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π-Conjugated Polyphenylenes with Diazaborole Side Chains Synthesized via 1,2-Phenylenediamine Polymer

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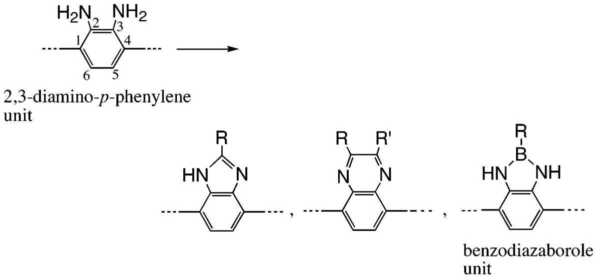
ABSTRACT: Pd-complex-catalyzed polycondensation of 3,6-dibromo-1,2-phenylenediamine (**1**) with 2,7-bis-(1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**2**) gave polymer **1a** which consisted of 1,2-phenylenediamine-3,6-diyl and 9,9-dioctylfluorene-2,7-diyl units in 99% yield. Polymer **1a** showed a weight-average molecular weight (M_w) of 78 000 in the light scattering analysis and gave an intrinsic viscosity of 0.74 dL g^{-1}. Reaction of polymer **1a** with aromatic boronic acids, Ar−B(OH)$_2$ (Ar = C_6H_5, C_6H_4-*p*-Bu, and C_6H_4-*p*-OMe), provided polymers **2a**−**2c** with a diazaborole ring in the side chain. A model compound of polymer **1a**, [1,4′;1′,1″;4″,1‴;4‴,1⁗]-quinquephenyl-2″,3″-diamine (model compound **1**), was also prepared by Pd-complex-catalyzed reaction of **1** with biphenyl-4-boronic acid. Structures of the polymers and the model compound were determined by ^{1}H NMR and IR spectroscopy as well as by elemental analyses. All the polymers and the model compound were photoluminescent in solution, and introduction of the diazaborole ring enhanced intensity of photoluminescence (PL). Cyclic voltammetry revealed that all the polymers and the model compound were electrochemically active in solutions, and the phenylenediamine and benzodiazaborole units behave as an electron-donating group. Thermal stability of polymer **1a** was improved by transformation of the diamino group to the diazaborole side chain.

Introduction

π-Conjugated polymers bearing reactive functional groups have been attracting interest.[1−10] For example, π-conjugated polymers having a sulfo group,[1−3] carboxylic group,[4−7] or hydroxy group[8,9] have been reported. However, π-conjugated polymer having a $-NH_2$ side group has received less attention,[10] in spite of the presence of a tremendous number of reports about polyanilines.

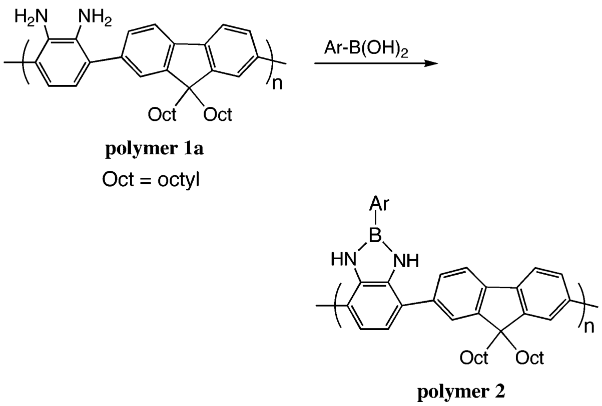
π-Conjugated poly(*p*-phenylene) with the following *o*-diamine side groups will be a useful starting polymer for various π-conjugated polymers because the *o*-diaminophenylene group will be able to be converted into various groups,[11,12] e.g.



(1)

It is known that 2,3-diamino-1,4-dibromobenzene can be converted into the corresponding dibromo benzimidazole and dibromoquinoxaline,[11,12] and π-conjugated polymers composed of the benzimidazole unit[11] and quinoxaline unit[12] have been synthesized by dehalogenative organometallic polycondensation of the corresponding dibromo monomers. However, synthesis of a similar π-conjugated polymer composed of the benzodiazaborole unit has no precedent to our knowledge.

