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Catalyst-Transfer Suzuki−Miyaura Coupling Polymerization for Precision Synthesis of Poly(*p*-phenylene)

Tsutomu Yokozawa,* Haruhiko Kohno, Yoshihiro Ohta, and Akihiro Yokoyama

Department of Material and Life Chemistry, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan

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ABSTRACT: Catalyst-transfer Suzuki−Miyaura coupling polymerization of 2,5-bis(hexyloxy)-4-iodophenylboronic acid (**1b**) with ^{t}Bu$_3$PPd(Ph)Br (**2**) was investigated. When **1b** was polymerized with **2** at 0 °C in the presence of 4 equiv of CsF, 8 equiv of 18-crown-6, and a small amount of water (to dissolve CsF), poly(*p*-phenylene) (poly**1b**) with a narrow molecular weight distribution was obtained. The conversion-number average molecular weight (M_n) and feed ratio−M_n relationships indicate that this polymerization proceeded in a chain-growth polymerization manner. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra showed that poly**1b** with moderate molecular weight uniformly had a phenyl group, derived from **2**, at one end of each polymer chain and a hydrogen atom at the other, indicating involvement of a catalyst-transfer mechanism. However, the molecular weight distribution of the polymer gradually became broader with increase of the feed ratio of **1b** to **2**, and polymer chains with other end groups were formed. Successive catalyst-transfer Suzuki−Miyaura coupling polymerization of 2-(7-bromo-9,9-dioctyl-9*H*-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**) and then **1b** yielded a well-defined block copolymer of polyfluorene and poly(*p*-phenylene).

Introduction

π-Conjugated polymers containing aromatic rings in the backbone are an attractive class of materials owing to their potential applications as organic electronic materials in devices such as field effect transistors (FETs),[1,2] organic light-emitting diodes (OLEDs),[3] and photovoltaic cells.[4] These polymers have generally been synthesized by conventional polycondensation with a metal catalyst,[5−7] and this approach results in a broad molecular weight distribution. However, the development of catalyst-transfer condensation polymerization has made it feasible to control the molecular weight, polydispersity, and end groups of π-conjugated polymers.[8,9] In catalyst-transfer Kumada−Tamao coupling polymerization with a Ni catalyst, the synthesis of poly(3-alkylthiophene)s,[8,10−12] poly(*p*-phenylene),[13] and poly(*N*-alkylpyrrole)[14,15] shows the character of living polymerization, whereas the polymerization leading to polyfluorene proceeds in a chain-growth polymerization manner accompanied by chain transfer reaction.[15,16] Among these polymerizations, the catalyst-transfer condensation polymerization leading to poly(3-alkylthiophene)s has been extensively developed. For example, block copolythiophenes with different alkyl side chains,[12,17−24] block copolymers of polythiophene and other π-conjugated polymers,[14,25−30] and block copolymers of polythiophene and vinyl polymers[31−40] have been obtained. Isolable Ni initiators[41−43] were found and applied to production of polythiophene brushes from the surface.[41,43−46] Furthermore, the mechanism of the catalyst-transfer condensation polymerization of poly(3-alkylthiophene)s has been investigated.[47,48]

In the case of catalyst-transfer Suzuki−Miyaura coupling polymerization, however, only polyfluorenes could be obtained in a controlled manner.[49,50] The polymerization of bromophenylboronic acid monomer **1a** with a Pd complex initiator **2** was attempted under the same conditions used for the polymerization of pinacol fluoreneboronate monomer **3** with aqueous Na_2CO_3 as a typical base but afforded polyphenylene with a broad molecular weight distribution.[49] In the present paper, we focus on the Suzuki−Miyaura coupling polymerization of iodophenylboronic acid monomer **1b** with **2** under various conditions. We found that the polymerization using CsF/18-crown-6 and a small amount of water instead of aqueous Na_2CO_3 proceeded in a chain-growth polymerization manner to yield polyphenylene with well-defined molecular weight and low polydispersity. The polymer end groups were also well controlled: a phenyl group, derived from **2**, was present at one end and a hydrogen atom at the other end (designated Ph/H). Furthermore, block copolymers of polyfluorene and polyphenylene were synthesized by successive catalyst-transfer Suzuki−Miyaura coupling polymerization of fluorene monomer **3** and then **1b** in one pot (Scheme 1).

Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra were obtained on JEOL ECA-600 and ECA-500 instruments using tetramethylsilane (0.00 ppm in ^{1}H NMR) and the midpoint of $CDCl_3$ (77.0 ppm in ^{13}C NMR) as internal standards, respectively. IR spectra were recorded on a JASCO FT/IR-410. Column chromatography was performed on silica gel (Kieselgel 60, 230−400 mesh, Merck). Analytical thin-layer chromatography (TLC) was performed on silica gel (silica gel 60 F_{254}, aluminum sheets, Merck). GC was performed on a Shimadzu GC-14B gas chromatograph equipped with a GL Science dimethylsilicone fluid OV-101 column (3 m) and a flame ionization detector (FID). The M_n and M_w/M_n values of polymers were measured with a TOSOH HLC-8020 gel permeation chromatography (GPC) unit [eluent: tetrahydrofuran (THF); calibration: polystyrene standards] using two TSK-gel columns (2 × Multipore H_{XL}-M). Isolation of poly**1b** for an NMR sample was carried out with a Japan Analytical Industry LC-908 Recycling Preparative HPLC (eluent: chloroform) using two TSK-gel columns (2 × G

