Syntheses and Characterization of Poly(1,3-phenylene-2-amino-1,3-phenylene)s and Dimer and Tetramer Model Compounds

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ABSTRACT: The Pd-catalyzed cross-coupling polycondensation of 2,6-dibromoaniline or 2,6-dibromo-4-*tert*-butylaniline with 1,3-phenylenebis(trimethylene boronate) in benzene−water in the presence of K_2CO_3 and Bu_4NCl gave poly(1,3-phenylene-2-amino-1,3-phenylene)s in 56−86% yields. The number average molecular weights of the poly(1,3-phenylene)s determined by GPC using styrene standards are 2500−5720, which correspond to the degree of polymerization of 15.0−25.6. The thermal stabilities of the polyphenylenes were evaluated by thermalgravimetry. The corresponding dimer and tetramer model compounds of poly(1,3-phenylene-2-amino-1,3-phenylene)s were prepared, and their properties were compared with those of the poly(1,3-phenylene)s.

Introduction

Polyphenylenes are one of potentially most useful polymers for organic conducting materials and organic polymeric ferromagnets because polyphenylenes have an extended planar conjugated π-system, along with high strength and high heat resistance. Polyphenylenes are classified to two types in the mode of linkage. One is the para-linked structure, and the other is the meta-linked structure. For conducting polymers, the former type is important,[1] and for organic polymeric ferromagnets the latter type is important.[2,3]

Synthetic methods of polyphenylenes have been developed in recent years. The oxidative coupling of benzene in the presence of Lewis acids and oxidants,[4] the Wurtz−Fittig reaction between dibromobenzene with metallic Na,[5] the Ni-catalyzed coupling reaction of Grignard reagents,[6] and the coupling reaction of dichlorobenzenes catalyzed by $NiCl_2$[7] have been the typical methods for the syntheses of polyphenylenes. Recently, the Pd-catalyzed cross-coupling reaction of dibromo- or diiodobenzenes with phenylenebis(boronic acid)s has attracted much attention as one of the best methods for syntheses of polyphenylenes.[8] This method has some advantages over those mentioned above. For example, the procedure is quite simple and the reaction is insensitive to moisture. Indeed, water is often used as a cosolvent. Furthermore, this coupling reaction can be applied to monomers carrying a functional group such as amino. In a previous paper we reported that the Pd-catalyzed cross-coupling reaction of dibromoanilines or tribromoaniline with phenylboronic acid gives biphenylamines or triphenylaniline in excellent yields (86−95%).[9]

In the present study we synthesized poly(1,3-phenylene-2-amino-1,3-phenylene)s (**4**) by the Pd-catalyzed cross-coupling polycondensation of 2,6-dibromoanilines with 1,3-phenylenebis(trimethylene boronate). The polyphenylenes obtained are potentially important as the intermediate for ferromagnetic polymers. Conversion of the amino groups to azide groups and subsequent photolysis yield ferromagnetic polynitrenes. Furthermore, we synthesized the corresponding dimer and tetramer model compounds of **4** (see Chart 1). The well-defined monodispersed oligomers are of recent interest because they are not only important as the model compounds of polymers but also potentially useful as modules for nanoscopic architectures. Herein we report the synthesis of poly(1,3-phenylene-2-amino-1,3-phenylene)s and the corresponding dimer and tetramer model compounds and their properties.

Results and Discussion

Synthesis of Dimer and Tetramer. Dimer **2** and tetramer **3** were prepared according to Schemes 1 and 2, respectively. Treatment of 4-*tert*-butylaniline with 2 equiv of benzyltrimethylammonium tribromide[10] (BTMA)Br_3 in CH_2Cl_2−MeOH in the presence of $CaCO_3$ gave 2,6-dibromo-4-*tert*-butylaniline (**5b**) in ~100% yield. The Pd-catalyzed cross-coupling reaction of the dibromo compound with 1 equiv of phenylboronic acid in benzene−H_2O at the reflux temperature for 24 h under nitrogen using $Pd(PPh_3)_4$ as catalyst and Na_2CO_3 as base gave **6** in 62% yield, along with **1** (31% yield).[8,9] Compound **6** was again subjected to the Pd-catalyzed cross-coupling reaction with 1,3-phenylenebis(trimethylene borate) (**7**). When **6** was treated with 0.5 equiv of **7** in a refluxing benzene−H_2O solution containing K_2CO_3 and Bu_4NCl for 24 h in the presence of $Pd(PPh_3)_4$, dimer **2** was obtained in 76% yield as colorless prisms. Bu_4NCl functions as a phase transfer catalyst, and no addition of Bu_4NCl reduced the yield to 54%.[11]

Tetramer **3** was synthesized via five steps, starting from 4-*tert*-butylaniline, as shown in Scheme 2. Monobromination of 4-*tert*-butylaniline was carried out by treating the aniline with 1 equiv of tetrabutylammonium tribromide[12] ((TBA)Br_3), giving **8** in 51% yield, along with byproduct **5b** (19%). (TBA)Br_3 is less active as a bromination agent than (BTMA)Br_3. The Pd-catalyzed cross-coupling reaction of two equiv of **8** with **7** afforded **9** in 72% yield. The subsequent bromination of **9** by (BTMA)Br_3 gave **10** in 65% yield. The Pd-

