

Synthesis of Novel σ - π Conjugated Polymers by Alternating Boration Copolymerization between 1,2-Diethynyl-1,1,2,2-tetramethyldisilane and Aromatic Diynes

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ABSTRACT: Novel σ - π conjugated polymers were prepared by alternating boration copolymerization between 1,2-diethynyl-1,1,2,2-tetramethyldisilane and aromatic diynes using diphenylbromoborane. The gel permeation chromatographic analysis (GPC) showed that the number average molecular weights (M_n) of the obtained polymers were several thousands. For example, M_n of the polymer produced from 2,7-diethynylfluorene was 5700 (yield 30%). The polymers were soluble in common organic solvents such as THF, chloroform and dichloromethane. The polymer having the fluorene unit was moderately fluorescent. The structures of the polymers were supported by ¹H NMR, ¹¹B NMR, ²⁹Si NMR, and IR spectra.

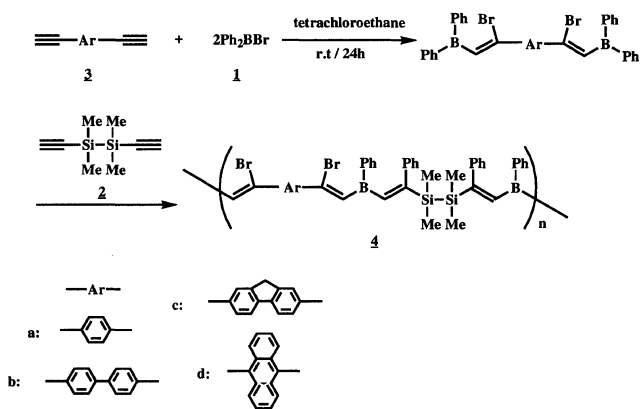
KEY WORDS Conjugated Polymer / Inorganic Polymer / Boration Polymerization / Organoboron Polymer / Organosilicon Polymer /

The preparation of the organosilicon polymers having silylene units and π -conjugated units in the alternating arrangement has been a very interesting subject due to the σ - π conjugative interaction¹ along the polymer chains. Since these materials are potentially important as semiconducting or conducting materials,² precursors for silicon carbide ceramics and light emitting materials,³ their preparative methods have also been widely developed. For example, a Wurtz type polymerization of bis(chloromethylphenylsilyl)benzene⁴ quenching of the aromatic bifunctional Grignard reagents (or organolithium reagents) with dichlorodisilane⁵ or a ring-opening polymerization of 1,1,2,2-tetramethyl-3,4-benzo-1,2-disilacyclobutene with a Lewis acid,⁶ each affords the corresponding poly(disilanylene-arylene)s respectively. On the other hand, we have previously explored various methodologies for the preparation of organoboron main-chain polymers by means of boration polymerization.⁷ During the course of the work, some polymers having relatively high stability toward air-oxidation and mois-

ture were prepared and they are interesting as a new class of boron containing materials.⁸ Very recently, it was found that the UV-*vis* spectra of organoboron polymers produced from aromatic diynes have the absorption maxima in the visible region, due to the extension of π -conjugation length *via* vacant p-orbital of boron atom.⁹ Furthermore, taking advantage of different reactivity between haloboration and phenylboration, an alternating boration polymerization method was explored.¹⁰ In this paper, an alternating boration polymerization between 1,2-diethynyl-1,1,2,2-tetramethyldisilane (**2**) and aromatic diynes (**3**) was undertaken to give the novel boron-containing σ - π conjugated polymers (Scheme 1).

RESULTS AND DISCUSSION

An alternating boration polymerization between 1,2-diethynyl-1,1,2,2-tetramethyldisilane (**2**) and 2,7-diethynylfluorene (**3c**) was first examined as follows. To a tetrachloroethane solution of **3c**, 2 molar equiv of diphenylbromoborane (**1**) were added under nitrogen atmosphere at room temperature and the reaction mixture was stirred for 24 h (1st step; selective haloboration). From the ¹H NMR measurement, disappearance of the acetylene proton (3.13 ppm) was observed. In the 2nd step, 1 molar equiv of **2** was added and the mixture was reacted at higher temperature (60–130°C) for 1–2 h (phenylboration polymerization). After reprecipitation into *n*-hexane, the polymer (**4c**) was obtained as a brown powder. The polymer was soluble in common organic solvents such as THF, chloroform and dichloromethane. The gel permeation chromatographic analysis (THF, PSt standards) showed that the number average molecular weights of the polymers were several thousands. The results of the polymerization under various reaction conditions of the 2nd step are summarized in Table I. From these results, the best condition was optimized to be at 80°C for 2 h (Run 3). Under the severe reaction conditions (Runs 5 and 6), relatively high molecular weights



Scheme 1.

