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Synthesis and Photostability of Poly(*p*-phenylenevinylene-borane)s

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Introduction

Organic field-effect transistors (OFETs) based on π-conjugated system have received considerable interest as they are indispensable components in organic electronics.[1] Poly(*p*-phenylene-vinylene)s (PPVs) have been extensively investigated for this application,[2] and great achievement for p-type organic semiconductors have been reported.[3] One of the most urgent aspects for the development of OFETs is the design and synthesis of new conjugated systems for electronically complementary n-type organic semiconductors.[4] Thus, the incorporation of electron-withdrawing groups such as cyano and trifluoromethyl substituents on the vinylene units of PPVs has been a part of ongoing efforts to lower and tune their molecular orbital energy levels, which leads to increasing electron affinity. Further, PPV derivatives containing their electron-withdrawing groups at vinylene units have revealed photooxidative stability, undesirable conformation changes arise from this substitution as a result of increased steric hindrance.[5] Recently, Swager et al. have demonstrated novel synthesis of PPVs containing perfluoroalkyl groups attached to the phenyl rings and the dramatic improvement in their stability against photooxidation.[6]

We have also synthesized a wide variety of n-type organoboron polymers, poly(*p*-phenylenevinylene-borane)s (PPVBs), including boron atoms in the polymer backbone by hydroboration polymerization.[7] Despite of their interesting properties due to the high electron deficiency of boron atoms, that is, strong fluorescence emission, n-type electronic conductivity, and third-order nonlinear optical properties,[7] photooxidative stability of PPVBs similar structures to PPVs has not been fully explored. Therefore, introduction of side groups such as perfluoroalkyl, alkoxy, and so on, in the PPVB backbones leads to increase of their solubility and improvement of their photooxidative durability and stability. The incorporation of side groups into their polymer backbones further allows for small tuning of the emission color of the polymers.

In this paper we report the synthesis and optical properties of novel electron donor−acceptor type PPVBs with various side groups, and the detailed investigation on the photooxidative stability of their PPVBs. The obtained polymers emitted blue-to-green light at 437−505 nm, and their quantum yields were Φ_F = 0.3−0.5. The photostabilities of the polymers were conducted under continuous UV irradiation using a UV lamp. Their stabilities depended on electron density of the substituents in the comonomers except for a comonomer with trifluoromethyl CF_3 group.

Experimental Section

Instrumentation. ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on a JEOL JNM-EX400 instrument. The chemical shift values were expressed relative to Me_4Si (^{1}H and ^{13}C NMR) as an internal standard and $BF_3{\cdot}OEt_2$ (^{11}B NMR) as an external standard. UV−vis spectra were obtained on a SHIMADZU UV-3600 spectrophotometer, and samples were analyzed in $CHCl_3$ at room temperature. Fluorescence spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in $CHCl_3$ at room temperature. Number-average molecular weight (M_n) and molecular weight distribution [weight-average molecular weight/number-average molecular weight (M_w/M_n)] values of all polymers were estimated by size exclusion chromatography (SEC) with a TOSOH 8020 series [a dual pump system (DP-8020), a column oven (CO-8020), and a degasser (SD-8020)] equipped with three consecutive polystyrene gel columns [TOSOH gels: α-3000] and a refractive index (RI-8020) and an ultraviolet detector (UV-8020) at 40 °C. The system was operated at a flow rate of 1.0 mL/min with tetrahydrofuran as an eluent. Polystyrene standards were employed for calibration. Monomer syntheses were performed under nitrogen atmosphere, and polymer syntheses were performed under an argon atmosphere in the drybox.

Materials. THF was distilled from sodium benzophenone ketyl before use. ^{i}Pr$_2$NH was distilled from KOH and kept with KOH. 1,4-Diethynylbenzene (**1a**) was obtained commercially, and used after purification by sublimation. 1,4-Diethynyl-2,5-bis(trifluoromethyl)benzene (**1d**)[8] and tripylborane (**2**)[9] were prepared as described in the literature. 1,4-Diethynyl-2,5-dimethylbenzene (**1b**)[10] and 1,4-diethynyl-2,5-dimethoxybenzene (**1c**)[11] were prepared according to the literature with minor modification.