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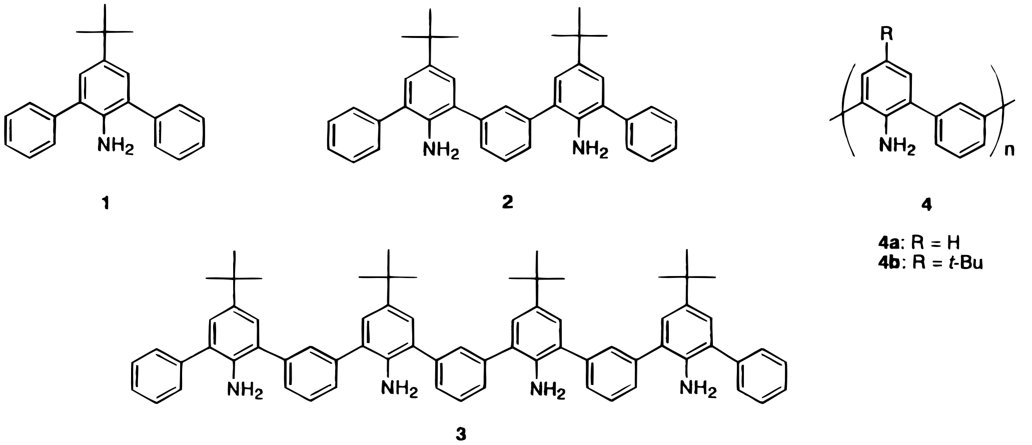
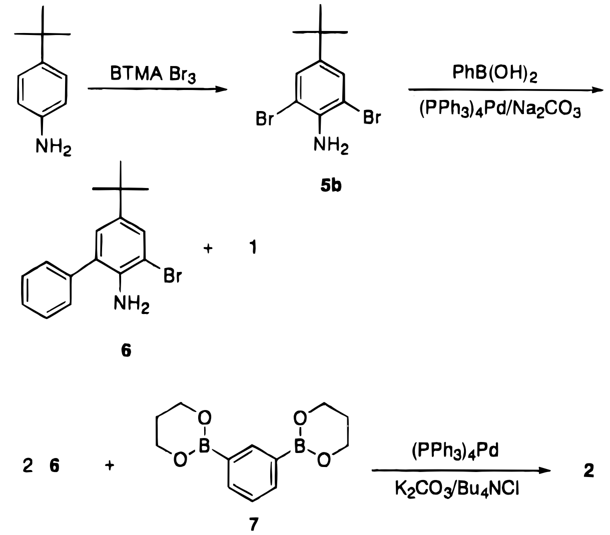
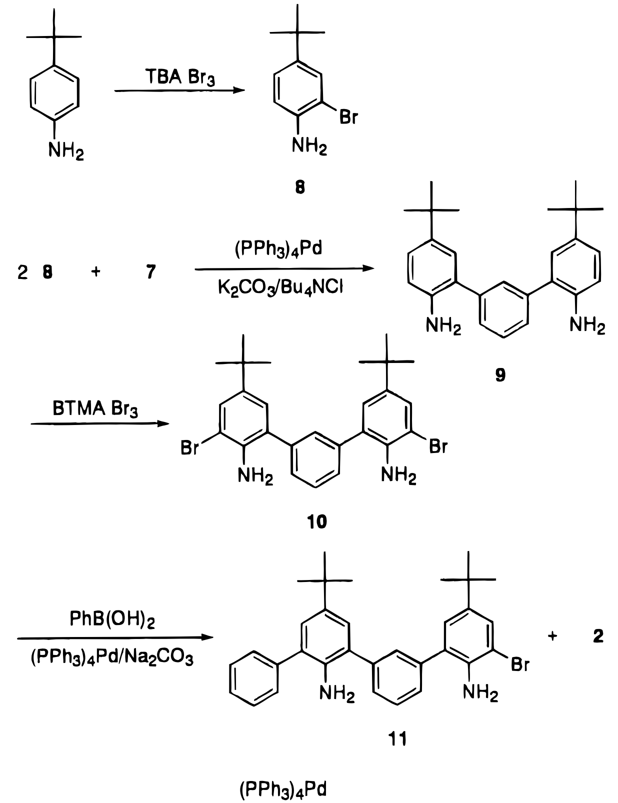
Chart 1



Scheme 1



Scheme 2



catalyzed cross-coupling reaction of **10** with phenylboronic acid gave **11** in 22% yield, along with byproduct **2** (15%). The final Pd-catalyzed cross-coupling reaction of 2 equiv of **11** with **7** in a refluxing benzene–H_2O solution containing K_2CO_3 and Bu_4NCl gave tetramer **3** in 75% yield as colorless prisms.

Characterization of Dimer and Tetramer. The structures of dimer **2** and tetramer **3** were confirmed by ^1H and^{13}C NMR spectra, FT-IR spectra, high resolution (HR) FAB (positive) mass spectra, and elemental analyses. The ^1H NMR spectrum of **2** showed a singlet peak due to the *tert*-butyl protons (18H) at 1.33 ppm and a broad singlet due to the amino protons (4H) at 3.84 ppm. On the other hand, the aromatic region is complex and analyzed by a H,H-COSY NMR spectrum (Figure 1a). The doublets at 7.18 and 7.22 ppm are correlated to each other, and the triplet at 7.47 ppm is correlated with the triplet at 7.36 ppm and doublet at 7.54 ppm. Therefore, the singlet at 7.55 (3H) is assigned to H2 + H3 and the singlet at 7.72 ppm (1H) to H1. The doublet with $J = 7.4$ Hz at 7.54 ppm is assigned to H6, and the two doublets with $J = 2.4$ Hz at 7.18 (2H) and 7.22 (2H) ppm to H4 and H5. On the other hand, the two triplets with $J = 7.4$ Hz at 7.36 (2H) and 7.47 ppm (4H) are assigned to H8 and H7, respectively. The ^{13}C NMR spectrum gave the theoretically expected 16 peaks. Two peaks are in the aliphatic region and 14 peaks are in the aromatic region (see Figure 1b). The two peaks in the aliphatic region are due to the primary and quarternary carbons of the *tert*-butyl group. The ^1H NMR spectrum of **3** is more complex (see Figure 2) than that of **2**, and assignments were made as follows based on the ^1H NMR spectra of **1** and **2**: δ 1.329 (s, 18H, *t*-Bu), 1.334 (s, 18H, *t*-Bu), 3.88 (s, br, 8H, NH_2), 7.17 and 7.22 (d, $J = 2.4$ Hz, 4H, H4 and H5 or H10 and H11), 7.23 (s, 4H, H10 and H11 or H4 and H5), 7.36 (t, $J = 7.4$ Hz, 2H, H14), 7.46 (t, $J = 7.4$ Hz, 4H, H13), 7.54 (d, $J = 7.4$ Hz, 4H, H12), 7.56 (s, 9H, H2 and H3, and H7–9), 7.72 (s, 3H, H1 and H6). The^{13}C NMR spectrum of **3** showed two peaks due to the primary and quarternary carbons of the *tert*-butyl group in the aliphatic region and 20 peaks in the aromatic region. The theoretically expected maximum number of peaks in the aromatic region is 26 and, if C4 and C5, C7 and C9, C15 and C16, and C17 and C18 (see Figure 2) are magnetically equivalent, the theoretically expected number of peaks is 22. Accordingly, at least four peaks in the

