 1.93 mmol), Pd(OAc)$_2$ (0.0079 g, 0.035 mmol), tri-*tert*-butylphosphine (34.0 μL, 0.14 mmol), and dry THF (15 mL) under nitrogen. The mixture was stirred at reflux for 24 h. After cooling to room temperature, the mixture was poured in water. An insoluble solid was filtered off, and the filtrate was extracted with chloroform. The organic layer was dried with MgSO$_4$ and concentrated by a rotary evaporator. The resulting solid was washed with diethyl ether. The yield was 3.35 g. ^{1}H NMR (CDCl$_3$): δ 7.86 (d, J = 8.7 Hz, 2H), 7.75 (s, 2H), 7.67 (d, J = 8.7 Hz, 2H), 7.22–6.79 (m, 14H), 4.12 (d, J = 4.5 Hz, 2H), 3.90–3.52 (m, 200H), 3.38 (s, 3H).

General Procedure for C–N Coupling Polymerizations. To a two-necked flask equipped with a stopcock and a condenser were added monomer (2.50 mmol), sodium *tert*-butoxide (0.264 g, 2.75 mmol), and dry THF (5.0 mL) under nitrogen. A solution of 4-bromotoluene (0.0086 g, 0.05 mmol), Pd(OAc)$_2$ (0.0112 g, 0.05 mmol), and tri-*tert*-butylphosphine (48.5 μL, 0.2 mmol) in THF (5 mL) was added to the flask, and the mixture was stirred at reflux for 24 h. To the reaction mixture was added a solution of diphenylamine (0.042 g, 0.25 mmol) in THF (1 mL), and then stirring was continued for 1 h. After cooling to room temperature, the mixture was poured into methanol. The precipitate was filtered, dissolved in THF, and reprecipitated in acetone. The polymer was collected and dried. A similar procedure was applied to the preparation of block copolymers with PEO segment, where PEO-Br or PEO-BTH was used instead of 4-bromotoluene.

Measurement of Hole Mobility (Time-of-Flight Method). Aluminum (100 nm) was vacuum-deposited on a well-cleaned glass slide as an anode. Thin charge generating layer was laminated on aluminum by spin-coating from dispersion of titanium phthalocyanine at a rate of 2500 rpm for 30 s. Sequentially, the polymer layer was deposited by bar-coating from 10 wt % of 1,1,2,2-tetrachloroethane solution. The thickness of the polymer layer was in the range 10–20 μm. After the polymer layer was dried in vacuum, the semitransparent gold layer was sputtered on the polymer layer as a cathode. The pulsed light was illuminated on the device to generate charges in the phthalocyanine layer by a xenon lamp, and the photocurrent was recorded on an oscilloscope.

Measurements. ^{1}H and ^{13}C NMR spectra were obtained on a JEOL ALPHA400 instrument at 300 and 75 MHz, respectively. Deuterated chloroform or acetone was used as a solvent with tetramethylsilane as an internal standard. Number- and weight-average molecular weights (M_n and M_w) were determined by gel permeation chromatography (GPC) analysis with JASCO RI-2031 and UV-970 detectors eluted with chloroform at a flow rate of 0.5 mL min^{-1} and calibrated by standard polystyrene samples. Differential scanning calorimetry (DSC) analyses were performed on a Rigaku DSC-8230 under a nitrogen atmosphere at heating and cooling rate of 10 °C min^{-1}. The cyclic voltammetry (CV) was measured at room temperature using a typical three-electrode system with a working (carbon wire), a reference (Ag/AgCl), and a counter electrode (Pt spiral) under a nitrogen atmosphere at a sweep rate of 10 mV s^{-1}. The block copolymer film was spin-coated on the carbon electrode from chloroform solution. A 0.1 M solution of tetra-*n*-butylammonium perchlorate in anhydrous acetonitrile was used as an electrolyte. UV–vis and photoluminescent (PL) analyses were conducted on a JASCO V-570 spectrophotometer and a JASCO FP-6500 spectrofluorometer, respectively.