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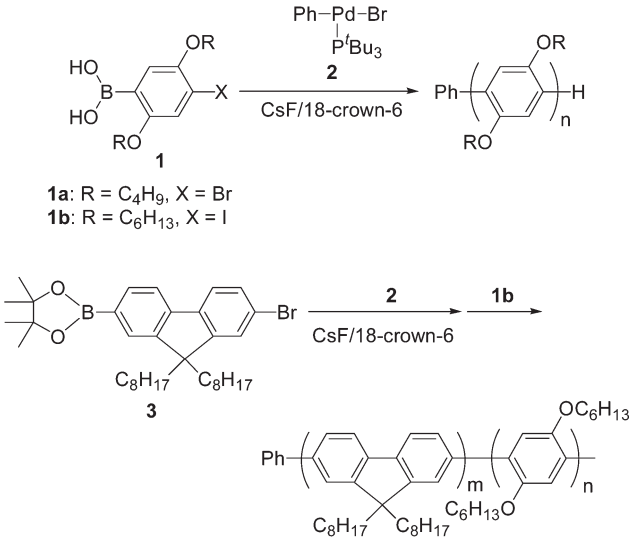
*Corresponding author. E-mail: yokozt01@kanagawa-u.ac.jp.

Scheme 1



$2000H_{HR}$). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Shimadzu/Kratos AXIMA-CFR plus in the reflectron or linear mode by use of a laser (λ = 337 nm). Dithranol (1,8-dihydroxy-9[10*H*]-anthracenone) was used as the matrix for the MALDI-TOF mass measurements.

Materials. 1,4-Bis(hexyloxy)benzene was prepared by the reported procedure.[51] ^{t}Bu$_3$PPd(Ph)Br (**2**)[52] and 2-(7-bromo-9,9-dioctyl-9*H*-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**)[53] were prepared according to the established procedures.[49] Dry tetrahydrofuran (THF) and other reagents were commercial products and were used without further purification.

Synthesis of 1b. Monomer **1b** was prepared by diiodination of 1,4-bis(hexyloxy)benzene, followed by boronation in a similar manner to the literature method.[54,55] A flask was charged with glacial acetic acid (55 mL), H_2SO_4 (2 mL), water (9 mL), and CCl_4 (12 mL), and into the flask were added 1,4-bis(hexyloxy)benzene (5.04 g, 18.1 mmol), iodine (4.14 g, 16.3 mmol), and iodic acid (1.90 g, 10.8 mmol). The resulting mixture was heated at 70 °C for 24 h. After this time, a solution of sodium thiosulfate was added to remove any unreacted iodine. The solution was extracted with diethyl ether and washed successively with 5% NaOH solution and water. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Column chromatography on silica gel with hexane, followed by recrystallization from hexane, afforded 1,4-bis(hexyloxy)-2,5-diiodobenzene as a white powder (4.67 g, 49%); mp 54.2–55.0 °C. IR (KBr): 2950, 2918, 2857, 1450, 1213, 849, 526 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.17 (s, 2 H), 3.93 (t, *J* = 6.5 Hz, 4 H), 1.80 (quint, *J* = 6.5 Hz, 4 H), 1.53–1.47 (m, 4 H), 1.37–1.32 (m, 8 H), 0.91 (t, *J* = 7.0 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 152.8, 122.7, 86.3, 70.3, 31.5, 29.1, 25.7, 22.6, 14.0.

The diiodinated product (4.03 g, 7.60 mmol) was placed in a flame-dried flask, and the flask was evacuated and then filled with argon. THF (40 mL) was added to the flask, and the solution was cooled to −78 °C. Butyllithium (1.6 mol/L in hexane, 4.8 mL, 7.7 mmol) was slowly added, and then the mixture was stirred at that temperature. After 2 h, when the starting material had been consumed, tri(isopropoxy)borane (3.4 mL, 15 mmol) was added at −78 °C, and the mixture was stirred at that temperature for 2 h. The reaction was quenched with 1 mol/L hydrochloric acid, and the product was extracted with diethyl ether. The organic layer was washed with water and brine and then dried over $MgSO_4$, and the solvent was evaporated. Recrystallization of the residue from ethyl acetate/hexane gave **1b** (1.75 g, 52%); mp 100.7–101.4 °C. IR (KBr): 3378, 2938, 2856, 1587, 1384, 1311, 1050, 881, 476 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31 (s, 1 H), 7.24 (s, 1 H), 6.02 (s, 2 H), 4.01 (t, *J* = 6.9 Hz, 2 H), 4.00 (t, *J* = 6.9 Hz, 2 H), 1.85–1.79 (m, 4 H), 1.54–1.43 (m, 4 H), 1.38–1.31 (m, 8 H), 0.91 (t, *J* = 7.4 Hz, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 158.3, 152.5, 122.4, 119.0, 91.4, 70.0, 69.3, 31.5, 31.4, 29.2, 25.7, 25.6, 22.6, 22.5, 14.0, 13.9.

Table 1. Polymerization of 1b with 2 by Using Aqueous Na_2CO_3[a]

entry	temp (°C)	[**1b**]$_0$/[**2**]$_0$	M_n[b]	M_w/M_n[b]
1	40	50	22 200[c]	2.71[c]
2	reflux	20	9 600	1.87
3	reflux	50	17 900	1.79

[a] Polymerization was carried out in the presence of Na_2CO_3 in THF–H_2O ([**1b**]$_0$ = 0.02 mol/L in THF, [Na_2CO_3]$_0$ = 2 mol/L in water, THF/water = 3/1 (v/v)). [b] Estimated by GPC based on polystyrene standards (eluent: THF). [c] Polymer was precipitated during polymerization.