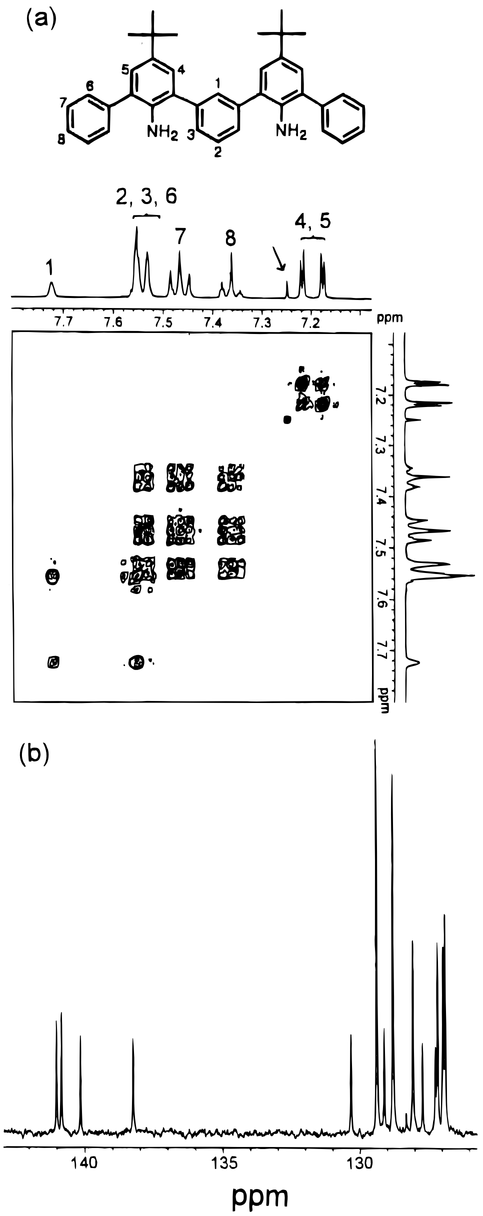


Figure 1. (a) H,H-COSY NMR spectrum of **2** in $CDCl_3$; (b) ^{13}C NMR spectra of **2** in $CDCl_3$. The absorption peak due to $CHCl_3$ is indicated by arrow.

aromatic region are suggested to overlap. In the HR FAB (posi) mass spectra of **2** and **3** a molecular ion (M^+) was observed at *m/z* 524.3196 (**2**) or 970.5942 (**3**), which is in agreement with the calculation (**2**, 524.3191 as $C_{38}H_{40}N_2$; **3**, 970.5913 as $C_{70}H_{74}N_4$). The elemental analyses for both compounds gave satisfactory agreements with the calculations.

Polycondensation. The Pd-catalyzed polycondensation of **5** with **7** using $Pd(PPh_3)_4$ as a catalyst was carried out in benzene–H_2O under nitrogen in the presence of Na_2CO_3 or K_2CO_3–Bu_4NCl (Scheme 3). After being refluxed for 72 h, the reaction mixture was extracted with benzene and chromatographed on silica gel. Elution with benzene gave the catalysts and decomposition products from the catalysts, and subsequent elution with ethyl acetate gave polymer **4**. The polymers were then refluxed in methanol to remove low molecular portions. The results of the polycondensations are summarized in Table 1.

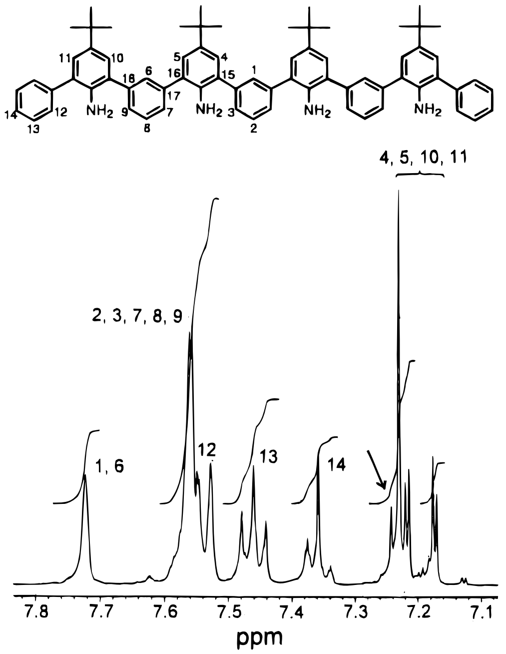
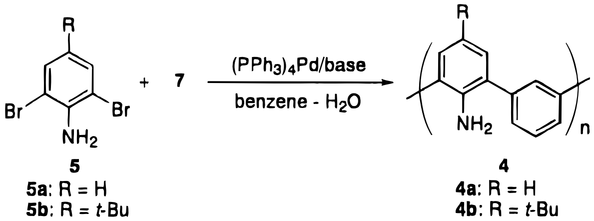


Figure 2. The ^1H NMR spectrum of **3** in $CDCl_3$. The absorption peak due to $CHCl_3$ is indicated by an arrow.