■ RESULTS AND DISCUSSION

Previously, we have demonstrated that poly(4-butyltriphenylamine) was synthesized by C–N coupling polymerization of self-condensing monomer using palladium catalyst.[12] In a similar regime, novel photoconductive polymers based on TPA backbone were designed. The monomers containing BTH (**4**) or EDOT (**8**) units were prepared in four-step reactions as shown in Scheme 1. One equivalent of 4-butylaniline was coupled with 4,7-bis(4′-bromophenyl)-2,1,3-benzothiadiazole (**3**) or 2,5-bis

Scheme 2. C−N Coupling Polymerization of Monomers

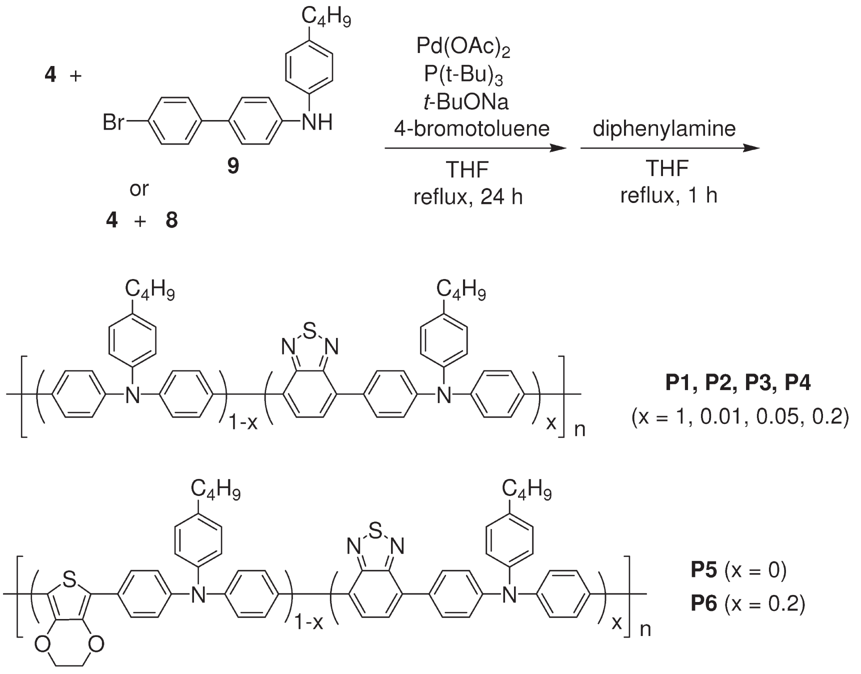


Table 1. Characteristics of TPA-Polymers Prepared by C−N Coupling Polymerization[a]

polymer	monomer	yield (%)	M_n[b]	M_w[b]	PDI[b]	mole ratio in polymer[c]	T_g (°C)[d]
P1	**4**	99 (10[e])	1 600[e]	3 900[e]	2.48[e]		
P2	**4** and **9** (1/99)	99	9 500	25 000	2.58	98.1/1.9	207
P3	**4** and **9** (5/95)	99	7 000	38 000	5.39	94.7/5.3	225
P4	**4** and **9** (20/80)	93	21 000	40 000	1.95	80.5/19.5	238
P5	**8**	94	20 000	38 000	1.90		234
P6	**4** and **8** (20/80)	99	13 000	23 000	1.85	79.0/21.0	208

[a] Reaction conditions: 2.5 mmol of monomer, 1.1 equiv of *t*-BuONa, 2 mol % of Pd(OAc)$_2$, 8 mol % of P(*t*-Bu)$_3$, and 2 mol % of 4-bromotoluene in 10 mL of THF at reflux for 24 h. [b] Determined by GPC with polystyrene standards. [c] Estimated from ^{1}H NMR spectra. [d] Determined by DSC profiles in the second heating. [e] Soluble part in chloroform.

(4′-bromophenyl)-3,4-ethylenedioxythiophene (**7**) using palladium catalyst in order to obtain the monomers with bromophenyl and diphenylamine moieties. Because these reactions gave the mixture of the desired product and oligomeric byproduct, the amount of sodium *tert*-butoxide was optimized at 1.4 equiv to 4-butylaniline to maximize the yield of the monomers. The isolation of **4** and **8** from the mixture was carried out by column chromatography. The structures of monomers were confirmed by ^{1}H and ^{13}C NMR spectra, in which the characteristic signals at 7.72 and 4.38 ppm derived from BTH and EDOT units were observed, respectively. The signal assignable to the proton of secondary arylamine was also observed for both monomers.