Polymerization of 1b. Compound **2** (1.5 mg, 3.3 μmol) was placed in a round-bottomed flask, and a vacuum was applied. The flask was filled with argon, then THF (3 mL) was added, and the solution was degassed with argon by using a diaphragm pump. In a pear-shaped flask, **1b** (28 mg, 0.063 mmol), CsF (42 mg, 0.28 mmol), 18-crown-6 (140 mg, 0.53 mmol), and naphthalene (7.5 mg, 0.059 mmol) as an internal standard were charged, and THF (4.5 mL) and water (0.4 mL) were added. The solution was similarly degassed. The polymerization was initiated by addition of the solution in the pear-shaped flask to the solution containing **2** in the round-bottomed flask with a cannula at 0 °C. After 2 h at 0 °C, the reaction was quenched with 12 mol/L hydrochloric acid. The solution was extracted with dichloromethane, and the organic layer was dried over $MgSO_4$. The solution was concentrated under reduced pressure, and the residue was purified by HPLC to remove 18-crown-6 to yield poly**1b** (M_n = 6100, M_w/M_n = 1.24). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.10 (m, 2 H), 3.92 (m, 4 H), 1.68 (m, 4 H), 1.36 (m, 4 H), 1.28 (m, 8 H), 0.87 (t, *J* = 6.9 Hz, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 150.1, 127.5, 117.3, 69.6, 31.7, 29.5, 25.8, 22.6, 14.0.

Block Copolymerization of 3 and 1b. Compound **2** (1.0 mg, 2.1 μmol) was placed in a round-bottomed flask, and a vacuum was applied. The flask was filled with argon, THF (2 mL) was added, and then the solution was degassed with argon by using a diaphragm pump. In a pear-shaped flask, **3** (23 mg, 0.042 mmol), CsF (70 mg, 0.46 mmol), 18-crown-6 (0.29 g, 1.1 mmol), and naphthalene (5.5 mg, 0.043 mmol) as an internal standard were charged, and THF (4 mL) and water (0.6 mL) were added. The solution was similarly degassed. The polymerization was initiated by addition of the solution in the pear-shaped flask into the solution containing **2** in the round-bottomed flask via a cannula at 0 °C. The mixture was stirred at 0 °C for 4 h (conversion of **3** = 94%, poly**3**: M_n = 7300, M_w/M_n = 1.19). A solution of **1b** (19 mg, 0.043 mmol) in THF (3 mL), which had been degassed, in a pear-shaped flask was added to the solution of poly**3**. The reaction mixture was stirred at 0 °C for 1 h (conversion of **1b** = 92%), and then the reaction was quenched with 12 mol/L hydrochloric acid. The solution was extracted with dichloromethane, and the organic layer was dried over $MgSO_4$, followed by concentration under reduced pressure to give 18.2 mg (68%) of poly**3**-*b*-poly**1b** (M_n=13 000, M_w/M_n=1.29).

Results and Discussion

Polymerization of 1b with Aqueous Na_2CO_3. The polymerization of **1b** with **2** was first carried out by using aqueous Na_2CO_3 as a base in THF in a similar manner to the case of catalyst-transfer polymerization of **3** (Table 1). In the polymerization at 40 °C, poly**1b** was precipitated during the polymerization (entry 1), although the same polyphenylene that was synthesized by catalyst-transfer Kumada–Tamao coupling polymerization[13] is soluble in THF. The precipitation

Table 2. Polymerization of 1b with 2 by Using Various Bases[a]

entry	base	time (h)	M_n[b]	M_w/M_n[b]
1	K_3PO_4	96[c]	2790	1.43
2	TBAF	120[c]	1550	2.01
3	CsF[d]	48[c]	3480	1.44
4	CsF/18-crown-6[d,e]	4	6400	1.26
5	CsF/18-crown-6[d]	20	6200	1.49

[a] Polymerization of **1b** was carried out with **2** ($[\mathbf{1b}]_0/[\mathbf{2}]_0 = 20$) in the presence of 4 equiv of base in THF ($[\mathbf{1b}]_0 = 0.02$ mol/L) at room temperature. [b] Estimated by GPC based on polystyrene standards (eluent: THF). [c] Monomer **1b** remained. [d] 8 equiv of 18-crown-6 was used. [e] A small amount of water was added (water/THF = 1/25 (v/v)).

Table 3. Polymerization of 1b with 2 at Various Temperatures[a]

entry	temp (°C)	$[\mathbf{1b}]_0/[\mathbf{2}]_0$	time (h)	M_n[b]	M_w/M_n[b]
1	rt	60	20	18 300	1.84
2	0	60	3.5	16 100	1.47
3	0	80	5	21 200	1.52
4	0	100	6	15 500[c]	1.44
5	−20	60	48	18 700	1.45
6	−20	80	4	15 100[c]	1.89
7	−50[d]	60	48[e]	5 300[c]	1.25

[a] Polymerization of **1b** was carried out with **2** in the presence of 4 equiv of CsF and 8 equiv of 18-crown-6 in THF ($[\mathbf{1b}]_0 = 8.0$ mmol/L) and water (water/THF = 1/17 (v/v)). [b] Estimated by GPC based on polystyrene standards (eluent: THF). [c] Polymer was precipitated during polymerization. [d] CsF was precipitated. [e] Monomer **1b** remained.

might be responsible for the bimodal GPC elution curve of the obtained poly**1b**. Since aqueous Na_2CO_3 was used, water dissolved in THF might decrease the solubility of poly**1b** in the reaction solvent, resulting in precipitation of poly**1b**. On the other hand, polymerization under reflux proceeded homogeneously to afford polymer with a monomodal GPC trace. When the feed ratio of **1b** to **2** ($[\mathbf{1b}]_0/[\mathbf{2}]_0$) was increased from 20 to 50, the M_n value almost doubled from 9600 to 17 900 (entries 2 and 3). However, the molecular weight distribution was broad. Accordingly, we expected that poly**1b** with a narrower molecular weight distribution would be obtained when the polymerization was carried out homogeneously at lower temperature by using a nonaqueous base.