Scheme 3



As found in Table 1, no addition of Bu_4NCl to the polymerization system (entries 1 and 3) gave no polymeric products. The products isolated using column chromatography were methanol-soluble low molecular compounds with M_n of 220–320. On the other hand, addition of Bu_4NCl prompted the polycondensation significantly to give polymeric products with M_n of 2500–5720 in 56–86% yields. Particularly interesting is the polycondensation of **5b** with **7**, which gave a higher molecular weight polymer in a good yield. Polymers **4** obtained are a light yellow powder which is soluble in benzene, ethyl acetate, chloroform, and THF and insoluble in hexane and MeOH.

Characterization of 4. The structures of **4** were confirmed by IR and ^1H and ^{13}C NMR spectra. In the IR spectra strong absorption peaks due to NH_2 were observed at 3470 and 3380 cm^{-1}. The ^1H NMR spectrum of **4b** showed five peaks at 1.33 (s, 9H), 3.93 (br s, 2H), 7.23 (s, 2H), 7.56 (m, 3H), and 7.72 ppm (s, 1H). The peak at 1.33 ppm is due to the *tert*-butyl protons, and the peak 3.93 ppm is due to the amino protons. The remaining three peaks appear in the aromatic region, as shown in Figure 3a. The integration curves showed that the peak at 7.23 ppm corresponds to 2H, the peaks at ~7.56 ppm correspond to 3H, and the peak at 7.72 ppm corresponds to 1H, respectively. Accordingly, the peak at 7.23 ppm is assigned to H5 and H6, the peaks at ~7.56 ppm are assigned to H2, H3, and H4, and the peak at 7.72 ppm is assigned to H1. These assignments are in harmony with those for **2** and **3**. The ^{13}C NMR spectrum gave the theoretically expected 10 peaks. The peaks due to primary and quartenary carbons in the *tert*-butyl group appear at 31.6 and 34.1 ppm, respec-

Table 1. Results of the Palladium-Catalyzed Polycondensation of 5 with 7[a]

entry	monomer[b]	base	polymer	yield/%	M_n[c]	M_w[c]	M_w/M_n	DP[d]
1	**5a**	Na_2CO_3[e]	**4a**	∼0[f]				
2	**5a**	$K_2CO_3 + Bu_4NCl$[g,h]	**4a**	56	2500	4900	1.96	15.0
3	**5b**	Na_2CO_3[e]	**4b**	∼0[i]				
4	**5b**	$K_2CO_3 + Bu_4NCl$[g,h]	**4b**	86	5720	13200	2.31	25.6

[a] Conditions: Monomer **7**, 2.0 mmol; $Pd(PPh_3)_4$, 0.12 mmol; solvent, benzene 20 mL; temperature, reflux; time 72 h. [b] Conditions: Monomer **5**, 2.0 mmol. [c] Determined by GPC based on polystyrene standard. [d] Degree of polymerization. [e] Aqueous 2 M Na_2CO_3, 2 mL. [f] A low molecular product with M_n of 220 was obtained in 96% yield. [g] Aqueous 2 M K_2CO_3, 2 mL. [h] Bu_4NCl, 5.3 mmol. [i] A low molecular product with M_n of 323 was obtained in 67% yield.

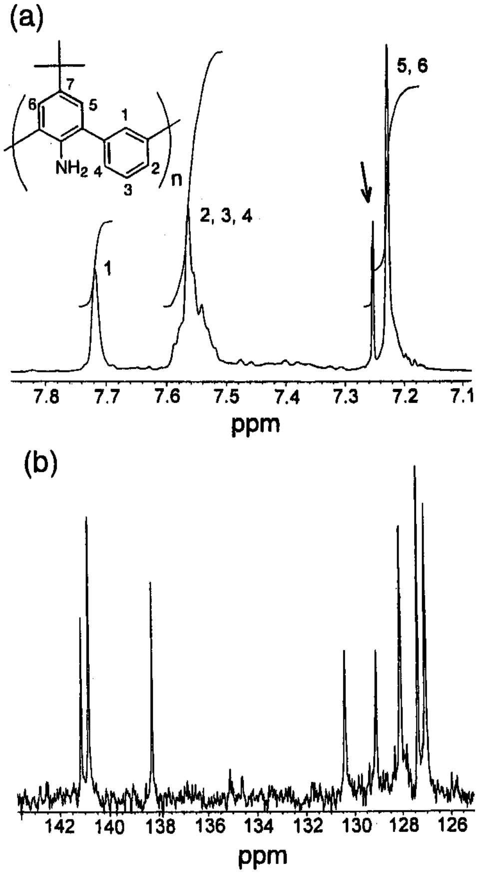


Figure 3. (a) ^1H NMR spectrum of **4a** in $CDCl_3$; (b) ^{13}C NMR spectrum of **4b** in $CDCl_3$. The absorption peak due to $CHCl_3$ is indicated by an arrow.

tively. The remaining eight peaks are found at 127.1, 127.4, 128.1, 129.1, 130.4, 138.3, 140.9, and 141.2 ppm in the aromatic region, as shown by Figure 3b.