The C−N coupling polymerization of monomers was conducted using palladium(II) acetate and tri-*tert*-butylphosphine as a catalytic system in THF at reflux for 24 h (Scheme 2). For end-capping of terminals, 4-bromotoluene (2 mol % to monomer) was initially added to modify the diphenylamine terminal, whereas excess amount of diphenylamine (10 mol % to monomer) was added at the end of polymerization to modify the bromophenyl terminal. The characteristics of the polymers are summarized in Table 1. At first, polymerizations of **4** and **8** were carried out in order to obtain homopolymers (**P1** and **P5**) whose backbone composed of alternative sequence of TPA with BTH or EDOT, respectively. Homopolymerization of **4** gives the insoluble polymer in any common solvents, with small amount of soluble part. On the other hand, the homopolymer of **8** shows high M_n up to 20 000 and good solubility in chloroform and THF. Random copolymerizations of **4** with **9**, a monomer for PTPA component, were conducted with various feeding ratios. The polymers with different BTH unit contents ranging from 1 to 20 mol % were synthesized as shown in Table 1 (**P2** to **P4**). The molecular weights of the random copolymers are high up to 21 000 in M_n for **P4**. Polydispersity indices of **P2** and **P3** are broadened compared with **P4**, probably because of the formation of cyclic oligomers as reported in the previous work.[12] In addition, the random copolymer of **4** and **8** was also prepared only for 20 mol % of BTH unit (**P6**).

The polymer structures were characterized by ^{1}H NMR spectra, and all the signals were reasonably assigned as shown in Figure 1. Besides the signals derived from 4-butyltriphenylamine backbone, the characteristic signals assignable for BTH and EDOT units were observed at 7.70−7.87 and 4.31 ppm, respectively. Because no signal at around 8.0 ppm derived from the unreacted bromophenyl terminal in ^{1}H NMR spectra, it was indicated that the diphenylamine unit was quantitatively introduced at the bromophenyl terminal of the polymers. For the random copolymers, the mole ratios of **4** and **9** (or **8**) units in the polymers were estimated from ^{1}H NMR spectra. The signal at 7.87 ppm derived from BTH unit was compared with the signal at 2.58 ppm assignable to the methylene protons of butyl group attached to TPA. As the results are listed in Table 1, all the random copolymers showed similar mole ratios in the polymers with feeding ratios. The thermal property of the polymers was investigated by DSC analysis. A glass transition temperature (T_g) was observed at over 200 °C for all the polymers except for **P1**, as listed in Table 1. The more BTH unit is introduced in the random copolymers, the higher the T_g becomes up to 238 °C.

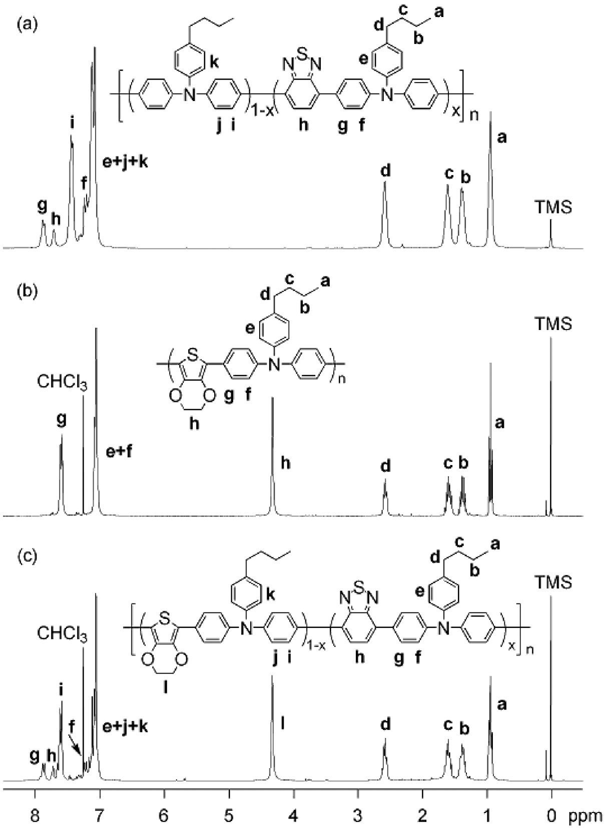


Figure 1. ^{1}H NMR spectra of (a) **P4**, (b) **P5**, and (c) **P6**.

Introduction of PEO as the second block at the diphenylamine terminal of the polymers containing BTH and/or EDOT units was achieved by end-capping reaction. As terminal modifiers, two kinds of PEO derivatives with M_n of 2000 were used instead of 4-bromotoluene. One is PEO with a bromophenyl group at a terminal (PEO-Br) as reported before.[12] The other was synthesized from PEO-Br in two steps. PEO-Br was treated with aniline to prepare PEO derivative with a diphenylamine terminal (PEO-DPA). The coupling reaction between PEO-DPA and **3** gave PEO derivative containing a BTH unit at a terminal (PEO-BTH, shown in Chart 1). Random copolymerization of **4** and **9** (5/95 in molar feed ratio) or homopolymerization of **8** was performed in the presence of 5 mol % of PEO-Br (**B1** and **B2** in Chart 1). On the other hand, **9** and **8** were polymerized in the presence of 5 mol % of PEO-BTH (**B3** and **B4** in Chart 1). After the polymerization, fractional reprecipitations from methanol and acetone were carried out for the removal of unreacted PEO terminal modifiers. All the polymerizations provided diblock copolymers containing PEO as the second segment. **B3** and **B4** possess BTH unit only at the junction point between TPA-polymers and PEO segments. The contents of BTH unit in the diblock copolymers (**B1**, **B3**, and **B4**) were constant around 5 mol % in feed ratios. The results are summarized in Table 2. The diblock copolymers