Study of Base. The polymerization of **1b** with **2** was then carried out by using various bases in THF at room temperature (Table 2). We first examined K_3PO_4, which was effective for selective diarylation of dihaloarenes with arylboronic acids via intramolecular Pd-catalyst transfer.[56] However, K_3PO_4 was not soluble in THF, and **1b** remained unreacted even after 96 h. The obtained polymer had low molecular weight (entry 1). We next tried fluoride-mediated Suzuki–Miyaura polymerization.[57] When tetrabutylammonium fluoride (TBAF), which is soluble in THF, was used, **1b** remained and low-molecular-weight polymer was obtained (entry 2). The use of CsF dissolved in a small amount of water gave similar results (entry 3). However, addition of 18-crown-6 to the former reaction mixture accelerated the polymerization, and **1b** was consumed within 4 h. Furthermore, the molecular weight distribution narrowed to 1.26 (entry 4). We further checked the polymerization with CsF/18-crown-6 in the absence of water, but the polymerization became slower, affording poly**1b** with a broader molecular weight distribution (entry 5). Consequently, it turned out that CsF along with 18-crown-6 and a small amount of water for dissolving CsF was the best base system for obtaining poly**1b** with a narrow molecular weight distribution.

Effect of Polymerization Temperature. Using the above conditions with CsF/18-crown-6, the polymerization was carried out with increasing values of $[\mathbf{1b}]_0/[\mathbf{2}]_0$ ratio from 20 to 60 in order to obtain higher-molecular-weight polymer. Indeed, the M_n value of the polymer increased almost 3-fold, but the molecular weight distribution became broad (Table 3, entry 1), implying that side reactions took place at room temperature. The polymerization was then examined at lower temperature. When the polymerization was carried out at $[\mathbf{1b}]_0/[\mathbf{2}]_0 = 60$ at 0, −20, and −50 °C, the polydispersity was narrower at 0 and −20 °C (entries 2 and 5), whereas CsF was precipitated at −50 °C, leaving unreacted **1b** (entry 7). The polymerization was then carried out at $[\mathbf{1b}]_0/[\mathbf{2}]_0 = 80$ at 0 and −20 °C. At 0 °C, the reaction mixture was homogeneous, whereas at −20 °C polymer was precipitated during the polymerization (entries 3 and 6). When the polymerization was carried out at 0 °C and $[\mathbf{1b}]_0/[\mathbf{2}]_0 = 100$, polymer was also precipitated (entry 4). Consequently, it has become apparent that **1b** should be polymerized at 0 °C with an $[\mathbf{1b}]_0/[\mathbf{2}]_0$ ratio of 80 or less.

Polymerization Behavior. With the optimized conditions in hand, we studied the polymerization behavior and evaluated the polymerization. We first analyzed the M_n and M_w/M_n values of poly**1b** at each conversion in the polymerization of **1b** with **2** ($[\mathbf{1b}]_0/[\mathbf{2}]_0 = 30$) at 0 °C. The M_n values increased in proportion to the conversion, and the M_w/M_n ratios were 1.25 or less over the whole conversion range (Figure 1A), indicating that **1b** was polymerized in a chain-growth polymerization manner. When **1b** was polymerized with various feed ratios ($[\mathbf{1b}]_0/[\mathbf{2}]_0$), the M_n values of the polymer increased linearly in proportion to $[\mathbf{1b}]_0/[\mathbf{2}]_0$ (Figure 1B). The polydispersity, however, gradually increased with increasing $[\mathbf{1b}]_0/[\mathbf{2}]_0$ ratio (see later discussion). The chain-growth nature of the polymerization was also examined by means of a monomer-addition experiment. A fresh feed of **1b** ($[\text{added } \mathbf{1b}]_0/[\mathbf{2}]_0 = 20$) was added to the prepolymer ($[\mathbf{1b}]_0/[\mathbf{2}]_0 = 40$, conversion = 98%, $M_n = 11\,600$, $M_w/M_n = 1.33$) in the reaction mixture. The GPC chromatogram of the product clearly shifted toward the higher-molecular-weight region (conversion = 96%, $M_n = 16\,500$, $M_w/M_n = 1.47$) (Figure 2). This result indicates that the added **1b** was polymerized from the polymer end group of the prepolymer due to the chain-growth nature of this polymerization.

In the ^1H NMR spectra of poly**1b** obtained at $[\mathbf{1b}]_0/[\mathbf{2}]_0 = 20$ and 50, the signals **a**, **c**, and **d** due to the terminal phenyl group derived from initiator **2** were observed (Figure 3). On the basis of the integral ratio of the phenylene proton signal **b** in the repeat unit to the signal **a** of the terminal phenyl group, the average values of degree of polymerization (DP_n) of poly**1b** obtained at $[\mathbf{1b}]_0/[\mathbf{2}]_0 = 20$ and 50 were estimated to be 20 and 54, respectively. The DP_ns were in good agreement with the feed ratios $[\mathbf{1b}]_0/[\mathbf{2}]_0$, implying that one initiator **2** molecule forms one polymer chain.