Polymer 3a. Hydroboration polymerization between **1a** and **2** was examined as follows. A freshly distilled THF (3 mL) was added to **2** (64.9 mg, 0.30 mmol) and **1a** (37.9 mg, 0.30 mmol). After stirring the mixture for 24 h at room temperature, the solvent was evaporated and the resulting polymer was purified by reprecipitation into methanol. After the product was dried under reduced pressure, the polymer **3a** (yield = 64%, 65.7 mg) was obtained as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08−7.76 (8H, Ar−H and B-CH=CH), 7.00 (2H, Ar−H (tripyl)), 5.91−6.78 (HB-C*H*=C*H*), 2.76−3.01 (1H, CH (tripyl)), 2.39−2.64 (2H, CH (tripyl)), 0.92−1.48 (18H, CH_3 (tripyl)) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 149.3, 147.8, 138.7, 135.1, 132.3, 127.2−128.8, 119.8, 34.8−35.6, 34.3, 23.8−24.9 ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ 31.2 ppm.

Polymer 3b. The reaction was carried out by following the procedure described above. The polymerization between 46.3 mg (0.30 mmol) of **1b** and 64.9 mg (0.30 mmol) of **2** gave 87.7 mg of the corresponding polymer **3b** (yield = 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07−7.74 (8H, Ar−H and B-CH=CH), 6.97 (2H, Ar−H (tripyl)), 5.98−6.87 (> B-CH=CH), 2.74−2.99 (1H, CH (tripyl)), 2.39−2.68 (2H, CH (tripyl)), 1.91−2.39 (6H, CH_3), 0.97−1.41 (18H, CH_3(tripyl)) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 149.2, 147.8, 137.4, 136.3, 134.9, 132.3, 128.4, 119.3−120.0, 34.8−35.5, 34.4, 23.4−24.9, 18.9−19.6 ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ 31.2 ppm.

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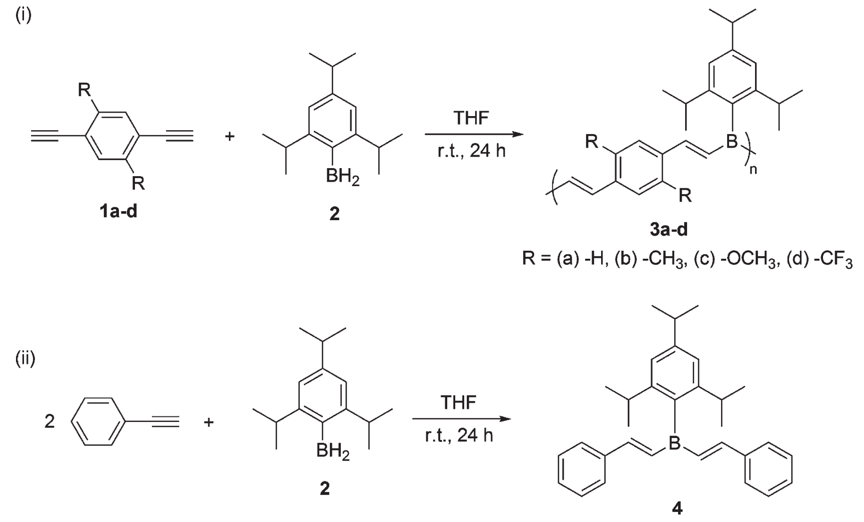
Scheme 1. (i) Hydroboration Polymerization of 2 with Various Diyne Monomers and (ii) Synthesis of Model Compound 4