Chart 1. Chemical Structures of Diblock Copolymers Consisting of TPA-Polymers and PEO

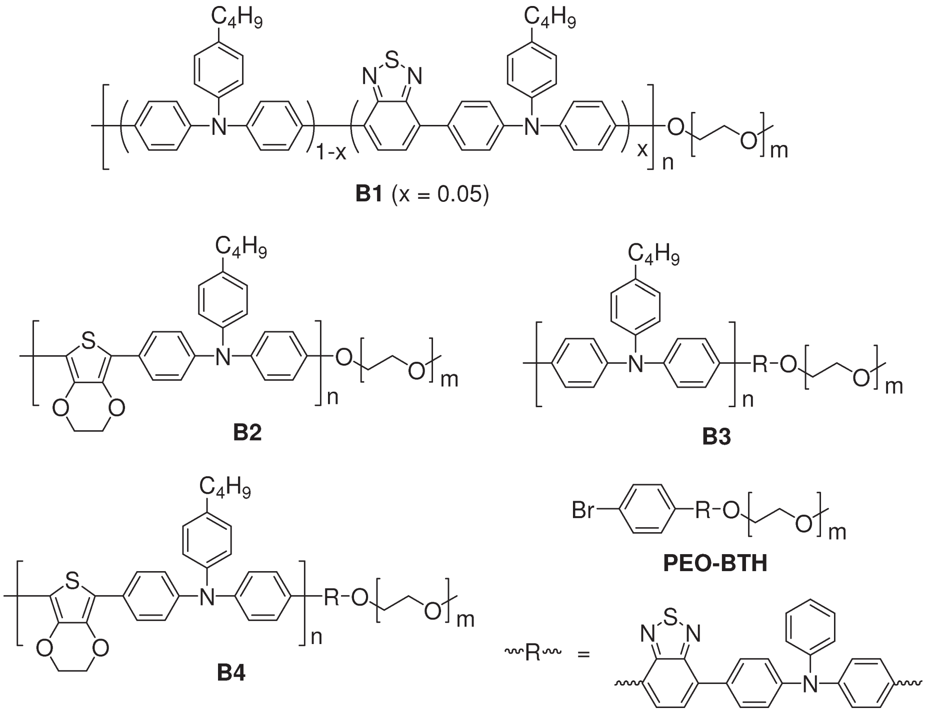


Table 2. Characteristics of Block Copolymers Based on TPA-Polymers[a]

polymer	monomer	terminal modifier	yield (%)	M_n[b]	M_w[b]	PDI[b]	T_m[c] (°C)	T_g[c] (°C)
B1	**4** and **9** (5/95)	PEO-Br	86	7 500	19 000	2.55	75	172
B2	**8**	PEO-Br	94	11 000	21 000	1.83	73	172
B3	**9**	PEO-BTH	98	8 000	16 000	2.03	74	167
B4	**8**	PEO-BTH	88	8 100	14 000	1.71	73	195

[a] Reaction conditions: 2.5 mmol of monomer, 1.1 equiv of *t*-BuONa, 2 mol % of $Pd(OAc)_2$, 8 mol % of $P(t\text{-}Bu)_3$, and 5 mol % of terminal modifier in 10 mL of THF at reflux for 24 h. [b] Determined by GPC with polystyrene standards. [c] Determined by DSC profiles in the second heating.