The ^1H NMR spectrum of **4a** showed a broad singlet at 3.94 ppm (2H) and singlets at 6.87 (1H), 7.15 (2H), 7.49 (3H), and 7.64 ppm (1H) in the aromatic region. On the basis of the integration curves, the broad singlet at 3.94 ppm was assigned to amino protons, the singlet at 6.87 to H7, the singlet at 7.15 ppm to H5 and H6, the singlet at 7.49 ppm to H2−4, and the singlet at 7.64 ppm to H1 (see Figure 3a), respectively. On the other hand, the ^{13}C NMR spectrum showed eight peaks at 118.3, 127.6, 127.9, 128.1, 128.3, 129.3, 129.9, 130.2, 134.6, 140.3, and 140.7, in accordance with the theoretically expected number of peaks. On the basis of the ^1H and ^{13}C NMR spectra the structures of **4** could be unequivocally confirmed.

The elemental analyses of **4**, however, deviated from the calculations (Anal. Calcd for $(C_{12}H_9N)_n$, **4a**: C, 86.20; H,5.42; N, 8.38. Found: C, 79.96; H, 5.41; N, 6.41; Br, 2.86. Anal. Calcd for $(C_{16}H_{17}N)_n$, **4b**: C, 86.06; H, 7.67; N, 6.27. Found: C, 82.42; H, 7.28; N, 5.29; Br, 2.20). The deviations in the elemental anlyses are obviously attributable to the influences from the terminal groups because the poly(1,3-phenelene)s do not have molecular weights large enough to be able to ignore the influences of the terminal structures of the polymers. As shown by the elemental analyses, the polymers obtained contain bromine of 2.86% (**4a**) or 2.20% (**4b**), suggesting that substantial polymer chains are terminated by **5**.

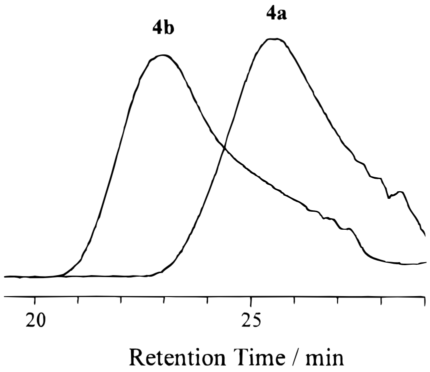


Figure 4. GPC traces of **4a** and **4b**.

Molecular weights of **4** were determined by GPC using polystyrene standards. The GPC elution curves obtained are shown in Figure 4, and the M_n and M_w values are summarized in Table 1. Both **4a** and **4b** show a unimodal molecular weight dispersion, and Table 1 shows that the polycondensation of **5a** with **7** gives a polymer with M_n of 2500 (DP = 15.0), while the polycondensation of **5b** with **7** gives a higher molecular weight polymer with M_n of 5720 (DP = 25.6). This difference in the molecular weights may be attributable to the good solubility of **4b** due to the presence of *tert*-butyl groups.

We measured M_n's of **1**, **2**, and **3** by GPC under the same conditions to evaluate the reliability for M_n. It is a generally accepted recognition that determination of M_n by GPC based on polystyrene standards often yields a relatively large deviation from the calculations when the structures of polymers are largely different from that of polystyrene. The M_n values of **1**, **2**, and **3** determined by GPC are 299, 569, and 1209, respectively, while the calculated values are 301 (**1**), 525 (**2**), and 971 (**3**), respectively. Therefore, the GPC results give larger M_n values than the calculations, and the deviation between the observed and calculated values increases with an increasing in M_n. Accordingly, the M_n values for **4** determined by GPC would be somewhat larger than the true values.

The UV−vis spectra of **1**, **2**, **3**, and **4b** were measured using CH_2Cl_2 as the solvent. The λ_{max} and ϵ are as follows: **1**, 231 (ϵ 29 900) and 320 nm (5220); **2**, 233 (58 400) and 322 nm (11 100); **3**, 233 (120 000) and 323 nm (24 000); **4b**, 233 (27 700), 324 nm (5530).[13] There-

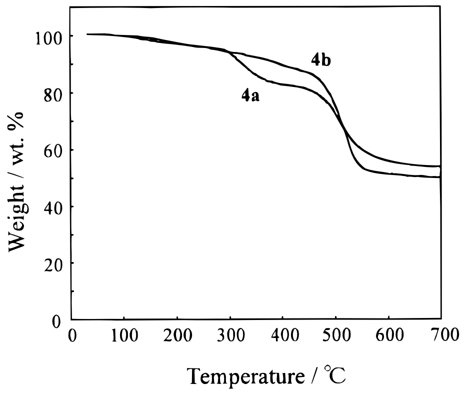


Figure 5. TG traces of **4a** and **4b** in nitrogen (10 °C/min).

fore, there is no significant shift in the $\lambda_{\max}$, and the unit molar absorption coefficients [29 900 and 5220 (**1**), 29 200 and 5550 (**2**), 30 000 and 6000 (**3**), and 27 700 and 5530 (**4b**)] are almost constant irrespective of the number of the repeating unit. Consequently, it can be said that there is no or a negligibly small extension in the π-conjugated system of the dimer, tetramer, and poly(1,3-phenylene), in accordance with the fact that those of **2**, **3**, and **4** are a cross-conjugated π-system.

The thermal stabilities of **4** were evaluated by thermalgravimetry (TG) under nitrogen. The results are shown in Figure 5. In the case of **4a**, two-step thermal decompositions were observed below 600 °C and a 10% weight loss was found at 323 °C. For **4b** a 10% weight loss was found at 390 °C. In both cases a gradual decomposition in the low-temperature range of 100−290 °C was observed, suggesting that the polymers have a thermally unstable end structure.