The polymer end groups were further analyzed by means of matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry. The spectrum of poly**1b** ($M_n = 6100$, $M_w/M_n = 1.24$, Figure 4A(a)), obtained by the polymerization of **1b** with **2** at $[\mathbf{1b}]_0/[\mathbf{2}]_0 = 20$, followed by quenching with 12 mol/L HCl, contains only one series of peaks, which correspond to the polymer with a phenyl group at one end and a hydrogen atom at the other end (designated as Ph/H) (Figure 4B). For example, the exact mass of a single isotope of the 14-mer with Ph/H is expected to produce a signal at 3944.99 Da, and in fact a signal was observed at 3945.07 Da, as shown in the magnified spectrum in Figure 4B. Since the Ph and H end groups are thought to be derived from the Ph group of **2** and the Pd complex end group by quenching, respectively, the results of the ^1H NMR and the MALDI-TOF mass spectra of poly**1b** indicate that the polymerization of **1** with **2** involves the catalyst-transfer polymerization mechanism.

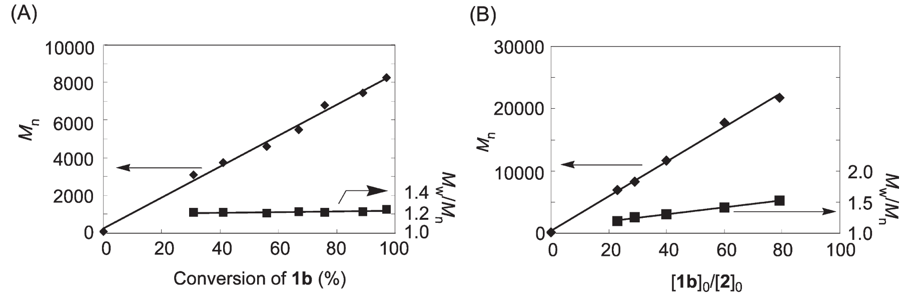


Figure 1. M_n and M_w/M_n values of poly**1b** as a function of (A) monomer conversion, obtained by the polymerization of **1b** with **2** ($[\mathbf{1b}]_0/[\mathbf{2}]_0$ = 30), and (B) the feed ratio of **1b** to **2**. All the polymerizations were carried out in the presence of 4 equiv of CsF and 8 equiv of 18-crown-6 in THF ($[\mathbf{1b}]_0$ = 8.0 mM) and water (water/THF = 1/17 (v/v)) at 0 °C. M_n and M_w/M_n values were determined by GPC based on polystyrene standards.

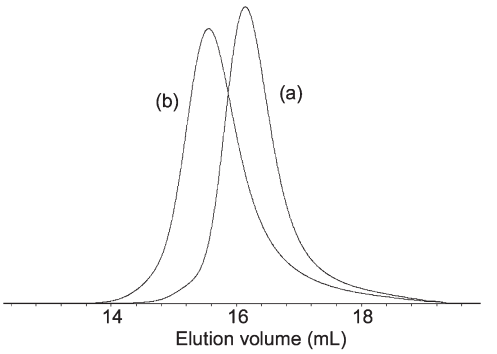


Figure 2. GPC profiles of (a) prepolymer ($[\mathbf{1b}]_0/[\mathbf{2}]_0$ = 40, conversion = 98%, M_n = 11 600, M_w/M_n = 1.33) and (b) postpolymer ([added $\mathbf{1b}]_0/[\mathbf{2}]_0$ = 20, conversion = 96%, M_n = 16 500, M_w/M_n = 1.47) obtained in a monomer addition experiment.

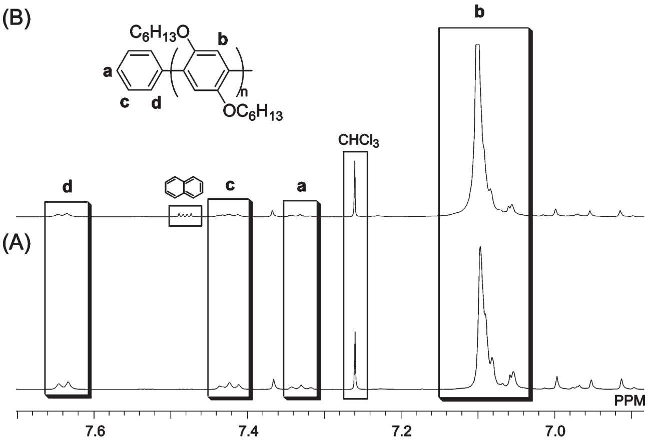


Figure 3. ^{1}H NMR spectra of poly**1b**, obtained at $[\mathbf{1b}]_0/[\mathbf{2}]_0$ = (A) 20 (M_n = 6100, M_w/M_n = 1.24) and (B) 50 (M_n = 15 200, M_w/M_n = 1.51) at 0 °C, in $CDCl_3$ at 25 °C.

However, poly**1b** (M_n = 17 300, M_w/M_n = 1.43), obtained by the polymerization at $[\mathbf{1b}]_0/[\mathbf{2}]_0$ = 60, showed tailing toward the low-molecular-weight region in the GPC chromatogram (Figure 4A(b)). The product in the tailing region was isolated by means of HPLC, and the MALDI-TOF mass spectrum was taken (Figure 4C). The main series of peaks were similarly due to the polymer with Ph/H, but peaks of the polymers with Ph/I and H/H were also observed as well as other peaks that could not be assigned. Therefore, termination and chain transfer of the catalyst might occur to some extent during propagation, resulting in the formation of low-molecular-weight polymer, when high-molecular-weight polymer is synthesized at a high $[\mathbf{1b}]_0/[\mathbf{2}]_0$ ratio.