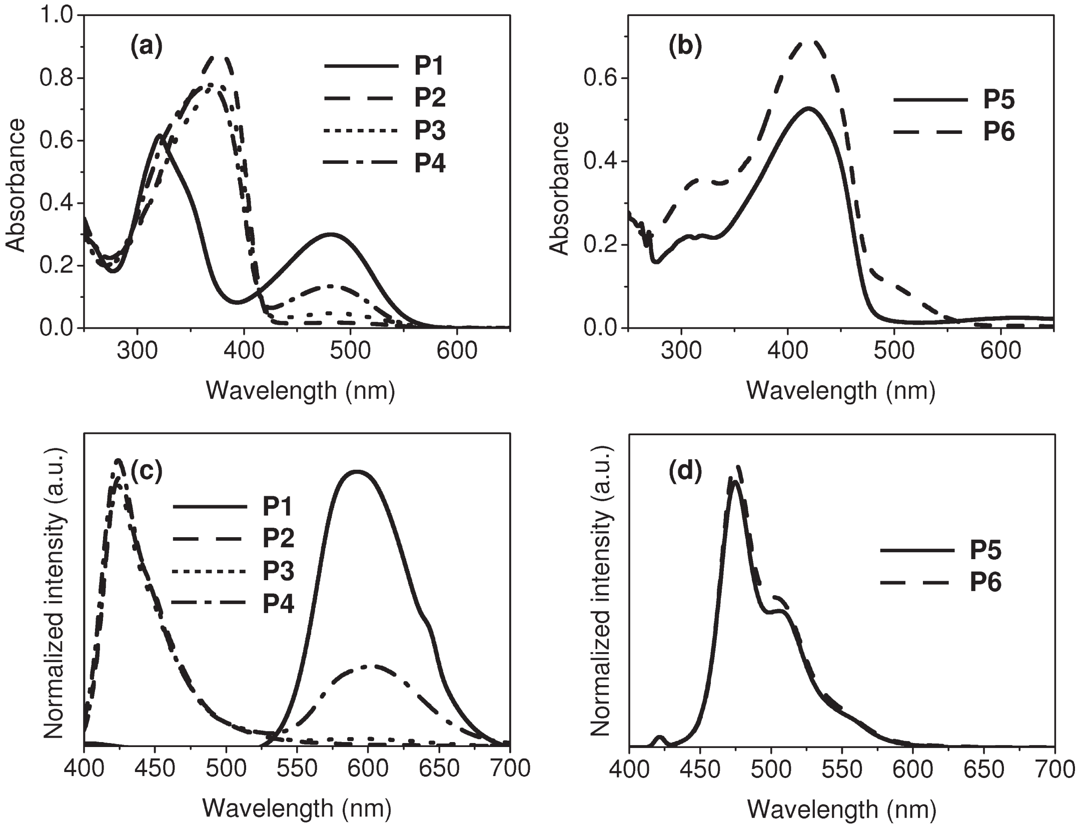


Figure 2. UV–vis absorption spectra of (a) BTH- and (b) EDOT-containing polymers and PL spectra of (c) BTH- and (d) EDOT-containing polymers.

showed the M_ns from 7500 to 11 000 with reasonable PDI values from 1.71 to 2.55. In the ^{1}H NMR spectra of block copolymers, a new signal derived from the methylene protons of PEO segment appeared at 3.65 ppm (see Supporting Information). No signal assignable to the terminal secondary amine of undesired homopolymer was observed at around 5.7 ppm. The mole ratio of ethylene oxide monomer unit to TPA monomer unit was around 33/67, which is comparable to the feeding ratio, confirming that almost all of PEO terminal modifier was introduced at the end of TPA-polymers. From these results, the formation of diblock copolymers without undesired homopolymers was confirmed.

DSC analysis was conducted for the block copolymers, and the results are listed in Table 2. The melting point (T_m) of PEO segment at 75 °C as well as the T_g of TPA-polymer was clearly observed for all the block copolymers. This may be an evidence for microphase separation of the block copolymers. However, the T_gs of TPA-polymer segments decreased because the M_ns were lower than those of corresponding homopolymers.

Photophysical properties of the polymers were investigated by UV–vis absorption and PL measurements in chloroform solution. The UV–vis and PL spectra of the polymers are shown in Figure 2. In addition to the absorption band around 350 nm derived from PTPA backbone, the polymers containning BTH unit (**P1** to **P4**) showed a maximum absorption wavelength at 480 nm. The absorption edge of the polymers with BTH unit reached 590 nm. Increasing BTH unit in the PTPA backbone gave a gradual increase in the absorption at 480 nm. On the other hand, the polymers containing EDOT unit (**P5** and **P6**) showed a bathochromic shift to 420 nm compared with PTPA. In the UV–vis spectrum of **P6**, a shoulder was observed at 500 nm derived from BTH unit.