Experimental Section

General Data. IR spectra were run on a JASCO A-202 spectrophotometer, and UV−vis spectra were recorded with a Shimadzu UV-2200 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained using a JEOL α-400 spectrometer (400 MHz); chemical shifts are expressed in parts per million downfield from tetramethylsilane (TMS) used as internal standard. HR FAB mass spectra were recorded on a JEOL JMS-HX 100 spectrometer using 3-nitrobenzyl alcohol as matrix. Gel permeation chromatographic (GPC) analyses were performed on a Tosoh CCP & 8020 series equipped with TSKgel GMH$_{HR}$-L and TSKgel G5000H$_{HR}$ columns using THF as eluant and using polystyrene standards. The thermalgravimetry (TG) experiments were carried out on a Seiko TG/DTA320 instrument at a heating rate of 10 °C/min under nitrogen. Column chromatography was performed using Wako gel C200.

Materials. Phenylboronic acid, 4-*tert*-butyl-2,6-dibromoaniline, and $(PPh_3)_4Pd$ were obtained by the reported methods. 1,3-Dibromobenzene, 4-*tert*-butylaniline, and 2,6-dibromoaniline were commercially available. (BTMA)Br$_3$ (benzyltrimethylammonium tribromide)[10] and (TBA)Br$_3$ (tetrabutylammonium tribromide)[12] were prepared according to the reported methods.

1,3-Bis(trimethylsilyl)benzene. This compound was prepared according to the same procedure as that for 1,3-bis(trimethylsilyl)-5-tetradecylbenzene[14] and obtained as a colorless oil in ~100% yield. ^1H NMR ($CDCl_3$): δ 0.29 (s, 9H), 7.36 (t, J = 7.3 Hz, 1H), 7.54 (d, J = 7.3 Hz, 2H), 7.69 (s, 1H).

1,3-Phenylenebis(trimethylene boronate) (7). This compound was prepared by a procedure analogous to that for 5-tetradecyl-1,3-phenylenebis(1,3,2-benzodioxaborole)[14,15] and obtained as colorless needles (methanol) with mp 130−132 °C in 47% yield; ^1H NMR ($CDCl_3$) δ 2.04 (q, J = 5.4 Hz, 4H), 4.16 (t, J = 5.4 Hz, 8H), 7.33 (t, J = 7.3 Hz, 1H), 7.81 (d, J = 7.3 Hz, 2H), 8.20 (s, 1H).

2-Amino-3-bromo-5-*tert*-butylbiphenyl (6). To a solution of 4-*tert*-butyl-2,6-dibromoaniline (3.07 g, 10.0 mmol) in benzene (70 mL) were added a solution of phenylboronic acid (1.71 g, 14 mmol) in EtOH (7.0 mL), 2 M aqueous Na_2CO_3 (14 mL), and $(PPh_3)_4Pd$ (0.35 g, 0.30 mmol). After the resulting heterogeneous mixture was purged with nitrogen, it was gently refluxed for 24 h with stirring under nitrogen. After cooling, the organic layer was separated, and the aqueous solution was extracted with benzene. The combined organic layers were dried ($MgSO_4$) and evaporated, and the residue was chromatographed on using silica gel with 1:1 benzene−hexane to give **6** in 62.1% yield (1.89 g, 6.21 mmol) as colorless prisms, along with 0.93 g of **1** (3.09 mmol, 30.9%). Mp: 49−51 °C. IR (KBr): 3480 and 3390 (NH_2), 2960 cm^{-1} (*t*-Bu); ^1H NMR ($CDCl_3$): δ 1.29 (s, 9H), 4.07 (s, br, 2H), 7.07 (d, J = 2.0 Hz, 1H), 7.36−7.48 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 31.4, 34.0, 109.8, 126.7, 127.5, 128.3, 128.7, 128.9, 129.0, 138.9, 139.5, 142.1.

Diamine 2. To a solution of **6** (1.83 g, 6.00 mmol) in benzene (20 mL) were added a solution of **7** (0.49 g, 2.00 mmol), 2 M aqueous K_2CO_3 (4.0 mL), Bu_4NCl (1.47 g, 5.30 mmol), and $(PPh_3)_4Pd$ (0.21 g, 0.18 mmol). The resulting heterogeneous mixture was purged with nitrogen and gently refluxed for 24 h with stirring under nitrogen. After cooling to room temperature, the organic layer was separated, and the aqueous solution was extracted with benzene. The combined organic layers were dried ($MgSO_4$), evaporated, and chromatographed on silica gel with benzene to give **2** in 75.5% yield (0.79 g, 1.51 mmol). Recrystallization from benzene-hexane gave **2** as colorless prisms with mp 194−196 °C. IR (KBr): 3450 and 3360 (NH_2), 2960 cm^{-1} (*t*-Bu). UV−vis (CH_2Cl_2): $\lambda_{\max}$ 233 (ϵ 58 400), 322 nm (11 100); ^1H NMR ($CDCl_3$): δ 1.33 (s, 18H), 3.84 (s, br, 4H), 7.18 (d, J = 2.4 Hz, 2H), 7.22 (d, J = 2.4 Hz, 2H), 7.36 (t, J = 7.4 Hz, 2H), 7.47 (t, J = 7.4 Hz, 4H), 7.54 (d, J = 7.4 Hz, 4H), 7.55 (s, 3H), 7.72 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 31.6, 34.0, 126.9, 127.0, 127.2, 127.2, 127.7, 128.1, 128.8, 129.1, 129.4, 130.3, 138.3, 140.2, 140.8, 141.0. HR−FABMS: m/z calcd for $C_{38}H_{40}N_2$, 524.3191; found, 524.3196. Anal. Calcd for $C_{38}H_{40}N_2$: C, 86.98; H,7.68; N, 5.34. Found: C, 86.61; H, 7.64; N, 5.21.

