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Poly(*p*-phenylene-borane)s. Novel Organoboron π-Conjugated Polymers via Grignard Reagent

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The heteroatom-including poly(phenylene)s such as poly(phenylene-oxide) (PPO),[1] poly(phenylene-sulfide) (PPS),[2] and polyaniline (PANI)[3] (Figure 1) have been industrially very important as engineering plastics or electronic materials. These polymers exhibit excellent mechanical properties, high stability, conductivity, energy storage ability, and so on. In this paper, we report the synthesis of novel poly(phenylene-borane)s (PPBs) by polycondensation between bifunctional Grignard reagents and aryldimethoxyborane (Scheme 1).

Previously, we have reported various methodologies for the synthesis of organoboron polymers.[4] Very recently, the polymers prepared by hydroboration polymerization between aromatic diynes and mesitylborane were found to be a novel type of π-conjugated polymers via the vacant p-orbital of the boron atom.[5] In their UV−vis absorption spectra, the absorption maxima were observed in the visible region. Furthermore, an intense blue light emission was observed upon excitation by UV light. Since these organoboron conjugated polymers can be regarded as polymer homologues of electron acceptors, they are expected as a new class of n-type conjugated polymers that are generally of great importance for the development of polymer energy storage systems.

The polymerization between bifunctional Grignard reagents and aryldimethoxyboranes was carried out under a nitrogen atmosphere in THF solution. For example, the reaction between tripyldimethoxyborane (tripyl = triisopropylphenyl) (**1y**) and 1,4-dibromo-2,5-*n*-dodecyloxybenzene (**2b**) in the presence of twice the molar amount of magnesium was performed in a freshly distilled THF at 80 °C (in a closed system). During vigorous stirring, the reaction mixture grew to be a fluorescent-yellow solution. After the mixture stirred for 3h, the solvent was removed, and the obtained yellow gum was dissolved in chloroform. The insoluble part was filtrated, and the filtrate was evaporated, washed with methanol repeatedly, and then dried in vacuo. The polymer [poly(di-*n*-dodecyloxyphenylene-tripylborane)] (**3by**) was obtained as a yellow powder in 99% yield. From gel permeation chromatographic analysis, the number-average molecular weight was estimated to be 3000 (THF, PSt standards). **3by** was very soluble in common organic solvents such as THF, chloroform, and benzene.

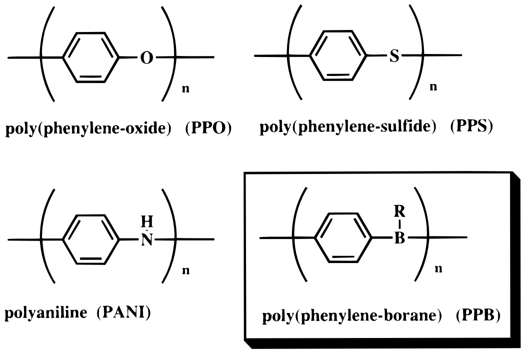
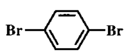
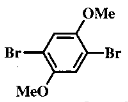
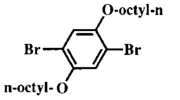
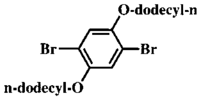


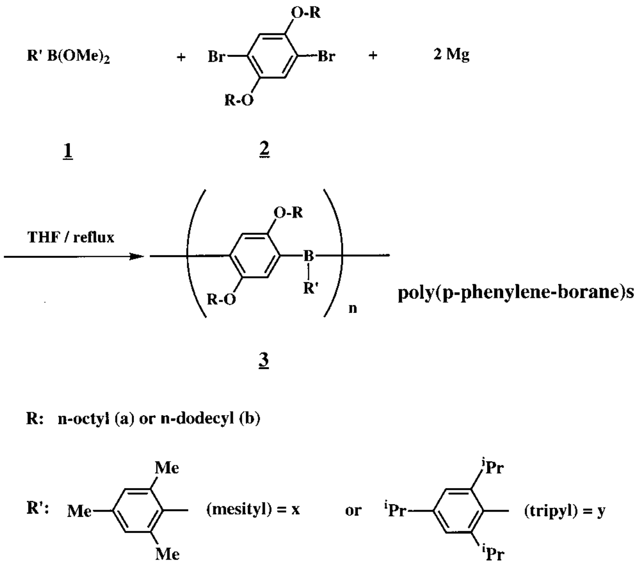
Figure 1. Heteroatom-containing poly(phenylene)s.