The PL spectra excited at each maximum absorption wavelength were obtained for the polymers. Figure 2c shows the PL spectra of BTH-containing polymers (**P1** to **P4**). When the content of BTH unit was below 1 mol % (**P2**), a blue emission was observed with a peak top at 424 nm, which corresponds to

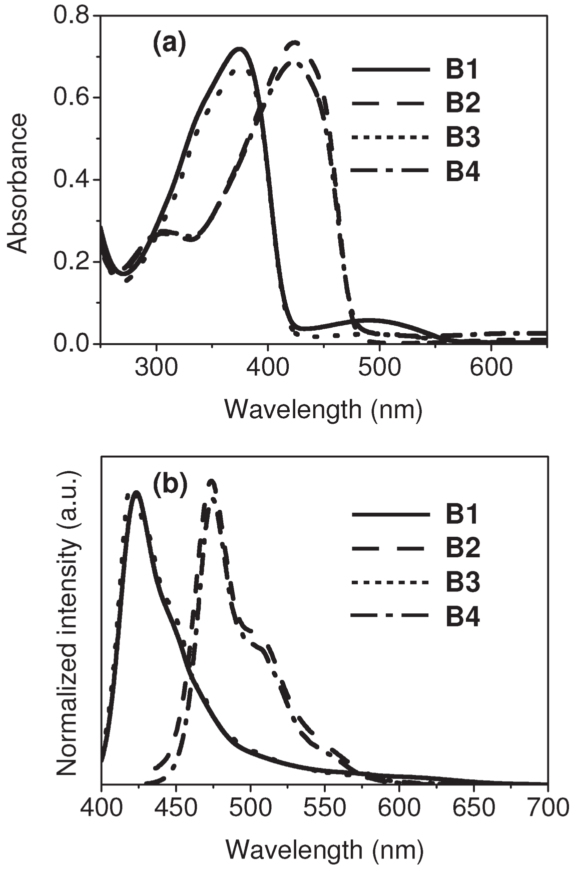


Figure 3. (a) UV–vis absorption spectra and (b) PL spectra of block copolymers.

the emission of PTPA. A new emission band at 600 nm appeared by increasing BTH unit for **P3** and **P4**, and the color of the emission turned to yellow and reddish orange, respectively. Homopolymer **P1** showed only the emission band at 600 nm colored red-violet. The energy transfer from TPA to BTH partially occurred during excitation at maximum absorption wavelengths around 350 nm. Therefore, the emission color can be tuned for the BTH-containing polymers by changing the content of BTH unit. On the other hand, an emission band at 475 nm with a shoulder at 507 nm was observed in the spectra of **P5** and **P6** (Figure 2d) excited at 420 nm. Although **P6** contains 20 mol % of BTH unit, the emission band around 600 nm derived from BTH moiety was not observed.

The UV–vis absorption and PL spectra of block copolymers in chloroform solution were also measured as shown in Figure 3. All the block copolymers showed similar spectra to those of corresponding homopolymers. In the UV–vis absorption spectra of **B3** and **B4**, a weak peak or a shoulder at 500 nm was attributed to BTH unit between blocks. In the PL spectra excited at the maximum absorption wavelengths, **B1** showed the yellow emission similar to that of **P3**, whereas the blue emission was observed for **B3** even with almost same the BTH content as **B1**. This resulted from the difference of the chemical structure. Energy transfer from TPA unit to BTH unit effectively took place in **B1** where BTH unit was randomly dispersed in the TPA-polymer backbone. In contrast, energy transfer rarely occurred in **B3** in which BTH unit located far from the excited TPA unit because the intrachain energy transfer is assumed to occur only on short segment length.[29]

Table 3. Electrical Properties of TPA-Polymers

polymer	E_{onset} (V)	$E_{\mathrm{pa}}{}^{a}$ (V)	$E_{\mathrm{pc}}{}^{a}$ (V)	$E^{\mathrm{o}\prime a}$ (V)	HOMO (eV)
P2	0.935	1.95	0.135	1.04	−5.69
P3	0.905	1.87	0.215	1.04	−5.69
P4	0.930	2.34	−0.335	0.990	−5.64
P5	0.745	1.65	−0.115	0.768	−5.41
P6	0.780	1.47	0.215	0.843	−5.49
B1	0.915	1.65	0.280	0.965	−5.61
B2	0.755	1.46	−0.035	0.710	−5.36
B3	0.880	1.98	−0.060	0.960	−5.61
B4	0.775	1.27	0.335	0.803	−5.45

[a] Formal potential $E^{\mathrm{o}\prime}$ was determined by the following equation: $E^{\mathrm{o}\prime} = (E_{\mathrm{pa}} + E_{\mathrm{pc}})/2$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively.