Polymer 3c. The reaction of 55.9 mg (0.30 mmol) of **1c** and 64.9 mg (0.30 mmol) of **2** gave 90.7 mg of the polymer **3c** (yield = 75%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.04−7.99 (8H, Ar−H and B-CH=CH), 7.00 (2H, Ar−H (tripyl)), 5.87−6.88 (> B-CH=CH), 3.52−3.97 (6H, OCH$_3$), 2.86−3.01 (1H, CH (tripyl)), 2.44−2.70 (2H, CH (tripyl)), 0.95−1.38 (18H, CH$_3$ (tripyl)) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 152.3, 151.6, 149.2, 146.5−147.9, 139.9, 135.4, 129.1, 119.7, 110.1, 55.3−55.6, 34.7−35.4, 34.3, 23.4−24.8 ppm. ^{11}B NMR (128 MHz, CDCl$_3$): δ 30.9 ppm.

Polymer 3d. The reaction of 78.7 mg (0.30 mmol) of **1d** and 64.9 mg (0.30 mmol) of **2** gave 45.9 mg of the polymer **3d** (yield = 32%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.06−8.29 (8H, Ar−H and B-CH=CH), 6.80−7.06 (2H, Ar−H (tripyl)), 5.96−6.80 (> B-CH=CH), 2.66−2.99 (1H, CH (tripyl)), 2.02−2.49 (2H, CH (tripyl)), 0.51−1.64 (18H, CH$_3$ (tripyl)) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 154.0, 148.7−149.8, 115−145, 119.7−120.5, 35.0−35.8, 34.0−34.5, 22.8−25.0 ppm. ^{11}B NMR (128 MHz, CDCl$_3$): δ 31.6 ppm.

Model Compound 4. Tripylborane (130 mg, 0.60 mmol) in THF (3 mL) was added to phenylacetylene (123 mg, 1.20 mmol). After stirring the mixture for 24 h at room temperature, the solvent was evaporated and the crude product was purified by recrystallization from hexane. After the product was dried under reduced pressure, the model compound **4** (yield = 54%, 135 mg) was obtained as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.56−7.62 (4H, Ar−H), 7.29−7.42 (10H, Ar−H and B-CH=CH), 7.00 (s, 2H, Ar−H (tripyl)), 2.95 (m, 1H, CH (tripyl)), 2.50 (m, 2H, CH (tripyl)), 1.33 (d, J = 6.8 Hz, 6H, CH$_3$ (tripyl)), 1.13 (d, J = 6.8 Hz, 12H, CH$_3$ (tripyl)) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 153.9, 149.3, 147.8, 139.3, 137.7, 134.3, 129.5, 128.6, 128.0, 119.8, 35.2, 34.2, 24.4, 24.2 ppm. ^{11}B NMR (128 MHz, CDCl$_3$): δ 64.5 ppm. Anal. Calcd for $C_{31}H_{37}B$: C, 88.56; H, 8.87. Found: C, 87.93; H, 9.12.

Results and Discussion

Polymer and Model Compound Synthesis. The polymerization of diyne monomers **1a−d** was conducted with tripylborane **2** in THF under an argon atmosphere at room temperature for 24 h (Scheme 1(i)). Although the yields of the obtained polymers **3a−c** were high enough, only a polymer **3d** was relatively lower yield, resulting from a low reactivity of diyne group in the **3d** due to the electron-withdrawing nature of trifluoromethyl groups. The results are summarized in Table 1. The obtained polymers were collected as a yellow or brown solid insoluble in methanol. The polymers were readily soluble in common organic solvents such as CHCl$_3$, CH$_2$Cl$_2$, and THF. The number-average molecular weights (M_n), measured by a GPC in THF, of the obtained polymers were almost same values ($M_n \approx 4000$), and the degrees of polymerization (DP), estimated by a GPC, of the obtained polymers were 8.8−12. The structures of the polymers were fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopies. Further, the model compound **4** was also prepared in a similar manner to the synthesis of the polymers, as shown in Scheme 1(ii). Single crystal of **4** was obtained by recrystallization from hexane. X-ray analysis indicated that **4** forms three-coordination states on the central boron atom (Figure 1). The structure of **4** was also confirmed by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopies and by elemental analysis. In comparison with ^{11}B NMR signals between the obtained polymers and the model compound, the signals of polymers showed significant upfield shift, probably originating from electron delocalization via vacant p-orbital of the boron atoms (discussion later).