Block Copolymerization. With two monomers that undergo catalyst-transfer Suzuki–Miyaura coupling polymerization in hand, we tried to synthesize block copolymers of polyfluorene and polyphenylene. McCullough and co-workers have recently reported similar block copolymers synthesized by means of Kumada–Tamao coupling polymerization.[30] In our previous paper, fluorene monomer **3** was polymerized by using aqueous Na_2CO_3 as a base.[49] For block copolymerization of **1b** and **3**, it should first be examined whether the polymerization of **3** with the CsF/18-crown-6 base system, instead of aqueous Na_2CO_3, proceeds in a catalyst-transfer mechanism. The polymerization of **3** with **2** ($[\mathbf{3}]_0/[\mathbf{2}]_0$ = 10) was then carried out in the presence of 4 equiv of CsF, 8 equiv of 18-crown-6, and a small amount of water at 0 °C to yield poly**3** with a narrow molecular weight distribution (M_n = 3800, M_w/M_n = 1.28) (Scheme 2). Furthermore, the feasibility of block copolymerization was also examined by means of a monomer-addition experiment, in which a fresh feed of **3** ([added $\mathbf{3}]_0/[\mathbf{2}]_0$ = 10) was added to the prepolymer ($[\mathbf{3}]_0/[\mathbf{2}]_0$ = 10, conversion = 92%, M_n = 3700, M_w/M_n = 1.28) in the reaction mixture. The added **3** was smoothly polymerized (conversion = 96%), and the M_n value of the resulting polymer doubled, while a narrow molecular weight distribution was maintained (M_n = 7300, M_w/M_n = 1.19).

The good result of the polymerization of **3** with CsF/18-crown-6 prompted us to try block copolymerization. Because we have found that successive catalyst-transfer polymerizations should be conducted from a monomer with low π-donor ability to a monomer with high π-donor ability,[28] the fluorene monomer **3** was polymerized first in the presence of **2** ($[\mathbf{3}]_0/[\mathbf{2}]_0$ = 20) and CsF/18-crown-6 at 0 °C for 4 h to afford well-defined poly**3** (conversion of **3** = 94%, poly**3**: M_n = 7300, M_w/M_n = 1.19). Then 1.0 equiv of phenylene monomer **1b** was added to the reaction mixture, and the second polymerization was conducted at 0 °C for 1 h (Scheme 1). The conversion of **1b** reached 92%, and the GPC elution curve shifted toward the higher-molecular-weight region, although with tailing toward the low-molecular-weight region (Figure 5). The obtained polymer showed M_n = 13 000 and M_w/M_n = 1.29. These results indicate that the second monomer **1b** was polymerized in a chain-growth polymerization manner from the polymer end group of the first polymer to yield diblock copolymer poly**3**-*b*-poly**1b**.

The block copolymerization in the reverse order was also examined, even though it is considered an inappropriate polymerization order on the basis of our previous observations.[28] Phenylene monomer **1b** was polymerized first in the presence of **2** ($[\mathbf{1b}]_0/[\mathbf{2}]_0$ = 20) and CsF/18-crown-6 at 0 °C for 1 h to afford poly**1b** (conversion of **1b** = 97%, poly**1b**: M_n = 6870, M_w/M_n = 1.18). Equimolar **3** was then added to the reaction mixture, and the polymerization was conducted at 0 °C. The conversions of **3** in 4 and 6 h were 23 and 26%, respectively; the polymerization almost stopped. The GPC profile of the polymer obtained at 6 h showed M_n = 9110 and

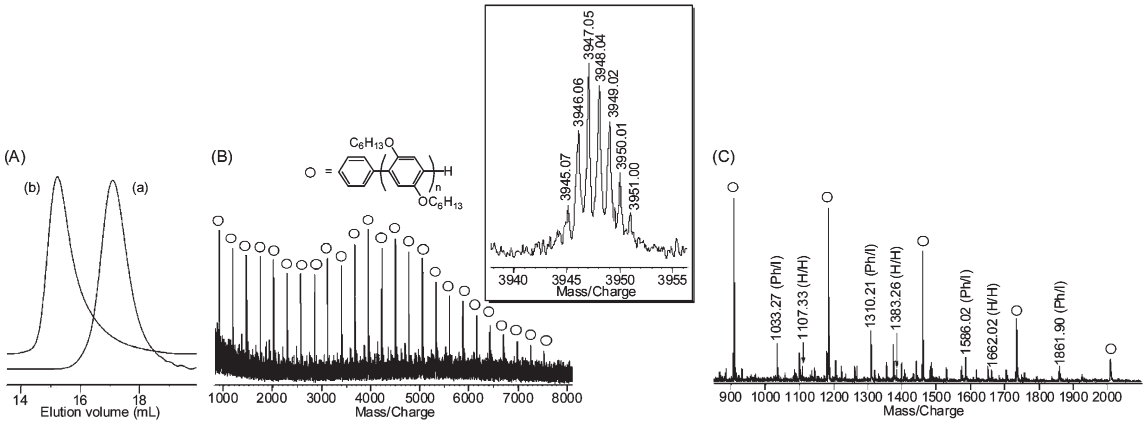
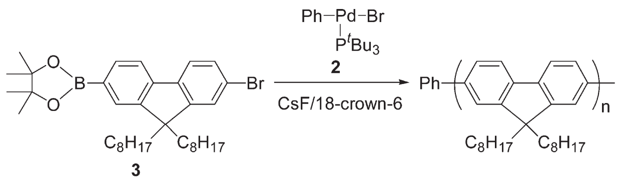


Figure 4. (A) GPC profiles of the polymer obtained at $[\mathbf{1b}]_0/[\mathbf{2}]_0$ = (a) 20 and (b) 60. (B) MALDI-TOF mass spectra of the polymer obtained at $[\mathbf{1b}]_0/[\mathbf{2}]_0$ = 20. (C) MALDI-TOF mass spectrum of the product in the tailing part of the GPC profile (b).