Herein we report synthesis of new π-conjugated *p*-phenylene-type polymer constituted of the 2,3-diamino-*p*-phenylene unit and conversion of the 2,3-diamino-*p*-phenylene unit of the polymer to the benzodiazaborole unit:



polymer 1a

Oct = octyl

polymer 2

(2)

Boron-containing polymers are the subject of recent interest because of their important chemical and physical functionalities.[13] They show blue emission,[14,15] large third-order nonlinear optical susceptibility,[16,17] and high thermal stability.[14,18,19] A large number of polymers containing boron in the main chain have recently been reported.[20−22] The polymers are considered to have an expanded electron system through the B−C and B−N bonds in the main chain by using the p_z orbital on boron.

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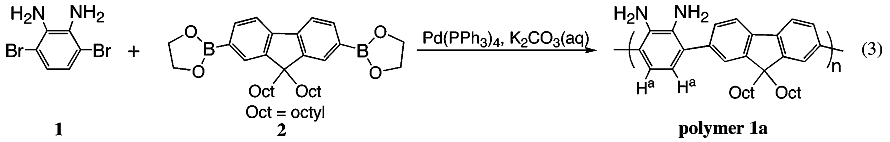
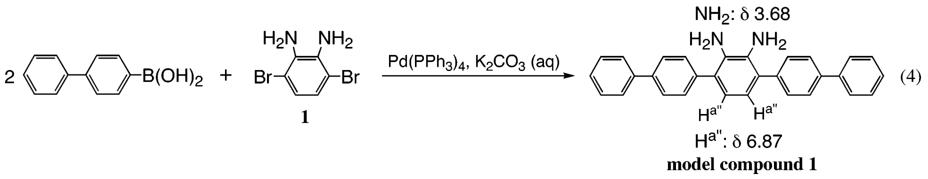
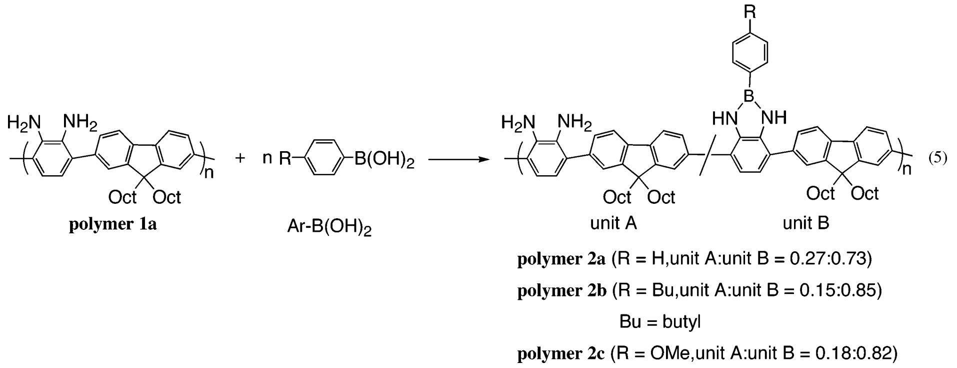
Scheme 1. Synthesis of the PPP-Type Polymer Having the NH_2 Side Group



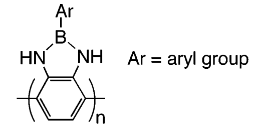
Scheme 2. Synthesis of a Model Compound for Polymer 1a



Scheme 3. Transformation to the Diazaborole Ring



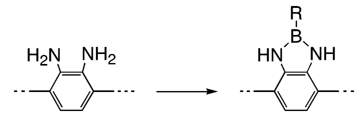
π-Conjugated polymers bearing a diazaborole ring at side chain, e.g.



Poly(*p*-phenylene) with the diazaborole side chain

are also expected to show interesting optical and electronic functionalities.

On these bases, we first synthesized a π-conjugated poly(*p*-phenylene)-type polymer with the 1,2-phenylenediamine building unit and then converted the 1,2-diphenylene unit into the diazaborole unit. It is known that aromatic diamines react with boronic acids to give diazaboroles.[23,24]



Herein we report preparation of the new π-conjugated polymer of 1,2-phenylenediamine, conversion of the diamino polymer into the diazaborole polymers, and chemical properties of the diamino and diazaborole polymers. Synthesis of a model compound is also reported.