Table 1. Hydroboration Polymerization of 2 with Diyne Monomers 1a−d[a]

	yield (%)[b]	M_n (M_w)[c]	M_w/M_n[c]	DP[d]
3a	64	4100 (6900)	1.68	12
3b	79	4700 (9500)	2.00	13
3c	75	4200 (7100)	1.71	10
3d	32	4200 (5900)	1.41	8.8

[a] Polymerization of **2** (0.30 mmol) with diyne monomers **1a−d** (0.30 mmol) was carried out in THF (0.2 M) at room temperature for 24 h. [b] Insoluble part in methanol. [c] Measurement by GPC (THF, polystyrene standards). [d] Estimated by GPC.

Optical Properties. The optical properties of the obtained polymers **3a−d** and model compound **4** were investigated by UV−vis absorption and photoluminescence (PL) spectroscopies (Figure 2). The absorption maxima of **3a** and **3b** at around 400 nm, corresponding to the $\pi \rightarrow \pi^*$ transition, are red-shifted as compared with that of **4** at 336 nm, indicating extended conjugation by overlap of π-orbitals of the vinyl moieties via vacant p-orbital of the boron atom.[7] The larger bathochromic shift of **3c** was further observed at 438 nm, resulting from donor−acceptor interaction between boron atom and methoxy group. In contrast, the maximum of **3d** was observed at 317 nm and was blue-shifted as compared with that of **4**. This blue-shift should be caused by fragmentating the π-conjugation of the polymer backbone through

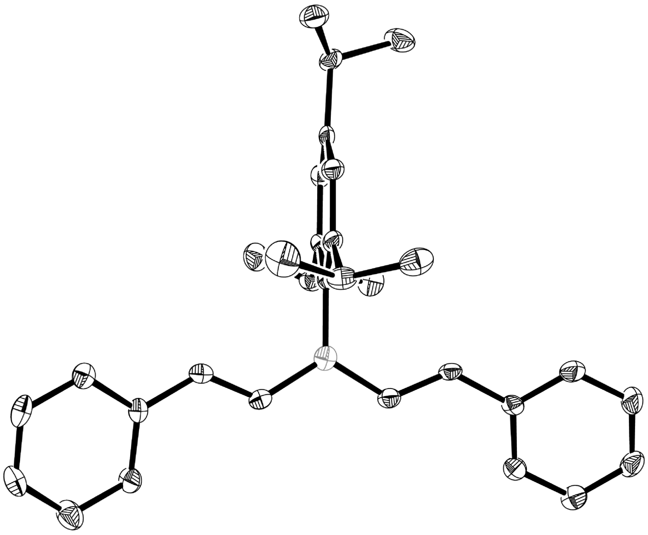


Figure 1. X-ray crystal structure of model compound **4** with thermal ellipisoids drawn to the 50% probability level.

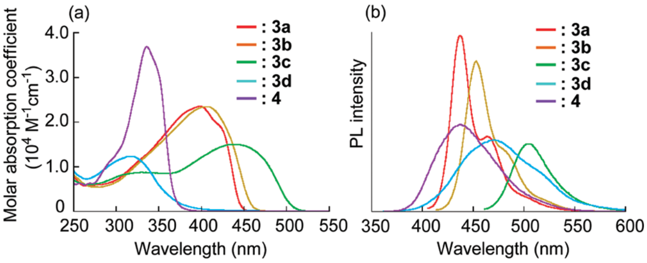


Figure 2. (a) UV−vis absorption spectra ($CHCl_3$: c = 5.0 × 10^{-5} M) and (b) photoluminescence spectra of **3a−d** and **4** ($CHCl_3$: c = 1.0 × 10^{-7} M).