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Table I. Alternating haloboration-phenylboration copolymerization between 2,7-diethynylfluorene (**3c**) and 1,2-diethynyl-1,1,2,2-tetramethyldisilane (**2**) using diphenylbromoborane (**1**) under various reaction conditions^a

Run	Temp/°C	Time/h	Conc./M ^b	Ratio/mol (1/3c/2)	M_n^c	M_w^c	M_w/M_n^c	Yield/% ^d
1	60	2	2.0	2.00/0.974/0.907	3500	9700	2.8	35
2	80	1	2.0	2.00/0.962/0.924	2000	5300	2.6	47
3	80	2	2.0	2.00/0.934/0.893	5700	19500	3.4	30
4	80	2	0.5	2.00/0.960/0.884	3900	13700	3.5	18
5	115	2	2.0	2.00/0.928/0.928	7700	38700	5.1	24
6	130	2	2.0	2.00/0.975/0.937	4900	27600	5.6	32

^a All reactions were carried out under nitrogen using tetrachloroethane as a solvent. ^b Concentration of **1**. ^c GPC (THF) polystyrene standards. ^d Isolated yields after reprecipitation into *n*-hexane.

were attained, however, the produced polymers had fairly crosslinked structure due to further phenylboration of B-Ph in the side-chain.

The structures of the polymers were supported by ¹H, ¹¹B, ²⁹Si NMR, and IR spectra. For example, in the ¹H NMR spectrum of **4c** (Figure 1a), methyl groups on the silylene moiety appeared at 0.23 ppm and the methylene protons and other aromatic protons (including vinyl group) were observed at 3.85 ppm and 7.45 ppm respectively. The ¹¹B NMR spectrum of **4c** (Figure 1b) had mainly only one peak (30.3 ppm) attributable to dialkenylborane. In the ²⁹Si NMR spectrum (Figure 1c), simple one peak due to the disilanylene unit was observed at -27.8 ppm. This indicates that the disilanylene structure was not affected by the polymerization condition.

The results of the polymerization using various aromatic diynes are listed in Table II. As diyne monomers, 1,4-diethynylbenzene (**3a**) and 1,6-diethynylbiphenyl (**3b**) also gave the corresponding soluble polymers. However, the reaction using 1,9-diethynylanthracene (**3d**) was unsuccessful due to poor solubility of **3d**.

The optical properties of the polymers obtained were investigated by the measurements of UV-*vis* spectra (in CHCl₃, at room temperature) and the fluorescence emission spectra (in CHCl₃ at room temperature; excitation wavelength at 300 nm). The both spectra of **4c** are represented in Figure 2. In the UV-*vis* spectrum (a), two absorption maxima were observed at 284 and 315 nm, the latter might be due to σ - π interaction *via* boron atom.¹² In the fluorescence emission spectrum (b), blue light emission (419 and 449 nm) was observed in a moderate intensity. However, in the case of the polymer **4a** and **4b**, just a weak emission was observed. This implies that σ - π interaction *via* boron atom is not so effective.

The air stability of **4c** was investigated by an air-bubbling experiment. Air was bubbled into a THF solution of **4c** and the change of the molecular weight was monitored by the GPC measurement. After the air bubbling for 48 h, no obvious decrease in molecular weight was observed. This indicates the relatively high stability of the organoboron unit. However, in the IR spectrum of **4c** after the air-bubbling, a strong Si-O-Si stretching was observed at 1030–1070 cm⁻¹.¹²

In conclusion, a novel methodology for the preparation of σ - π conjugated polymers was explored by alternating boration copolymerization between 1,2-diethynyl-1,1,2,2-tetramethyldisilane (**2**) and aromatic diynes (**3**). The polymers obtained (**4**) were soluble in common organic solvents such as THF, chloroform and dichloromethane. However, σ - π interaction *via* boron atom