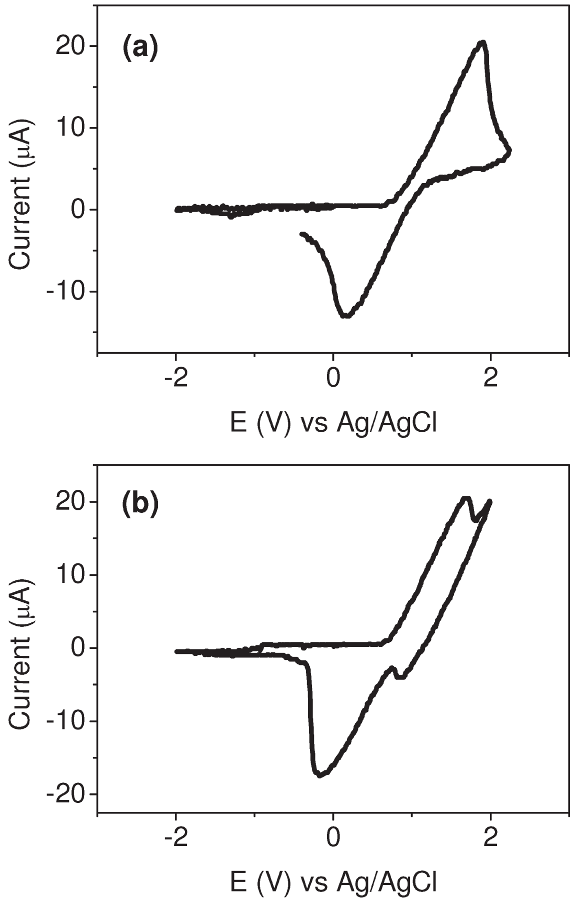


Figure 4. Cyclic voltammograms of (a) **P3** and (b) **P5** in film vs Ag/AgCl.

Cyclic voltammetry was conducted for the thin polymer films on a glassy carbon electrode using Ag/AgCl as a reference electrode. All the polymers except **P1** showed the redox peaks in the anodic sweep whereas no noticeable peak was observed in the cathodic sweep. The oxidation potentials and the highest occupied molecular orbital (HOMO) levels were estimated and are summarized in Table 3. The first set of redox peaks is assumed to be derived from the oxidation of TPA moiety. The HOMO levels of the BTH-containing polymers are slightly deeper than

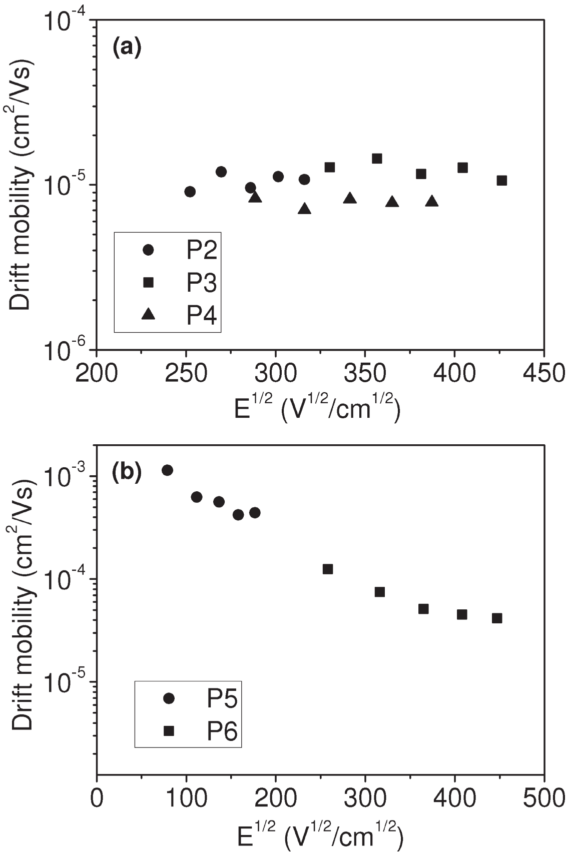


Figure 5. Dependence of the hole drift mobility on the applied field for (a) BTH- and (b) EDOT-containing polymers.

that of PTPA[10] because of the electron deficient nature of BTH unit. On the other hand, the EDOT-containing polymers (**P5** and **B2**) give the HOMO levels of around −5.4 eV, which is comparable to the HOMO level of PTPA.