Results and Discussion

Polymerization. Pd-complex-catalyzed polycondensation of 2,3-dibromo-1,4-phenylenediamine (**1**) and 2,7-bis(1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**2**) gave polymer **1a** in 99% yield, as shown in Scheme 1. The polymer essentially has a poly(*p*-phenylene) **PPP**-type π-conjugated main chain.

Figure 1a shows the ^1H NMR spectrum of polymer **1a**. A peak at δ 3.72 is assigned to the amine hydrogen, and its peak area reveals that the amine groups are intact in the polymerization. Signals of aliphatic and aromatic hydrogens are observed in ranges of δ 0.7−2.2 and δ 6.8−8.0, respectively. A model compound of polymer **1**, model compound **1**, was also synthesized according the method shown by eq 4, and comparison of the ^1H NMR spectrum of model compound **1** with that of polymer **1a** revealed that the ^1H NMR peak of polymer **1a** at δ 6.93 was assigned to the aromatic −H of the diamino-*p*-phenylene unit (H^a shown in Scheme 1).

Observed areas of the amine signal, aliphatic signal, and aromatic signals agreed with structure of polymer **1a** shown in Scheme 1. Data from elemental analysis also agreed with the structure of polymer **1a** with hydration water; the presence of the hydrophilic NH_2 groups in polymer **1a** seems to be the reason for the hydration.

The IR spectrum of polymer **1a** depicted in Figure 2a shows two distinct ν(NH) peaks at 3423 and 3338 cm^{-1}. A peak assigned to δ(N−H) is observed at 1609 cm^{-1}. Polymer **1a** had high thermal stability with 5% weight loss temperature at 372 °C and was soluble in organic solvents such as toluene and chloroform. However, polymer **1a** was not soluble in DMF. It has been reported that π-conjugated polymers such as poly(3-alkylthiophene)s with long side chains are soluble in halogenated hydrocarbons and hydrocarbon whereas as they have poor solubility in polar solvents such as DMF and acetone.[25] Light scattering analysis[26] of a toluene solution of polymer **1a** gave an M_w (weight-average molecular weight) of 78 000 as described below. Toluene solutions of polymer **1a** afforded an intrinsic viscosity of 0.74 dL g^{-1}.

Transformation of the *p*-Phenylenediamine Unit to Diazaborole Units. Reactions of polymer **1a** with aromatic boronic acids, $Ar-B(OH)_2$ ($Ar = C_6H_5$, C_6H_4-*p*-Bu, and C_6H_4-*p*-OMe), in toluene under reflux conditions gave the diazaborole polymers, polymers **2a**−**2c**, as exhibited in Scheme 3. The degree of the transformation of the diamino group to the diazaborole

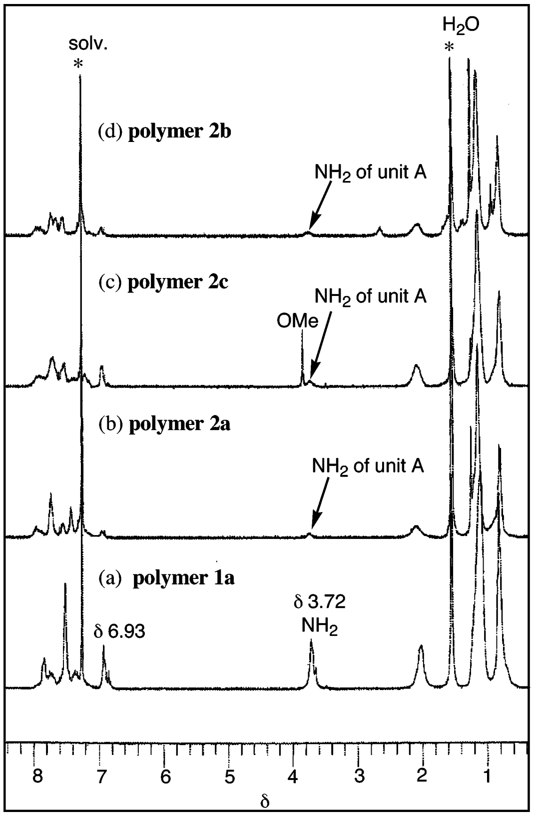


Figure 1. ^{1}H NMR spectra of polymers **1a** and **2a**−**2c** in $CDCl_3$. Polymer **1b** exhibits the same ^{1}H NMR spectrum as the polymer **1a**. Peaks marked with the * are due to the solvent impurity ($CHCl_3$ and H_2O).

group was estimated at 73−85% from ^{1}H NMR data and the boron content.