Table 1. Polymerization of Various Dibromides (**2**) with **1y**[a]

Bromide	1y/2	*Mw* [b]	*Mn* [b]	*Mw/Mn* [b]	yields [c]
	1.05	No Polymerization			
	1.01	1200	800	1.5	96
	1.06	3500	2900	1.2	quant.
	1.04	3400	3000	1.2	99

[a] The reactions were carried out under nitrogen atmosphere at 80 °C in THF for 3h. [b] GPC (THF), polystyrene standards. [c] Isolated yields after washing with methanol.

Scheme 1



The polymerization with various dibromide monomers (**2**) was performed, and the results are summarized in Table 1. As a dibromide monomer, 1,4-dibromo-2,5-*n*-octyloxybenzene (**2a**)

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(1) For example: (a) Hay, A. S. *Adv. Polym. Sci.* **1967**, *4*, 496. (b) Hay, A. S. *Polym. Eng. Sci.* **1967**, *16*, 1. (c) Hay, A. S.; Blanchard, H. S.; Endres, G. F.; Eustance, J. W. In *Macromolecular Synthesis* Overberger, C. G., Ed., John Wiley: New York, 1963; Vol. 1, p 75. (d) Hay, A. S.; Endres, G. F. *J. Polym. Sci., Polym. Lett. Ed.* **1965**, *3*, 887. (e) Hay, A. S. *Macromolecules* **1969**, *2*, 107.

(2) For example: (a) *Macromolecular Synthesis*; Moore, J. A., Ed., Wiley: New York, 1977; Vol. 1, p 345. (b) Tsuchida, E.; Yamamoto, K.; Nishide, H.; Yoshida, S. *Macromolecules* **1987**, *20*, 2030. (c) Freund, L.; Heitz, W. *Makromol. Chem.* **1990**, *191*, 815. (d) Tsuchida, E.; Yamamoto, K.; Jikei, M.; Nishide, H. *Macromolecules* **1990**, *23*, 930. (e) Yamamoto, K.; Jikei, M.; Nishide, H.; Tsuchida, E. *J. Chem. Soc., Chem. Commun.* **1991**, 596.

(3) For example: (a) Skotheim, T. A. In *Handbook of Conducting Polymers*; M. Dekker: New York, 1986; Vols. I and II. (b) MacDiarmid, A. G.; Chiang, J. C.; Epstein, A. J. *Synth. Met.* **1987**, *18*, 285. (c) Wudl, F.; Angus, R. O., Jr.; Lu, F. L.; Allemand, P. M.; Vachon, D. F.; Nowak, M.; Liu, Z, X.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 3677. (d) Lux, F. *Polymer* **1994**, *14*, 2915.

(4) (a) Chujo, Y.; Tomita, I.; Hashiguchi, Y.; Tanigawa, H.; Ihara, E.; Saegusa, T. *Macromolecules* **1991**, *24*, 345. (b) Chujo, Y.; Tomita, I.; Saegusa, T. *Polym. Bull.* **1992**, *27*, 375. (c) Chujo, Y.; Tomita, I.; Murata, N.; Mauermann, H.; Saegusa, T. *Macromolecules* **1992**, *25*, 27. (d) Matsumi, N.; Chujo, Y. *Polym. Bull.* **1997**, *38*, 531.

(5) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5112.

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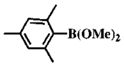
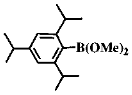
Table 2. Polymerization of **2b** with Various Borane Reagents[a]

Borane	1 / 2b	conc. (M)[b)]	time (h)	Mw[c)]	Mn[c)]	Mw/Mn[c)]	yield (%)[d)]
	1.10	0.2	12	2500	2200	1.1	77
	1.04	0.67	3	3400	3000	1.2	99
$B(OEt)_3$	1.02	0.67	3	No Polymerization			
$BF_3 \cdot OEt_2$	1.07	0.2	12	1800	1400	1.3	87

[a] The reactions were carried out under nitrogen atmosphere at 80 °C. [b] Concentration of **2**. [c] GPC (THF), polystyrene standards. [d] Isolated yields after washing with methanol.

Table 3. Optical Properties of Poly(p-phenylene-borane)s

polymers	UV λ_{max}[a] (nm)	ϵ[a]	PL λ_{max}[a,b] (nm)
3ax	359	2240	496
3ay	365	2510	481
3bx	359	1780	477
3by	367	1820	487

[a] Absorption and emission spectra were recorded in dilute $CHCl_3$ solutions at rt. [b] Excited at 350 nm.

also gave the corresponding polymer, although its number-average molecular weight had slightly decreased. However, the polymerization with 1,4-dibromo-2,5-dimethoxybenzene resulted in low molecular weight oligomer formation, and no polymerization was observed in the case of 1,4-dibromobenzene. This might be due to the poor solubility of the polymers and oligomers.