2-Bromo-4-*tert*-butylaniline (8). To a solution of 4-*tert*-butylaniline (14.9 g, 100 mmol) in $CHCl_3$ (750 mL) was added (TBA)Br$_3$ (57.9 g, 120 mmol) at room temperature. After the mixture was stirred for 10 min, 10% aqueous $Na_2S_2O_3$ (500 mL) was added, and the resulting mixture was extracted with $CHCl_3$. The organic layer was washed with brine, dried ($MgSO_4$), evaporated, and chromatographed on silica gel with benzene to give **8** in 51.0% yield (11.6 g, 51.0 mmol) as a red oil, along with 5.67 g of **5b** (18.5 mmol, 18.5%). IR (KBr): 3470 and 3380 (NH_2), 2960 cm^{-1} (*t*-Bu). ^1H NMR ($CDCl_3$): δ 1.26 (s, 9H), 3.95 (s, br, 2H), 6.71 (d, J = 8.3 Hz, 1H), 7.13 (dd, J = 8.3 and 2.0 Hz, 1H), 7.40 (d, J = 2.0 Hz, 1H).

2,2″-Diamino-5,5″-di-*tert*-butyl-*m*-terphenyl (9). To a solution of **8** (6.84 g, 30.0 mmol) in benzene (100 mL) were added a solution of **7** (1.66 g, 10.0 mmol), 2 M aqueous K_2CO_3 (20 mL), Bu_4NCl (7.50 g, 27.0 mmol), and $(PPh_3)_4Pd$ (1.04 g, 0.90 mmol). After the resulting heterogeneous mixture was purged with nitrogen, it was gently refluxed for 24 h with stirring under nitrogen. After cooling, the organic layer was separated, and the aqueous solution was extracted with benzene. The combined organic layers were dried ($MgSO_4$), evaporated, and chromatographed on silica gel with 1:4 ethyl acetate−benzene to give **9** in 71.7% yield (2.67 g, 7.17 mmol) as colorless needles. Mp: 122−124 °C. IR (KBr): 3440 and 3360 (NH_2), 2960 cm^{-1} (*t*-Bu). ^1H NMR ($CDCl_3$): δ 1.30 (s, 9H), 3.65 (s, br, 4H), 6.74 (d, J = 8.8 Hz, 2H), 7.20−7.22 (m, 4H), 7.47−7.54 (m, 3H), 7.60 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 31.52, 33.96, 115.55, 125.51, 126.86, 127.40, 127.71, 129.04, 129.80, 140.58, 140.94, 141.58.

2,2″-Diamino-3,3″-dibromo-5,5″-di-*tert*-butyl-*m*-terphenyl (10). To a solution of **9** (1.49 g, 4.00 mmol) in CH_2Cl_2 (40 mL)-MeOH (16 mL) were added (BTMA)Br$_3$ (3.43 g, 8.80 mmol) and $CaCO_3$ powder (1.00 g, 10.0 mmol) at room temperature. After the mixture was stirred for 1 h, the solvent was removed, and aqueous 10% NaHSO$_3$ (30 mL) was added. The mixture was then extracted with benzene, and the benzene layer was washed with brine, dried (MgSO$_4$), and evaporated to give **10** in 64.5% yield (1.37 g, 2.58 mmol) as colorless prisms with mp 239−241 °C. IR (KBr): 3480 and 3380 (NH$_2$), 2950 cm^{-1} (*t*-Bu). ^{1}H NMR (CDCl$_3$): δ 1.29 (s, 9H), 4.14 (s, br, 4H), 7.10 (d, J = 2.0 Hz, 2H), 7.50 (d, J = 2.0 Hz, 2H), 7.46−7.48 (m, 2H), 7.52−7.56 (m, 2H). Anal. Calcd for C$_{26}$H$_{30}$Br$_2$N$_2$: C, 58.88; H, 5.70; N, 5.28. Found: C, 58.97; H, 5.72; N, 5.09.

3-Bromo-2,2″-Diamino-5,5″-di-*t*-butyl-*m*-terphenyl (11). To a solution of **10** (2.65 g, 5.00 mmol) in benzene (35 mL) were added a solution of phenylboronic acid (0.85 g, 7.00 mmol) in EtOH (3.5 mL), 2 M aqueous Na$_2$CO$_3$ (7.0 mL), and (PPh$_3$)$_4$-Pd (0.17 g, 0.15 mmol). After the resulting heterogeneous mixture was purged with nitrogen, it was gently refluxed for 24 h with stirring under nitrogen. After cooling, the organic layer was separated, and the aqueous layer was extracted with benzene. The combined organic layers were dried (MgSO$_4$), evaporated, and chromatographed on silica gel with benzene to give **11** in 22.4% yield (0.59 g, 1.12 mmol) as colorless needles with mp 138−140 °C, along with 0.39 g of **2** (0.74 mmol, 14.9%). IR (KBr): 3460 and 3370 (NH$_2$), 2960 cm^{-1} (*t*-Bu). ^{1}H NMR (CDCl$_3$): δ 1.26 (s, 9H), 1.29 (s, 9H), 4.13 (s, br, 4H), 7.13 (d, J = 2.0 Hz, 1H), 7.18 (d, J = 2.4 Hz, 1H), 7.19 (d, J = 2.0 Hz, 1H), 7.37 (t, J = 7.3 Hz, 1H), 7.44−7.49 (m, 4H), 7.53−7.58 (m, 4H), 7.62 (s, 1H). ^{13}C NMR (CDCl$_3$): δ 31.4, 31.6, 34.0, 34.1, 110.0, 126.8, 127.1, 127.2, 127.7, 127.8, 128.0, 128.5, 128.8, 129.3, 129.4, 130.0, 138.2, 138.8, 140.0, 140.2, 141.0, 141,1, 142.3. Anal. Calcd for C$_{32}$H$_{35}$BrN$_2$: C, 72.86; H,6.69; N, 5.31. Found: C, 72.81; H, 6.77; N, 5.25.