According to the boronation reaction expressed by eq 5, the intensity of the NH_2 signal of polymer **1a** at δ 3.7 decreases, as shown in Figure 1. The intensity of the H^a (cf. Scheme 1) signal at δ 6.93 is also decreased, and the peak pattern in the aromatic region is changed after the boronation reaction. These ^{1}H NMR data agree with the formation of the unit B. The molar ratio between the unit A and unit B was calculated from the content of boron determined by ICP (inductively coupled plasma) spectroscopy, and the data agreed with the ^{1}H NMR data. The molar ratios between the unit A and unit B in polymers **2a**−**2c** thus evaluated were 0.27:0.73, 0.15:0.85, and 0.18:0.82, respectively. These data are shown in Table 1.

As described above and depicted in Figure 2, the IR spectrum of polymer **1a** exhibits two ν(NH) peaks, ν_{asym}(HNH) and ν_{sym}(HNH), at 3423 and 3338 cm^{-1}. According to the formation of the diazaborole ring, these two IR peaks decrease, and a new sharp peak of NH group of the diazaborole ring appears at 3479 cm^{-1} in the IR spectrum of polymers **2a**−**2c**.

As described above, polymers **2a**−**2c** have the mixed structure with the unreacted unit A. As an attempt to obtain a pure polymer consisting of only the unit B, polymerization of **2** with the following compound **3**, which was synthesized by reaction of **1** with benzeneboronic acid, was carried out as shown in Scheme 4. However, the expected polymer, polymer **3**, was not obtained, and a product, whose ^{1}H NMR and IR spectra were essentially the same as those of polymer **1a**, was obtained. It was reported that diazaborole compounds undergo hydrolysis under basic conditions,[27] and **3** and/or polymer **3** seemed to receive the hydrolysis during the polymerization under the basic conditions. On the other hand, reaction expressed by eq 5 did not require such basic conditions, and polymers **2a**−**2c** were obtained.

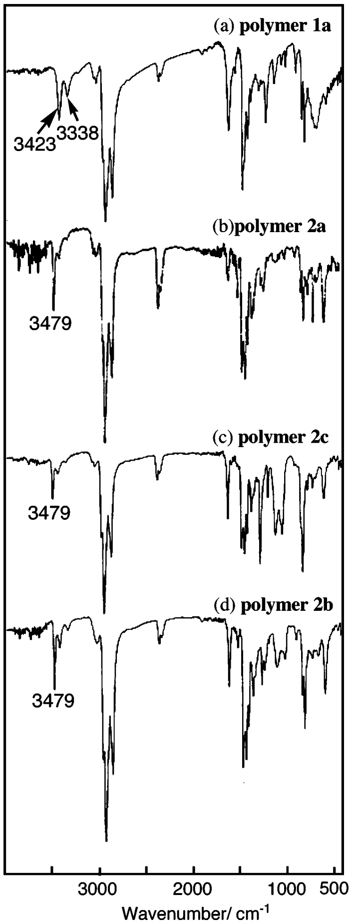


Figure 2. IR spectra of polymers **1a** and **2a**−**2c.** The peak at about 2360 cm^{-1} is due to CO_2 in air.

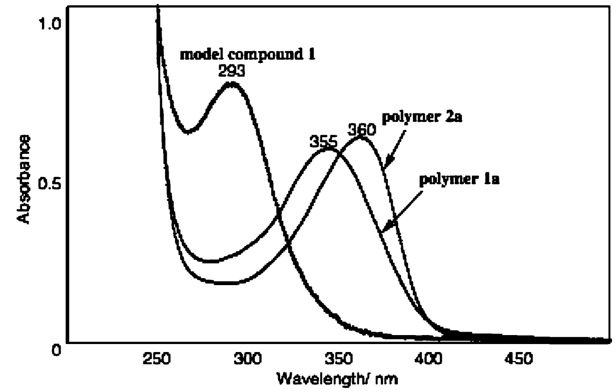


Figure 3. UV−vis spectra of polymers **1a** and **2a** and model compound **1** in $CHCl_3$.