Scheme 2



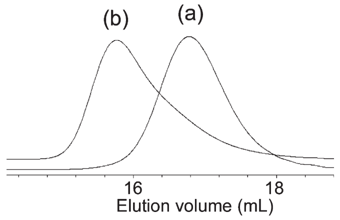


Figure 5. GPC profiles of the polymer obtained by block copolymerization: (a) poly**3** as a prepolymer ($[\mathbf{3}]_0/[\mathbf{2}]_0$ = 20, conversion of **3** = 94%, M_n = 7300, M_w/M_n = 1.19) and (b) poly**3**-*b*-poly**1b** as a postpolymer ([added $\mathbf{1b}]_0/[\mathbf{2}]_0$ = 20, conversion of **1b** = 92%, M_n = 13 000, M_w/M_n = 1.29).

M_w/M_n = 1.20. The polymerization temperature was then raised to room temperature so as to consume **3**. As a result, the conversion of **3** reached 94% in 12 h at room temperature to afford poly**1b**-*b*-poly**3** with a broader molecular weight distribution (M_n = 16 900, M_w/M_n = 1.45). Consequently, block copolymerization in Suzuki–Miyaura catalyst-transfer coupling polymerization should be also conducted from a monomer with low π-donor ability to a monomer with high π-donor ability.

Conclusion

We have demonstrated that Suzuki–Miyaura coupling polymerization of iodophenylboronic acid monomer **1b** with ^{t}Bu$_3$PPd(Ph)Br (**2**) proceeded in a chain-growth polymerization manner to yield well-defined poly(*p*-phenylene) when CsF, 18-crown-6, and a small amount of water (for dissolving CsF) were used as the base system. The M_n value was controlled by the feed ratio of monomer **1b** to the Pd complex **2**. The MALDI-TOF mass spectra showed that poly**1b** with moderate molecular weight uniformly had a phenyl group, derived from **2**, at one end and a hydrogen atom at the other, indicating that this polymerization involves a catalyst-transfer mechanism. In the synthesis of higher-molecular-weight polymer, however, the molecular weight distribution became broader, and polymer end groups other than Ph/H were observed. The successive Suzuki–Miyaura coupling polymerization of fluorene monomer **3** and then *p*-phenylene monomer **1b** yielded block copolymer of polyfluorene and poly(*p*-pheneylene), which has many potential applications. Further experiments are in progress to evaluate catalyst-transfer Suzuki–Miyaura coupling polymerization of other monomers.

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References and Notes

(1) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99–117.
(2) Bao, Z.; Locklin, J. *Organic Field-Effect Transistors*, 1st ed.; CRC Press: Boca Raton, FL, 2007.
(3) Braun, D. *Mater. Today* **2002**, *5*, 32–39.
(4) Brabec, C.; Dyakonov, V.; Scherf, U. *Organic Photovoltaics; Materials, Device Physics, and Manufacturing Technologies*; Wiley-VCH: Weinheim, 2008.
(5) Yamamoto, T. *Macromol. Rapid Commun.* **2002**, *23*, 583–606.
(6) Babudri, F.; Farinola, G. M.; Naso, F. *J. Mater. Chem.* **2004**, *14*, 11–34.
(7) Barbarella, G.; Melucci, M.; Sotgiu, G. *Adv. Mater.* **2005**, *17*, 1581–1593.
(8) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169–1171.
(9) Sheina, E. E.; Liu, J. S.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526–3528.
(10) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Macromol. Rapid Commun.* **2004**, *25*, 1663–1666.
(11) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542–17547.
(12) Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, *38*, 8649–8656.
(13) Miyakoshi, R.; Shimono, K.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2006**, *128*, 16012–16013.
(14) Yokoyama, A.; Kato, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2008**, *41*, 7271–7273.
(15) Stefan, M. C.; Javier, A. E.; Osaka, I.; McCullough, R. D. *Macromolecules* **2009**, *42*, 30–32.
(16) Huang, L.; Wu, S. P.; Qu, Y.; Geng, Y. H.; Wang, F. S. *Macromolecules* **2008**, *41*, 8944–8947.
(17) Yokozawa, T.; Adachi, I.; Miyakoshi, R.; Yokoyama, A. *High Perform. Polym.* **2007**, *19*, 684–699.
(18) Benanti, T. L.; Kalaydjian, A.; Venkataraman, D. *Macromolecules* **2008**, *41*, 8312–8315.
(19) Zhang, Y.; Tajima, K.; Hirota, K.; Hashimoto, K. *J. Am. Chem. Soc.* **2008**, *130*, 7812–7813.
(20) Ohshimizu, K.; Ueda, M. *Macromolecules* **2008**, *41*, 5289–5294.
(21) Ouhib, F.; Khoukh, A.; Ledeuil, J. B.; Martinez, H.; Desbrieres, J.; Dagron-Lartigau, C. *Macromolecules* **2008**, *41*, 9736–9743.
(22) Van den Ber, K.; Huybrechts, J.; Verbiest, T.; Koeckelberghs, G. *Chem.—Eur. J.* **2008**, *14*, 9122–9125.