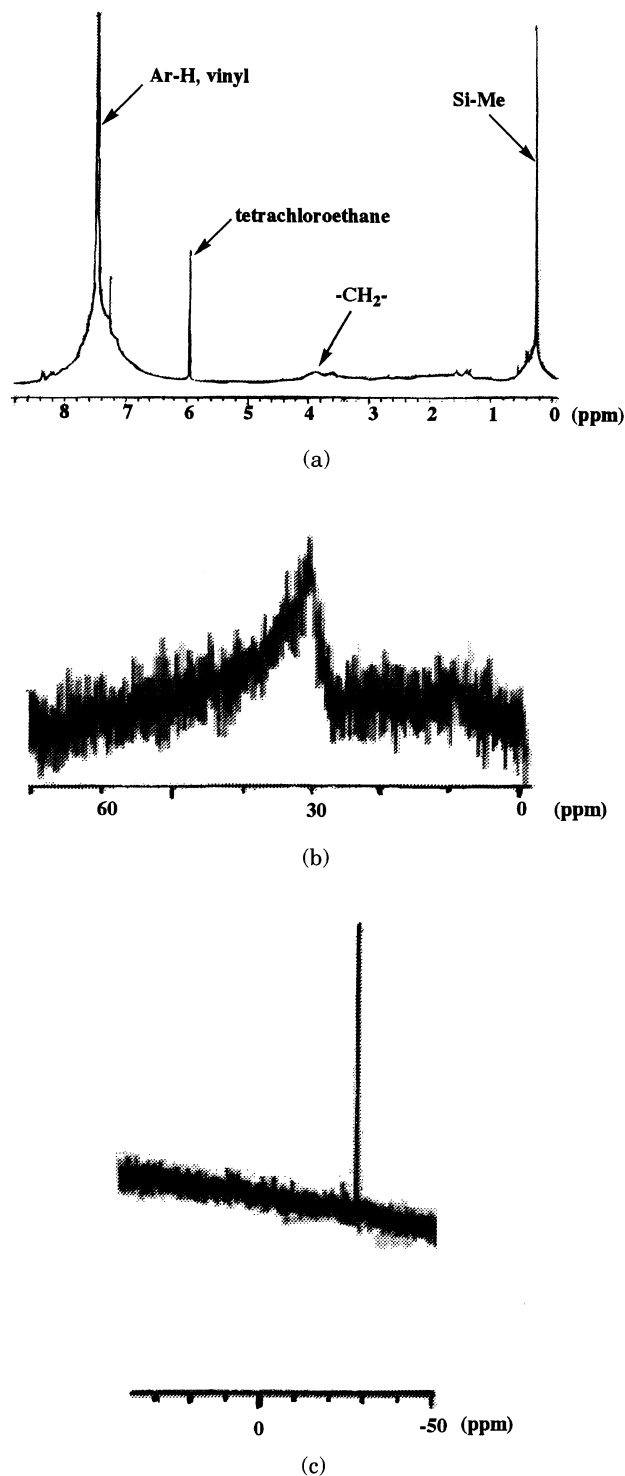
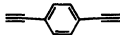
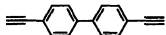
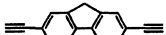
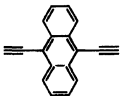
**Figure 1.** ¹H (a), ¹¹B (b), and ²⁹Si NMR (c) spectra of **4c**.

Table II. Alternating haloboration-phenylboration copolymerization between 1,2-diethynyl-1,1,2,2-tetramethyldisilane (**2**) and various diynes (**3**)^a

Diyne		1/3/2	Conc./M ^b	M _n ^c	M _w ^c	M _w /M _n ^c	Yield/% ^d
	(3a)	2.00/0.972/0.890	2.0	8400	34000	4.1	50
	(3b)	2.00/0.976/0.953	1.0	2500	4500	1.8	56
	(3c)	2.00/0.934/0.893	2.0	5700	19500	3.4	30
	(3d)	2.00/0.931/0.888	0.7	No Polymerization			

^a Reactions were carried out in tetrachloroethane at 80°C for 2 h. ^b Concentration of **1**. ^c GPC (THF) polystyrene standards. ^d Isolated yields after reprecipitation into *n*-hexane.

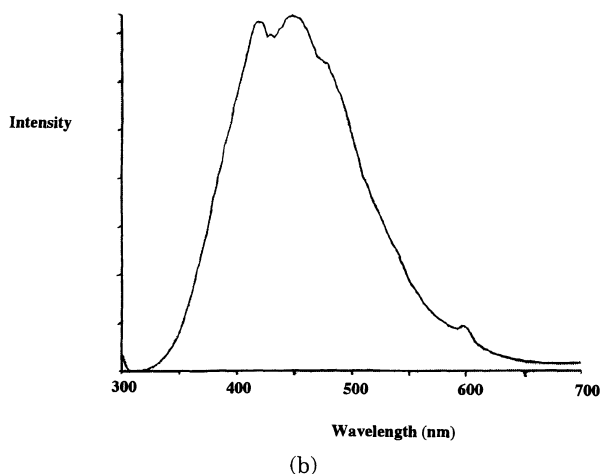
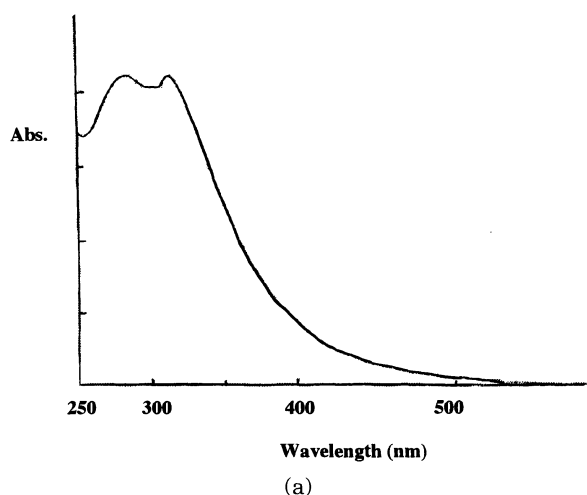