Molecular Weight. Polymers **1a**, **1b**, and **2a**−**2c** were soluble in chloroform and toluene. Molecular weights of the polymers were determined by light scattering methods and GPC, and the data are included in Table 1. Light scattering analysis[26] of polymer **1a** gave a weight-average molecular weight (M_w) of 78 000, a degree of depolarization (ρ_v) of 0.06, a second virial coefficient (A_2) of -19.2×10^{-4} cm^3 mol^{-1} g^{-2}, and a radius of gyration (R_g) of 23 nm in toluene. The medium ρ_v value suggested that polymer **1a** took an intermediate structure between a linear structure and a random coil structure in the solution. Determination of molecular weight of polymer **1a** by GPC was not possible, presumably due to a strong interaction

Table 1. Synthetic Results of the Polymers

polymer	yield, %	mol wt[a]/10^3	M_w/M_n	ρ_v[b]	A_2[c] × 10^4, $cm^3\ mol^{-1}\ g^{-2}$	R_g,[d] nm	[η],[e] dL g^{-1}	unit A:unit B[f]
1a	99	78 (LS)		0.060	−19.2	23	0.72	100:0
2a	85	188 (LS)		0.020	−0.91	33		
		8.6 (GPC)	6.37					27:73
2b	94	278 (LS)		0.11	0.59	36		
		5.7 (GPC)	1.23					15:85
2c	80	9.8 (GPC)	8.31					18:82

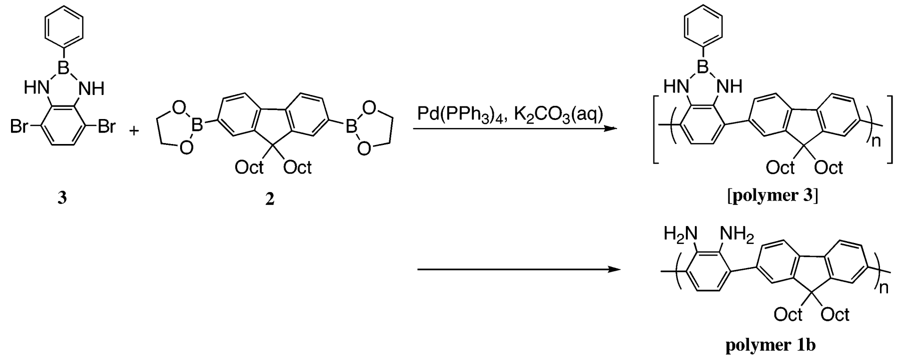
[a] LS: M_w (weight-average molecular weight determined by the light scattering method). GPC: M_n (number-average molecule weight) determined by GPC. [b] Degree of depolarization. [c] Second virial coefficient. [d] Radius of gyration. [e] Intrinsic viscosity measured with a toluene solution at 26 °C. [f] Estimated from ICP data.

Table 2. Optical, Electrochemical, and Thermal Data

polymer and model compound	absorption in $CHCl_3$, nm	photoluminescence in $CHCl_3$, nm (Φ,[a] %)	Ex,[b] nm	oxidation potential,[c] V	T_d,[d] °C
polymer **1a**	355	409 (11)	356	0.47	372
polymer **2a**	360	407 (32)	363	0.71	419
polymer **2b**	354	409 (48)	362	0.54	428
polymer **2c**	360	420 (20)	354	0.55	395
model compound **1**	293 (43100[e])	391 (46)	314	0.35, 0.79	

[a] Quantum yield. [b] Peak position observed in the excitation spectrum. [c] Peak oxidation potential E_{pa} vs Ag^+/Ag. Measured in a dichloromethane solution of $[Bu_4N]BF_4$ (0.10 M). [d] The 5% weight-loss temperature measured by TGA under N_2. [e] Molar coefficient in mol^{-1} L cm^{-1}.

Scheme 4. Polymerization Using the Diazaborole Monomer



(6)

of polymer **1a** with polystyrene gel in the GPC column. For polymers **2a**−**2c**, their molecular weights were able to be estimated by GPC, and the number-average molecular weights (M_n's) and M_w/M_n values estimated by GPC are shown in Table 1, together with M_w(LS) values of these polymers determined by the light scattering analysis. Comparison of the M_w(LS) value estimated from the light scattering method with M_w(GPC) suggests that polymers form a loose aggregate in the static solution used for the light scattering analysis. The smaller M_n(GPC) value of polymer **2b** than those of polymers **2a** and **2c** implies a change of polymer structure by introducing the flexible butyl group at the diazaborole side chain, which will affect the GPC data.