the intermediary of boron atom due to loss of donor−acceptor interaction in the electron poor state of **3d** having trifluoromethyl group as electron-withdrawing group. In the PL spectra, **3a** showed the PL maxima at 437 nm (excited at 398 nm) and its emission color was a strong blue. Further, strong blue-green emission colors of **3b** and **3c** were observed at 452 and 505 nm, respectively, originating from donor−acceptor interaction by electron-donating groups. The quantum yields (Φ_F) of the polymers **3a−c** were high enough (0.4−0.5). In contrast, **3d** showed a weaker blue-green emission at 470 nm (excited at 317 nm) due to longer Stokes shift (135 nm) than their shifts of **3a−c** (**3a**: 38 nm, **3b**: 52 nm, **3c**: 51 nm). Therefore, the Φ_F of **3d** was also very low (Φ_F = 0.3). These results indicate that emission of the obtained polymers originates from delocalization via vacant p-orbital of boron atom.

Theoretical Calculations. To survey the relationship between the conjugation length and the number of the repeating units for the obtained polymers, molecular orbital calculations of model compounds [**1-mer** (= model compound **4**), **2-mer**, **3-mer**, **4-mer**, and **5-mer**] for polymer **3a** were performed as shown in Figure 3a. Their geometry optimizations were carried out by using Gaussian 03[12] and examined by theoretical calculations using a density-functional theory (DFT) method at the B3LYP/6-31G (d,p)//B3LYP/6-31G (d,p) level of theory. The calculation results are summarized in Figure 3b. The band gaps dramatically decreased as increasing the number of the repeating units from **1-mer** to **3-mer**, meaning that the conjugation lengths were extended along the polymer main chain via vacant

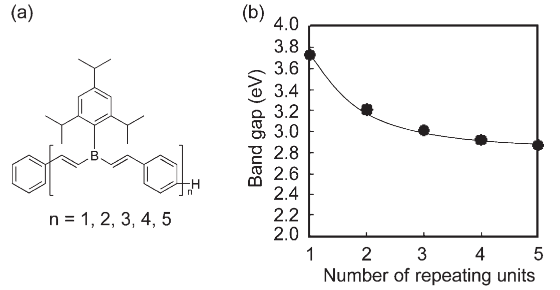


Figure 3. (a) Molecular structures (**1-mer**∼**5-mer**) and (b) relationship between the band gaps and the number of repeating units.

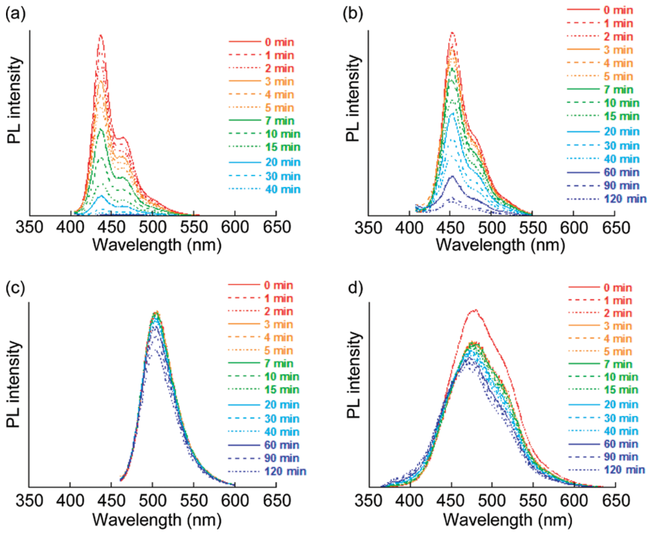


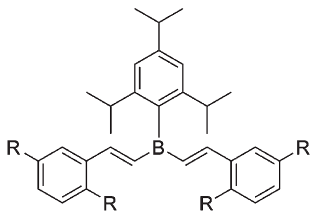
Figure 4. Photoluminescence spectra of (a) **3a** (c = 1.0 × 10^{-7} M), (b) **3b** (c = 1.0 × 10^{-7} M), (c) **3c** (c = 1.0 × 10^{-7} M), and (d) **3d** (c = 5.0 × 10^{-5} M) under continuous UV-irradiation in $CHCl_3$.

