Communications to the Editor

Extension of π-Conjugation Length via the Vacant p-Orbital of the Boron Atom. Synthesis of Novel Electron Deficient π-Conjugated Systems by Hydroboration Polymerization and Their Blue Light Emission

Noriyoshi Matsumi, Kensuke Naka, and Yoshiki Chujo*

Department of Polymer Chemistry
Graduate School of Engineering
Kyoto University, Yoshida
Sakyo-ku, Kyoto 606-8501, Japan

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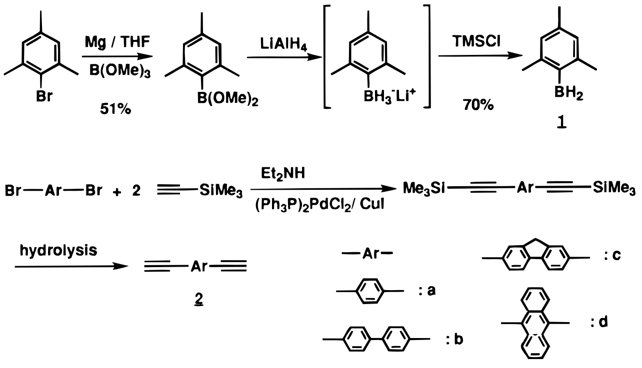
For the past decades, considerable attention has been focused on the construction of novel π-conjugated systems for their remarkable electrochemical and optical properties. Their potential utility ranges from light emitting diodes (LED), energy storage systems (batteries), nonlinear optical (NLO) materials, and so on. A large number of papers have been published about their preparative methods with electrochemical synthesis,[1] chemical oxidation,[2] and polycondensation[3] reactions. Here we report a facile synthesis of novel well-defined π-conjugated systems by polyaddition using the well-known hydroboration reaction.[4]

The conjugative interaction between the vinyl group and the boron atom has been investigated by using the spectral properties of low molecular weight vinylborane derivatives.[5] In the early studies, it was found that these spectroscopic data such as ^{11}B NMR and absorption maxima were in accordance with the calculated results with Hückel MO theory, which suggested considerable conjugative overlap of the π-orbitals of the vinyl groups with the p-orbital of the boron atom.[5a]

Previously, we have explored various methodologies for the preparation of organoboron main-chain polymers by hydroboration polymerization.[6] Although most of these polymers obtained were relatively unstable, several organoboron polymers were found to have relatively high stability toward air oxidation.[7] The air stability of these polymers might show the possibility of the application of these polymers as functional materials.

Scheme 1



Scheme 2

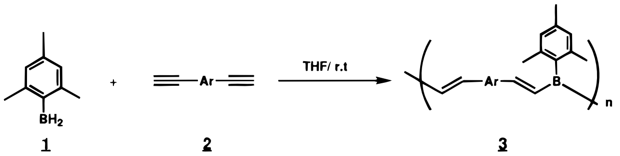
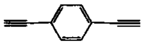
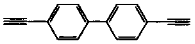
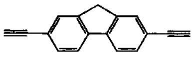
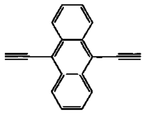


Table 1. Hydroboration Polymerization of Aromatic Diynes Using Mesitylborane[a]

Diynes	1/2	*Mw* [b]	*Mn* [b]	*Mw/Mn* [b]	Yield (%) [c]
 (2a)	1.17	16000	6500	2.5	71
 (2b)	1.27	10500	5100	2.1	95
 (2c)	1.24	4200	2800	1.5	71
 (2d)	1.22	1700	1300	1.3	67

[a] Reactions were carried out in THF at room temperature. [b] GPC (THF), polystyrene standards. [c] Isolated yields after reprecipitation into MeOH.

Generally, aromatic organoboron compounds such as triphenylborane or trimesitylborane[8] are known as strong electron acceptors. Therefore, the polymeric homologues of these materials are expected to possess unique properties as a novel type of n-type conjugated polymers. For example, these include high electron affinity or extened π-conjugation length via the vacant p-orbital of the boron atom.