The model compound **1** also exhibited good solubility in organic solvents, in contrast to poor solubility of *p*-quinquephenyl in organic solvents.

Optical Properties. Optical data of the polymers and the model compound are summarized in Table 2. Figure 3 depicts UV−vis spectra of polymer **1a**, polymer **2a**, and model compound **1** in chloroform. Polymer **1a** shows an absorption peak at 355 nm. The peak position locates at a longer wavelength than that of model compound **1**, in agreement with the expansion of the π-conjugation system along the polymer chain. The λ_{max} value, however, is shorter than that of a π-conjugated polymer consisting of 9,9-dihexylfluorene-2,7-diyl and *p*-phenylene units, which shows λ_{max} at 370 nm in chloroform.[29] This seems to be ascribable to a steric effect of the NH_2 group which will cause torsion of the main chain of polymer **1a**. In relation to this, the model compound **1** exhibits λ_{max} (293 nm), which is located at a shorter wavelength than that (λ_{max} = 303 nm) of *p*-quinquephenyl.

All the polymers exhibit blue emission in their solution when irradiated with UV light. The PL peak of the polymers appears at an onset position of the their absorption bands, as usually observed with photoluminescent aromatic compounds. Polymers **2a**−**2c** give the PL peak in a range of 407−420 nm, and it is seen from Table 2 that introduction of the diazaborole side chain increases the quantum yield of PL. It has been reported that aromatic diazaborole compounds give a strong emission with high quantum yields.[24b]

Electrochemical Response. The electrochemical behavior of the polymers was investigated by cyclic voltammetry (CV). Figure 4 depicts CV charts of polymers **1a** and **2a** in a dichloromethane solution containing $[Bu_4N]BF_4$. Polymer **1a** gives an oxidation (or p-doping) peak at about 0.47 V. It has been reported that *o*-phenylenediamine undergoes multiple electrochemical oxidation,[28a] and electrochemical oxidative polymerization of *o*-phenylenediamine can also proceed.[28b] Consequently, it is not easy to identify the electrochemical reaction; however, occurrence of a simple oxidation reaction of the *o*-phenylenediamine unit to *o*-phenylenediimine, similar to the electrochemical oxidation of *p*-phenylenediamine unit of poly(aniline) to *p*-phenylenediimine unit,[28c] is conceivable. A CV chart of model compound **1** is depicted in the Supporting Information (Figure 1S), and conceivable electrochemical oxidation processes are exhibited in Scheme 1S and Scheme 2S in the Supporting Information. As shown in Figure 4 and Table 2, polymers **2a**−**2c** received electrochemical oxidation at a

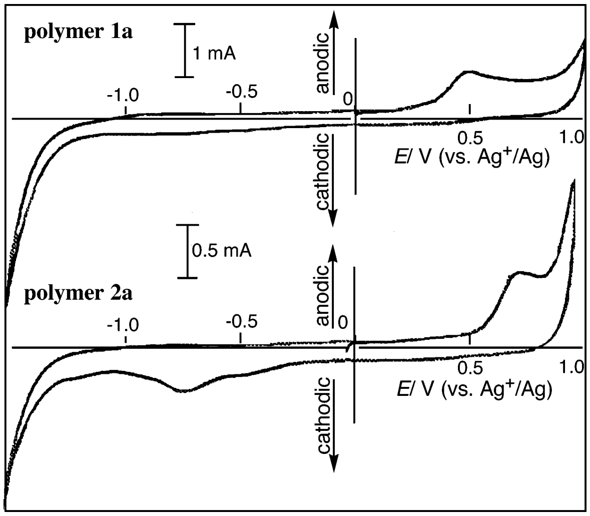
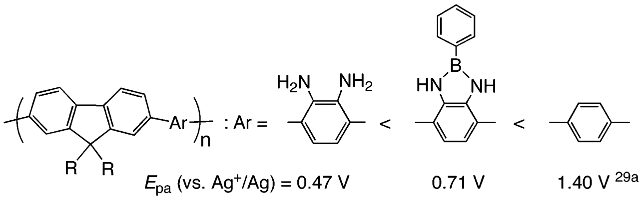