The photocurrent on the exposure of a pulsed light was measured for the polymer films with a thickness ranging from 10 to 20 μm, and the hole drift mobility (μ) was estimated from the transit time (τ) represented as the knee point of the photocurrent. The logarithm of drift mobility in the polymers was plotted versus the square root of electric field in Figure 5. The random copolymers containing BTH unit (**P2** to **P4**) showed almost constant drift mobility of around 1×10^{-5} cm^2 V^{-1} s^{-1} independent of the amount of BTH unit (Figure 5a). This value is slightly lower than the hole drift mobility of PTPA (around 3×10^{-5} cm^2 V^{-1} s^{-1}) reported in the literature.[10] Especially, although only 1.9% of BTH unit was involved in the polymer backbone of **P2**, the μ decreased compared with PTPA. This is probably due to the existence of dipoles resulting from the combination of electron deficient BTH unit with electron-rich TPA unit. It is reported that doping of polar molecules to hole transporting materials decrease the drift mobility.[30,31] In the meantime, the introduction of EDOT unit in the polymer backbone (**P5** and **P6**) increased drift mobility up to 1×10^{-3} cm^2 V^{-1} s^{-1} (Figure 5b). The μ of **P6** decreased to the values ranging from 5×10^{-5} to 1×10^{-4} cm^2 V^{-1} s^{-1} because of the existence of BTH unit but was still higher value compared with PTPA.

The hole drift mobility of block copolymers films was also measured as shown in Figure 6. All the block copolymers exhibited the drift mobilities over 1×10^{-5} cm^2 V^{-1} s^{-1} even

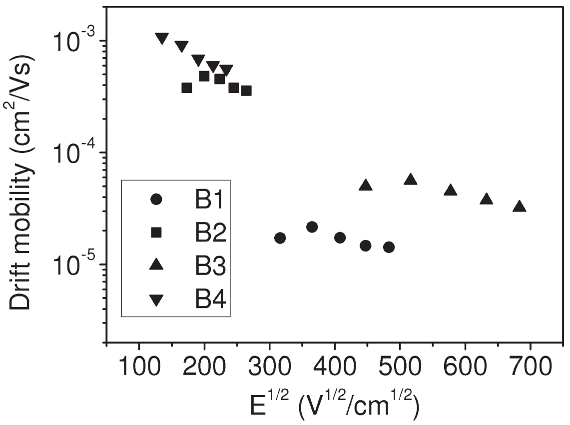


Figure 6. Dependence of the hole drift mobility on the applied field for block copolymers.

in the presence of electrically inert PEO block. **B1** and **B2** showed comparable μ values to those of corresponding homopolymers **P3** and **P5**, respectively. These results revealed that the existence of PEO block does not impede the transport of the generated hole. It is assumed that the generated hole transported through the TPA-polymer domain created by the microphase separation of block copolymers. The morphology of the surface of the polymer devices was confirmed by AFM measurement. The AFM image of **B1** and **B2** showed microphase-separated structures compared with that of homopolymer (see Supporting Information).

Furthermore, there is no influence of BTH unit on the drift mobility of the block copolymers with BTH unit at the junction point (**B3** and **B4**). Although **B3** contains BTH unit of 5 mol % at the junction point between PTPA and PEO, the μ of **B3** was from 4×10^{-5} to 5×10^{-5} cm^2 V^{-1} s^{-1}, which is slightly higher than that of PTPA. Similarly, the μ of **B4** was almost equivalent to that of **P5** in spite of BTH unit. The improved mobility of **B3** compared with **P3** or **B1**, the BTH contents of which are almost same of 5 mol %, may be attributed to the structural difference that BTH unit exists randomly in the polymer backbone or at the junction point. In the latter case, it is suggested that BTH unit lies only at the interface of the microphase-separated structure, i.e., between TPA-polymer and PEO domains. Therefore, the generated hole is assumed to pass through the TPA-polymer domain without being trapped at BTH unit.

■ CONCLUSIONS

The hole transporting polymers involving TPA unit in combination with BTH and/or EDOT unit(s) were synthesized via C−N coupling polymerization using palladium catalytic system. By chain-end modification using PEO terminal modifiers, the diblock copolymers consisting of TPA-polymer and PEO were prepared. Furthermore, the junction point between the segments of diblock copolymers was selectively functionalized using the BTH-modified PEO derivative. The optical and electrical measurements of the TPA-polymers revealed that the physical properties were influenced by the position where BTH unit was modified in the polymer backbone. High hole mobility up to 1.0×10^{-3} cm^2 V^{-1} s^{-1} was obtained by introduction of EDOT unit in PTPA backbone. Whereas the hole drift mobility of BTH-containing polymer films lowered because of hole trapping nature of BTH unit, the selective modification by BTH unit at the junction point of block copolymers does not impede the hole transporting ability.

■ ASSOCIATED CONTENT

Supporting Information. Figures S1−S28. This material is available free of charge via the Internet at http://pubs.acs.org.

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