(23) Ouhib, F.; Hiorns, R. C.; de Bettignies, R.; Bailly, S.; Desbrieres, J.; Dagron-Lartigau, C. *Thin Solid Films* **2008**, *516*, 7199–7204.
(24) Wu, P.-T.; Ren, G.; Li, C.; Mezzenga, R.; Jenekhe, S. A. *Macromolecules* **2009**, *42*, 2317–2320.
(25) Tu, G. L.; Li, H. B.; Forster, M.; Heiderhoff, R.; Balk, L. J.; Scherf, U. *Macromolecules* **2006**, *39*, 4327–4331.
(26) Scherf, U.; Gutacker, A.; Koenen, N. *Acc. Chem. Res.* **2008**, *41*, 1086–1097.
(27) Tu, G. L.; Li, H. B.; Forster, M.; Heiderhoff, R.; Balk, L. J.; Sigel, R.; Scherf, U. *Small* **2007**, *3*, 1001–1006.
(28) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Chem. Lett.* **2008**, *37*, 1022–1023.
(29) Wu, S.; Bu, L.; Huang, L.; Yu, X.; Han, Y.; Geng, Y.; Wang, F. *Polymer* **2009**, *50*, 6245–6251.
(30) Javier, A. E.; Varshney, S. R.; McCullough, R. D. *Macromolecules* **2010**, *43*, 3233–3237.
(31) Iovu, M. C.; Jeffries-El, M.; Sheina, E. E.; Cooper, J. R.; McCullough, R. D. *Polymer* **2005**, *46*, 8582–8586.
(32) Iovu, M. C.; Zhang, R.; Cooper, J. R.; Smilgies, D. M.; Javier, A. E.; Sheina, E. E.; Kowalewski, T.; McCullough, R. D. *Macromol. Rapid Commun.* **2007**, *28*, 1816–1824.
(33) Craley, C. R.; Zhang, R.; Kowalewski, T.; McCullough, R. D.; Stefan, M. C. *Macromol. Rapid Commun.* **2009**, *30*, 11–16.
(34) Lee, Y.; Fukukawa, K. I.; Bang, J.; Hawker, C. J.; Kim, J. K. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 8200–8205.
(35) Iovu, M. C.; Craley, C. R.; Jeffries-El, M.; Krankowski, A. B.; Zhang, R.; Kowalewski, T.; McCullough, R. D. *Macromolecules* **2007**, *40*, 4733–4735.
(36) Sommer, M.; Lang, A. S.; Thelakkat, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7901–7904.
(37) Zhang, Q.; Cirpan, A.; Russell, T. P.; Emrick, T. *Macromolecules* **2009**, *42*, 1079–1082.
(38) Richard, F.; Brochon, C.; Leclerc, N.; Eckhardt, D.; Heiser, T.; Hadziioannou, G. *Macromol. Rapid Commun.* **2008**, *29*, 885–891.
(39) Dai, C. A.; Yen, W. C.; Lee, Y. H.; Ho, C. C.; Su, W. F. *J. Am. Chem. Soc.* **2007**, *129*, 11036–11038.
(40) Kaul, E.; Senkovskyy, V.; Tkachov, R.; Bocharova, V.; Komber, H.; Stamm, M.; Kiriy, A. *Macromolecules* **2010**, *43*, 77–81.
(41) Senkovskyy, V.; Khanduyeva, N.; Komber, H.; Oertel, U.; Stamm, M.; Kuckling, D.; Kiriy, A. *J. Am. Chem. Soc.* **2007**, *129*, 6626–6632.
(42) Bronstein, H. A.; Luscombe, C. K. *J. Am. Chem. Soc.* **2009**, *131*, 12894–12895.
(43) Senkovskyy, V.; Tkachov, R.; Beryozkina, T.; Komber, H.; Oertel, U.; Horecha, M.; Bocharova, V.; Stamm, M.; Gevorgyan, S. A.; Krebs, F. C.; Kiriy, A. *J. Am. Chem. Soc.* **2009**, *131*, 16445–16453.
(44) Khanduyeva, N.; Senkovskyy, V.; Beryozkina, T.; Bocharova, V.; Simon, F.; Nitschke, M.; Stamm, M.; Grotzschel, R.; Kiriy, A. *Macromolecules* **2008**, *41*, 7383–7389.
(45) Khanduyeva, N.; Senkovskyy, V.; Beryozkina, T.; Horecha, M.; Stamm, M.; Uhrich, C.; Riede, M.; Leo, K.; Kiriy, A. *J. Am. Chem. Soc.* **2009**, *131*, 153–161.
(46) Sontag, S. K.; Marshall, N.; Locklin, J. *Chem. Commun.* **2009**, 3354–3356.
(47) Lanni, E. L.; McNeil, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16573–16579.
(48) Boyd, S. D.; Jen, A. K. Y.; Luscombe, C. K. *Macromolecules* **2009**, *42*, 9387–9389.
(49) Yokoyama, A.; Suzuki, H.; Kubota, Y.; Ohuchi, K.; Higashimura, H.; Yokozawa, T. *J. Am. Chem. Soc.* **2007**, *129*, 7236–7237.
(50) Beryozkina, T.; Boyko, K.; Khanduyeva, N.; Senkovskyy, V.; Horecha, M.; Oertel, U.; Simon, F.; Stamm, M.; Kiriy, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 2695–2698.
(51) Plater, M. J.; Sinclair, J. P.; Aiken, S.; Gelbrich, T.; Hursthouse, M. B. *Tetrahedron* **2004**, *60*, 6385–6394.
(52) Stambuli, J. P.; Incarvito, C. D.; Buhl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 1184–1194.
(53) Zhang, X.; Tian, H.; Liu, Q.; Wang, L.; Geng, Y.; Wang, F. *J. Org. Chem.* **2006**, *71*, 4332–4335.
(54) Daoud, W. A.; Turner, M. L. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 367–369.
(55) Rehahn, M.; Schlueter, A. D.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30*, 1060–1062.
(56) Dong, C. G.; Hu, Q. S. *J. Am. Chem. Soc.* **2005**, *127*, 10006–10007.
(57) Wright, S. W.; Hageman, D. L.; McClure, L. D. *J. Org. Chem.* **1994**, *59*, 6095–6097.