Figure 4. Cyclic voltammograms of polymer **1** and polymer **2a** in a dichloromethane solution of $[Bu_4N]BF_4$. Sweep rate was 50 mV s^{-1}.

higher potential than polymer **1a** probably due to presence of the electronegative boron atom. The oxidation of polymer **1a** and polymer **2a** occurs at a lower potential than that of a *p*-phenylene analogue (peak oxidation potential $E_{pa} = 1.40$ V[28d] vs SCE or 1.06 V vs Ag^+/Ag). These data indicate that the diazaborole unit behaves as a medium electron-donating unit.



Conclusion

New π-conjugated polymers constituted of the 2,3-diamino-1,4-phenylene unit have been obtained. The polymer is expected to be a starting polymer for various π-conjugated polymers, and conversion of the 2,3-diamino-1,4-phenylene unit of the polymer to the diazaborole unit has been carried out. The diazaborole polymers are soluble in organic solvents, photoluminescent, electrochemically active, and thermally stable. The diazaborole group behaves as a medium electron-donating group.

Experimental Section

Materials and Measurements. Solvents were dried, distilled, and stored under N_2. The starting monomer **1**,[11a,c] monomer **2**,[29] and $Pd(PPh_3)_4$[30] were prepared according to the literature.

Microanalysis of C, H, and N was carried out with a Yanagimoto type MT-2 CHN autocorder. Microanalysis of B was performed by using a Shimadzu ICPS-8100 sequential plasma spectrometer. IR and NMR spectra were recorded on a JASCO FT/IR-410 PLUS spectrophotometer and a JEOL GX-300 spectrometer, respectively. UV−vis and photoluminescence spectra were recorded on Shimadzu UV−vis 3100PC and Hitachi F4010 spectrometers, respectively. Quantum yields were calculated by using a diluted sulfuric acid (0.50 M) solution of quinine as the standard. GPC analyses were performed by a Toso HLC 8020 and a Shimadzu LA-6A equipped with polystyrene gel columns, using a DMF solution of LiBr (0.010 M), chloroform, or THF as the eluent with RI and UV detectors. Light scattering measurement was carried out by using He−Ne laser laser (632.8 nm) and toluene solutions of the polymers at 25 °C. TGA measurement was carried out by using a Shimadzu TGA-50 under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Cyclic voltammetry was performed in a dichloromethane solution containing 0.10 M $[Et_4N]BF_4$ with a Solartron SI 1287 electrochemical interface.

Synthesis of Polymer 1a. **1** (0.53 g, 2.0 mmol) and **2** (1.12 g, 2.0 mmol) were dissolved in 20 mL of dry toluene under N_2. To the solution were added K_2CO_3(aq) (2.0 M, 10 mL; N_2 bubbled before use), $Pd(PPh_3)_4$ (0.23 g, 0.20 mmol), and several drops of the phase transfer catalyst (Aliquat336). After the mixture was stirred for 3 days at 80 °C, the solvent was removed under vacuum. The resulting solid was dissolved in a small amount of chloroform and reprecipitated in methanol. Polymer **1a** was collected by filtration, dried under vacuum, and obtained as a dark brown powder (0.98 g, 99%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.9−7.3 (6H, except for solvent impurity), 6.93−6.83 (2H), 3.72 (4H), 2.02 (4H), 1.25−1.10 (20H), 0.83 (10H). Anal. Calcd for $(C_{35}H_{46}N_2{\cdot}0.5H_2O)_n$: C, 83.45; H, 9.40; N, 5.56. Found: C, 83.37; H, 9.50; N, 5.10.

Synthesis of Polymer 2a. After a toluene solution of polymer **1a** (0.25 g, 0.50 mmol) and benzeneboronic acid (0.06 g, 0.50 mmol) was refluxed for 3 days, the solvent was removed under vacuum. The resulting solid was dissolved in a small amount of chloroform and reprecipitated in methanol. Polymer **2a** was collected by filtration, dried under vacuum, and obtained as an orange powder (0.25 g, 85%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.0−6.9 (13.1H, except for solvent impurity), 3.75 (1.08H), 2.10 (4H), 1.25−1.15 (20H), 0.82 (10H). Anal. Calcd for $\{(C_{35}H_{46}N_2)_{0.27}(C_{41}H_{49}BN_2)_{0.73}(H_2O)\}_n$: C, 82.19; H, 8.79; N, 4.87. Found: C, 82.19; H, 9.49; N, 4.90. ICP: Calcd: B, 1.37. Found: B, 1.35.