p-orbital of the boron atoms as pointed before. In contrast, the band gaps of **4-mer** and **5-mer** were almost close to that of **3-mer**. Consequently, the π-conjugation length of this system is enough for more than three units.

Photostabilities. We have investigated photostabilities of the obtained polymers **3a−d** in $CHCl_3$ (Figure 4). The photooxidation studies were performed by continuous UV irradiation using a 16 W steady-state UV lamp (365 nm) as the irradiation source under aerobic conditions, and their behaviors of photodecomposition were quantified by monitoring decrease of PL spectra. The decrease of PL intensity of **3c** and **3d** was slight after 40 min, whereas the PL intensity of **3a** decreased rapidly and almost disappeared. Accordingly, the photostabilities of the polymers were on the order of **3c** > **3d** > **3b** > **3a**. Further, the molecular weights of **3a−d** irradiated with time were traced by GPC measurement, and the GPC traces were shifted to low molecular weight side (Figure S1), meaning the decomposition of each polymer backbone. These results might indicate that the photostability of the polymers depends on electronic density and/or steric hindrance of the substitutents.

To provide more effective role of side groups on the reactivity of the C=C bonds, the designs and geometry optimizations of model compounds were conducted by using Gaussian 03[12] and theoretical calculations (B3LYP/6-31G (d,p)//B3LYP/6-31G (d,p)). The bond order of C=C bonds was calculated using natural population analysis after their geometry was optimized. The bond order is a way of viewing influence for the electron density of side group.[5b] The results

Table 2. Theoretical Calculation Results for Substituted Model Compounds with the Structure Provided



run	R	bond order
1	H	1.2799
2	CH_3	1.2769
3	CF_3	1.2983
4	OCH_3	1.2722

of their calculations are summarized in Table 2. The bond order of model compounds was in the order of $OCH_3 < CH_3 < H$ except for CF_3-substituted model compound. This order of the side groups means increasing of electron density, that is, increasing of localized π-electrons in the C=C bond. On the other hand, the stability of the model compounds is the order of $OCH_3 > CH_3 > H$, which is consistent with experimental observations. In contrast, only CF_3-substituted model compound loses the planarity of the molecule (Figure S2). The bond order is shorter than those of other model compounds in despite of good photostable polymer with CF_3 group, probably resulting that the steric hindrance rather than electron density around the C=C bond is responsible for stability of the CF_3-substituted polymer.

In summary, we have synthesized n-type organoboron polymers, poly(*p*-phenylenevinylene-borane)s (PPVBs), including boron atoms in the polymer backbone by hydroboration polymerization of tripylborane and diyne monomers. The obtained polymers showed blue-to-green emission, and the quantum yields of **3a**−**c** were high enough ($\Phi_F = 0.4-0.5$), whereas the Φ_F of **3d** was very low due to large Stokes shift. The photostabilities of the polymers were examined by monitoring decrease of the PL spectra under continuous UV irradiation using a UV lamp under aerobic conditions. Their stabilities should be responsible for electron density of the substituents in the comonomers except for comonomer having trifluoromethyl group. Future work will focus on the design of superior photostable and water-soluble PPVBs via introduction of chirality into polymer main chain.

Acknowledgment.

Supporting Information Available: Figure S1 showing GPC traces of the UV-irradiated obtained polymers with time, Figure S2 showing optimized model molecular structures, and ^1H, ^{13}C, and ^{11}B NMR spectra of the obtained polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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