The synthesis of a series of conjugated organoboron polymers was examined by hydroboration polymerization of aromatic diynes with mesitylborane, utilizing the highly regioselective nature of the hydroboration reaction of mesitylborane with the acetylene bond. Aromatic diynes (**2**)[9] and mesitylborane (**1**)[6f,10] were prepared by the modified procedure shown in Scheme 1 according to the reported method.

A typical procedure for the polymerization (Scheme 2) is as follows. To a freshly distilled tetrahydrofuran solution of diyne monomer (**2**) was added dropwise a slightly excess amount of mesitylborane (**1**) in THF under nitrogen at room temperature,

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(1) For example: Kovacic, P.; Oziomek, J. *J. Am. Chem. Soc.* **1963**, *85*, 454.

(2) For example: (a) Goldfingger, G. *J. Polym. Sci.* **1949**, *93*, 4. (b) Yamamoto, T.; Hayashi, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2091. (c) MacDonald, D. N.; Campell, T. W. *J. Am. Chem. Soc.* **1960**, *82*, 4669. (d) Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun.* **1984**, *25*, 327. (e) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1497. (f) Amer, A.; Zimmer, H.; Mulligan, K. J.; Mark, H. B.; Pons, S., Jr.; MeAleer, J. F. *J. Polym. Sci. Part C. Polym. Symp.*, **1984**, *22*, 77.

(3) For example: (a) Diaz, A. F.; Logan, J. A. *J. Electroanal. Chem.* **1980**, 111, 111. (b) Sato, M.; Kaneko, K.; Yoshino, K. *J. Chem. Soc., Chem. Commun.* **1985**, 1629. (c) Dall'Olio, A.; Dascola, Y.; Varacca, V.; Bocchi, V. *C. R. Hebd. Seances Acad. Sci., Ser. C***1968**, *267*, 433. (d) Diaz, A. F.; Kanazawa, K. K.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* **1979**, 635.

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(5) For example: (a) Good, C. D.; Ritter, D. M. *J. Am. Chem. Soc.* **1962**, *84*, 1162. (b) Good, C. D.; Ritter, D. M. *J. Chem. Eng. Data, 1* **1962**, 416. (c) Zweifel, G.; Clark, G. M.; Leung, T.; Whitney, C. C. *J. Organomet. Chem.* **1976**, *117*, 303.

(6) (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.; Hashiguchi, Y.; Saegusa, T. *Macromolecules* **1992**, *25*, 33. (d) Matsumi, N.; Chujo, Y. *Polym. Bull.* **1997**, *38*, 531.

(7) Sasaki, Y.; Kinomura, N.; Chujo, Y. Unpublished data.

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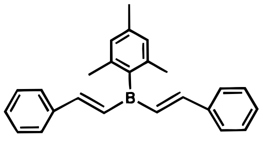
Table 2. Optical Properties of Organoboron Polymers **3a**−**d**

polymers	UV $\lambda_{max}{}^a$ (nm)	ϵ^a	PL $\lambda_{max}{}^{a,b}$ (nm)
3a	399	8470	441
3b	390	17700	440
3c	350, 390, 407	9670, 10230, 10800	455
3d	364, 383, 405	3520, 5360, 6120	412, 436, 462

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

and the resulting reaction mixture was stirred for several hours. After the complete addition of mesitylborane, the dark reaction mixture remained homogeneous and no gelation was observed. The reaction mixture was directly subjected to gel permeation chromatographic analysis (THF as an eluent, polystyrene standards). After removal of the solvent, a dark brown gum was obtained. The polymer was purified by reprecipitation into methanol. After freeze-drying, each polymer was obtained as a yellow powder (**3a**−**3c**) or as an orange powder (**3d**). The polymers obtained were highly soluble in common organic solvents such as THF, chloroform, and benzene, even in the case of **3d** having the anthracene unit. The structures of the polymers were supported by ^1H, ^{11}B NMR and IR spectra. In the ^1H NMR spectrum of **3a** in $CDCl_3$, the peak corresponding to the acetylene proton at 3.22 ppm almost disappeared while those of the mesityl group appeared at 2.18−2.42 (Me) and 6.93 (Ar−H) ppm.