The results of the polymerization of **2b** using various borane reagents are listed in Table 2. The polymerization with mesityldimethoxyborane (**1x**) also proceeded to give the corresponding polymers although the molecular weight was slightly lower. When trimethoxyborane was employed, no polymerization was observed. It is likely that a thermally stable aryl-type boron monomer is necessary to avoid thermal disproportionation of the main chain, as we had reported in other polymerization system.[6]

The structures of the polymers were supported by ^1H and ^{11}B NMR spectra. For example, in the ^1H NMR spectrum of **3by**, the peaks corresponding to tripyl group were observed at 1,27, 2.64, 2.88, and 6.84 ppm. The ^{11}B NMR spectrum of **3by** showed the main peak at 31.6 ppm due to the triarylborane unit, which indicates this polymer has mainly only one kind of unit structure.

The optical data of the polymers obtained are given in Table 3. In the UV−vis spectrum of **3by** (in chloroform, at room temperature), the absorption maximum was observed at 367 nm (Figure 2). This indicates the effective extension of π-conjugation length via the vacant p-orbital of the boron atom, despite the presence of bulky tripyl group substituent on the boron atom. The spectra of **3ax**, **3ay** and **3bx** also showed their λ_{max} around 360 nm. These values were not so much dependent on the reaction conditions.

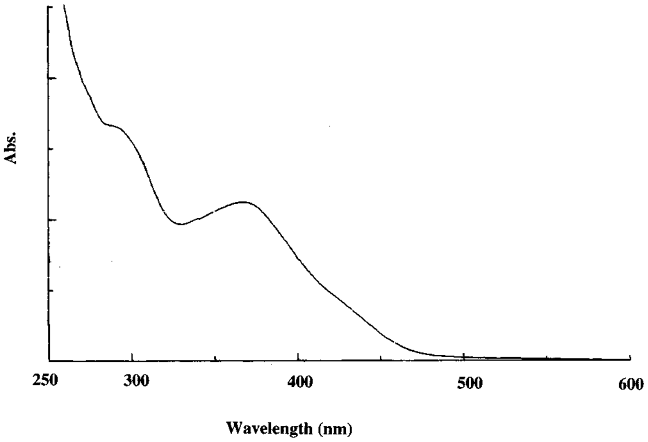


Figure 2. UV−vis absorption spectrum of **3by** in $CHCl_3$ at room temperature.

All of the polymers prepared were highly fluorescent. When the dilute chloroform solutions of the polymers were irradiated by UV light (350 nm), intense visible blue-green emissions were observed. For example, the fluorescence emission spectrum of **3by** (in chloroform, at room temperature, excitation wavelength at 350 nm) exhibited a peak at 487 nm, and the value of λ_{max} showed a slight dependence on the kind of solvents (480 nm in benzene). The Stokes shift (79 nm) was relatively large in comparison with those of the polymers prepared by hydroboration polymerization (less than 50 nm),[5] despite the fairly rigid structure of **3by**. This might be due to some energy transfer in the excited states.

To investigate the stability of the polymers, an air-bubbling experiment was carried out for **3by**. An stream of air was bubbled into a THF solution of **3by** and the change of the molecular weight was monitored by GPC measurements. The stability of **3by** toward moisture was similarly studied during the treatment with water. In both cases, after the air-bubbling or the treatment with water for 24 h, no significant decrease in the molecular weight was observed. This indicates fairly high stability of the polymers obtained in the present method.

In conclusion, novel poly(*p*-phenylene-borane)s (PPBs) were prepared by polycondensation between aryldimethoxyborane and bifunctional Grignard reagents. This provides a novel methodology for the preparation of organoboron conjugated polymers as a useful alternative to hydroboration polymerization. The polymers obtained are expected as novel n-type conjugated polymers with fairly high stability toward air and moisture. The higher thermal stability is also expected due to the absence of a retro-hydroboration (β-elimination) process during their thermal degradation. These characteristics of the polymers might allow their application for various electronic devices.

Acknowledgment. We thank Professor Susumu Kitagawa and Dr. Tadashi Mizutani (Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University) for their help to measure fluorescence emission spectra.

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(6) Matsumi, N.; Chujo, Y. *Macromolecules* **1998**, *31*, 3802. Alkoxyboration polymerization of diisocyanates with thermally stable mesityldimethoxyborane gave the corresponding poly(boronic carbamate)s. The polymerization using trimethoxyborane, triethoxyborane or cyclohexyldimethoxyborane was unsuccessful possibly due to disproportionation of the monomer or the main chain.