Polymers 2b and **2c** were prepared analogously. Spectroscopic and analytical data of the polymers are shown below.

Polymer 2b. Gray powder (yield = 94%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.0−6.9 (13.1H, except for solvent impurity), 3.88 (0.6H), 2.63 (1.7H), 2.1−0.7 (40H, except for solvent impurity). Anal. Calcd for $\{(C_{35}H_{46}N_2)_{0.15}(C_{45}H_{57}BN_2)_{0.85}(1.2H_2O)\}_n$: C, 82.01; H, 9.14; N, 4.40. Found: C, 81.43; H, 9.11; N, 4.74. ICP Calcd: B, 1.44. Found: B, 1.44.

Polymer 2c. Orange powder (yield = 80%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.0−6.8 (12.9H, except for solvent impurity), 3.84 (2.46H), 3.70 (0.72H), 2.12 (4H), 1.25−1.14 (20H), 0.88 (10H). Anal. Calcd for $\{(C_{35}H_{46}N_2)_{0.18}(C_{42}H_{51}BN_2O)_{0.82}(2.5H_2O)\}_n$: C, 77.08; H, 8.75; N, 4.41. Found: C, 77.39; H, 8.65; N, 4.15. ICP Calcd: B, 1.40. Found: B, 1.44.

Synthesis of Polymer 1b. 3 (351 mg, 1.0 mmol) and **2** (558 mg, 1.0 mmol) were dissolved in 20 mL of dry toluene under N_2. To the solution were added K_2CO_3(aq) (2.0 M, 10 mL; N_2 bubbled before use), $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), and several drops of the phase transfer catalyst, (Aliquat336). After the mixture was stirred for 3 days at 80 °C, the solvent was removed under vacuum. The resulting solid was dissolved in a small amount of chloroform and reprecipitated in methanol. Polymer **1b** was collected by filtration, dried under vacuum, and obtained as a dark brown powder (402 mg, 66%). ^1H NMR data agreed with those of polymer **1a**.

Synthesis of 3. After a mixture of 50 mL of toluene solution of **1** (2.57 g, 10 mmol) and benzeneboronic acid (1.22 g, 10 mmol) was refluxed for 3 days, the solvent was removed under vacuum. The resulting solid was recrystallized from hexane, collected by filtration, and dried under vacuum to give **3** as a white powder (2.63 g, 75%). ^1H NMR (300 MHz, DMSO-d_6): δ 9.29 (2H), 8.21 (2H), 7.43 (1H), 7.42 (2H), 7.01 (2H). Anal. Calcd for $C_{12}H_9BBr_2N_2$: C, 40.97; H, 2.58; N, 7.96; Br, 45.42. Found: C, 40.65; H, 2.62; N, 7.79; Br, 45.62.

Synthesis of Model Compound 1. **1** (0.80 g, 3.0 mmol) and 4-biphenylboronic acid (1.19 g, 6.0 mmol) were dissolved in 20 mL of dry toluene under N_2. To the solution were added K_2CO_3(aq) (2.0 M, 10 mL; N_2 bubbled before use), $Pd(PPh_3)_4$ (0.17 g, 0.15 mmol), and several drops of the phase transfer catalyst (Aliquat336). After the mixture was stirred for 3 days at 80 °C, the solvent was removed under vacuum. The resulting solid was dissolved in a small amount of chloroform and reprecipitated in methanol. Model compound **1** was collected by filtration, dried under vacuum, and obtained as a colorless powder (1.24 g, quantitative). ^1H NMR (300 MHz, $CDCl_3$): δ 7.76−7.34 (18H), 6.87

(2H), 3.68 (4H). Anal. Calcd for $C_{30}H_{24}N_2$: C, 87.35; H, 5.86; N, 6.79. Found: C, 87.07; H, 5.86; N, 7.09.

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Supporting Information Available: CV chart of model compound **1** and conceivable electrochemical oxidation processes of model compound **1** and polymer **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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