The results of the polymerization with various diyne monomers are summarized in Table 1. In every case, the corresponding polymers were obtained in good yields (67−95%). The relatively low molecular weight of **3d** is probably due to the low solubility of the monomer **2d**.



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The UV−vis absorption spectra data for the dilute chloroform solutions of **3a**−**d** are shown in Table 2. Figure 1 represents the spectrum of **3a**, in which the peak due to the $\pi-\pi^*$ transition of the polymer backbone is observed at 399 nm. The value was largely bathochromic shifted in comparison with the model compound **4**. From this result, it was confirmed that the π-delocalization length was highly extended via the boron atom. Furthermore, these spectra were independent of the type of solvents used. This result suggests the red shift should not be due to a charge transfer. A relatively large band gap might be, in part, due to a steric distortion of the main-chain by the bulky mesityl substituent.

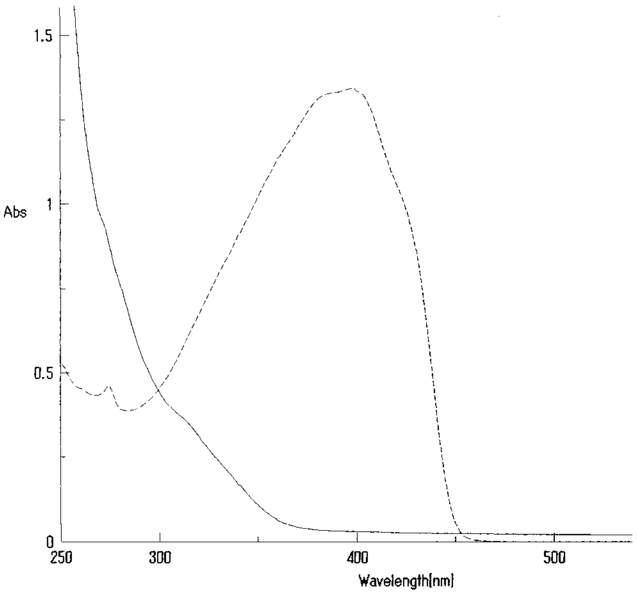

Figure 1. UV−vis spectra of **3a** (dot line) and **4** (solid line) in $CHCl_3$.

The polymers obtained were highly fluorescent. The fluorescence emission spectra data of **3a**−**d** are also summarized in Table 2. In every case, when a dilute chloroform solution was excited at 350 nm at room temperature, an intense emission was observed in a visible blue region. The value of λ_{max} was independent of the excitation wavelength. In the fluorescence emission spectrum of **3a** (2.00×10^{-4} M in chloroform), the emission maximum was observed at 441 nm, bathochromic shifted by 38 nm compared with that of the excitation spectrum of this sample (403 nm). This small Stokes shift indicates that the present polymer has a relatively rigid structure.

Thermogravimetric analysis (TGA) was recorded for **3a**, under both air and under nitrogen. In both cases, **3a** was stable up to 110−120 °C and was slightly more stable under nitrogen. However, the difference in both weight loss curves was much smaller than that of other organoboron polymers previously investigated by us. This result indicates that the thermal degradation of **3a** was not strongly affected by the insertion of oxygen into the C−B bond.

In conclusion, the extension of the π-conjugation length via the boron atom was observed in the organoboron main-chain polymers prepared by hydroboration polymerization. The polymers prepared had high solubility and are expected as novel n-type conjugated polymers. In addition, blue fluorescence emission was observed in every case. These results may stimulate interest for further physical studies about the electrochemical property, EL activity, conductivity, and so on.

Supporting Information Available: Experimental procedure and ^1H and ^{11}B NMR, IR, UV−vis, and PL spectra of **3a**−**d** (11 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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