Tetraamine 3. To a solution of **11** (0.63 g, 1.2 mmol) in benzene (4.0 mL) were added a solution of **7** (0.098 g, 0.40 mmol), 2 M aqueous K$_2$CO$_3$ (0.8 mL), Bu$_4$NCl (0.31 g, 1.10 mmol), and (PPh$_3$)$_4$Pd (0.042 g, 0.036 mmol). After the resulting heterogeneous mixture was purged with nitrogen, it was gently refluxed for 24 h with stirring under nitrogen. After cooling, the organic layer was separated, and the aqueous layer was extracted with benzene. The combined organic layers were dried (MgSO$_4$), evaporated, and chromatographed on silica gel with 1:20 ethyl acetate−benzene to give **3** in 74.8% yield (0.29 g, 0.299 mmol). Recrystallization from benzene−hexane gave **3** as colorless prisms with mp 202−204 °C. IR (KBr): 3480 (broad), 3440 (sharp), 3380 (broad), and 3360 (sharp) cm^{-1} (NH$_2$). UV−vis (CH$_2$Cl$_2$): $\lambda_{\max}$ 233 (ϵ 120 000), 323 nm (24 000). ^{1}H NMR (CDCl$_3$): δ 1.329 (s, 18H), 1.334 (s, 18H), 3.88 (s, br, 8H), 7.17 (d, J = 2.4 Hz, 2H), 7.22 (d, J = 2.4 Hz, 2H), 7.23 (s, 4H), 7.36 (t, J = 7.4 Hz, 2H), 7.46 (t, J = 7.4 Hz, 4H), 7.54 (d, J = 7.4 Hz, 4H), 7.56 (s, 9H), 7.72 (s, 3H). ^{13}C NMR (CDCl$_3$): δ 31.6, 34.0, 126.9, 127.0, 127.1, 127.17, 127.22, 127.4, 127.7, 128.1, 128.3, 128.8, 129.1, 129.4, 130.4, 138.3, 140.2 140.79, 140.84, 140.88, 141.0, 141.1. HR−FABMS: *m*/*z* calcd for C$_{70}$H$_{74}$N$_4$, 970.5913; found, 970.5942. Anal. Calcd for C$_{70}$H$_{74}$N$_4$: C, 86.55; H,7.68; N, 5.77. Found: C, 86.22; H, 7.68; N, 5.69.

Polymerization. To a solution of **5** (2.00 mmol) in benzene (20 mL) were added **7** (0.49 g, 2.00 mmol), aqueous 2 M Na$_2$CO$_3$ (4.0 mL) or aqueous 2 M K$_2$CO$_3$ (4.0 mL), Bu$_4$NCl (1.47 g, 5.30 mmol), and (PPh$_3$)$_4$Pd (0.14 g, 0.12 mmol). After the resulting heterogeneous mixture was purged with nitrogen, it was gently refluxed for 72 h with stirring under nitrogen. After cooling, the products were extracted with benzene, and the benzene extract was washed with brine, dried (MgSO$_4$), and evaporated, and the residue was chromatographed on silica gel. Elution with benzene gave low polar compounds, and subsequent elution with ethyl acetate gave **4**. Evaporation of the solvent from the eluant gave **4** as a yellow powder. Polymer **4** was then refluxed in methanol (20 mL) for 10 min to remove low molecular products. After filtration, the polymer was dried in vacuo. The results of polymerization are summarized in Table 1.

Polyphenylene 4a. IR (KBr): 3475 and 3381 cm^{-1} (NH$_2$). UV−vis (CH$_2$Cl$_2$):[13] 230 (ϵ 25 700), 317 nm (5570). ^{1}H NMR (CDCl$_3$): δ 3.94 (s, 2H), 6.87 (s, 1H), 7.15 (s, 2H), 7.49 (s, 3H), 7.64 (s, 1H). ^{13}C NMR (CDCl$_3$): δ 118.3, 127.6, 127.9, 128.1, 128.3, 129.3, 129.9, 130.2, 134.6, 140.3, 140.7. Anal. Calcd for (C$_{12}$H$_9$N)$_n$: C, 86.20; H,5.42; N, 8.38. Found: C, 79.96 H, 5.41; N, 6.41; Br, 2.86.

Polyphenylene 4b. IR (KBr): 3475 and 3386 (NH$_2$), 2954 cm^{-1} (*t*-Bu). UV−vis (CH$_2$Cl$_2$):[13] 233 (ϵ 27 700), 324 nm (5530). ^{1}H NMR (CDCl$_3$): δ 1.33 (s, 9H), 3.93 (s, 2H), 7.23 (s, 2H), 7.56 (s, 3H), 7.72 (s, 1 H); ^{13}C NMR (CDCl$_3$): δ 31.6, 34.1, 127.1, 127.4, 128.1, 129.1, 130.4, 138.3, 140.9, 141.2. Anal. Calcd for (C$_{16}$H$_{17}$N)$_n$: C, 86.06; H, 7.67; N, 6.27. Found: C, 82.42; H, 7.28; N, 5.29; Br, 2.20.

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