Figure 2. UV-*vis* absorption (in CHCl₃, at room temperature); (a) and PL emission (in CHCl₃, at room temperature; excited at 300 nm); (b) spectra of **4c**.

was not so effective except in **4c**, because of the presence of less planar trialkenylborane unit formed by further phenylboration reaction.

EXPERIMENTAL

Materials and Instruments

Tetrachloroethane was dried over calcium chloride

and distilled before use. Diphenylbromoborane (**1**),¹³ aromatic diynes (**3**)¹⁴ and 1,1,2,2-tetramethyl-1,2-diethynyldisilane (**2**)¹⁵ were prepared according to the reported procedures. ¹H, ¹¹B, and ²⁹Si NMR spectra were recorded in CDCl₃ on a JEOL EX-270 instrument. Gel permeation chromatographic analysis was carried out on a TOSOH G3000HXI by using THF as an eluent after calibration with polystyrene standards. IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. UV-*vis* spectra were recorded on a JASCO V-530 spectrophotometer. Fluorescence emission spectra were recorded on a Perkin-Elmer LS 50 B luminescence spectrometer.

Alternating Boration Copolymerization between **2** and **3**

Typically, the polymerization between **2** and **3c** was carried out as follows. To a tetrachloroethane solution of **3c** (103.2 mg, 0.482 mmol), 2 molar equiv of **1** (252.7 mg, 1.032 mmol) were added under nitrogen atmosphere at room temperature and the reaction mixture was stirred for 24 h (1st step; selective haloboration). From the ¹H NMR measurement, disappearance of the acetylene proton (3.13 ppm) was observed. In the 2nd step, 1 molar equiv of **2** (76.7 mg, 0.461 mmol) was added and the mixture was reacted at higher temperature (80°C) for 2 h (phenylboration polymerization). After reprecipitation into *n*-hexane, the polymer (**4c**) was obtained as a brown powder (120.5 mg, 30%). ¹H NMR (δ , ppm) 0.23 (Si-CH₃, 12H), 3.85 (CH₂, 2H), 7.45 (Ar-H, vinyl, 30H). ¹¹B NMR (δ , ppm) 30.3. ²⁹Si NMR (δ , ppm) -27.8. IR (cm⁻¹) 1600 ($\nu_{C=C}$).

4a and **4b** were similarly prepared as described for **4c**. **4a**; 251.6 mg (1.027 mmol) of **1**, 76.1 mg (0.457 mmol) of **2** and 63.0 mg (0.499 mmol) of **3a**; 178.0 mg of **4a** (50%) ¹H NMR (δ , ppm) 0.19 (Si-CH₃, 12H), 7.24 (Ar-H, vinyl, 28H). IR (cm⁻¹) 1600 ($\nu_{C=C}$). **4b**; 253.2 mg (1.033 mmol) of **1**, 81.8 mg (0.492 mmol) of **2** and 102.0 mg (0.504 mmol) of **3b**; 235.2 mg of **4b** (56%) ¹H NMR (δ , ppm) 0.25 (Si-CH₃, 12H), 7.39 (Ar-H, vinyl, 32H). IR (cm⁻¹) 1601 ($\nu_{C=C}$).

REFERENCES

1. a) M. Ishikawa and M. Kumada, *Adv. Organomet. Chem.*, **19**, 51 (1981). b) H. Sakurai, S. Tasaka, and M. Kira, *J. Am. Chem. Soc.*, **94**, 9285 (1972). c) H. Sakurai, *J. Organomet. Chem.*, **200**, 261 (1980). d) H. Shizuka, Y. Sato, Y. Ueki, M.

- Ishikawa, and M. Kumada, *J. Chem. Soc., Faraday Trans. 1*, **80**, 341 (1984).
2. a) J. Ohshita, D. Kanaya, M. Ishikawa, and T. Yamanaka, *Chem. Express.*, **5**, 489 (1990). b) J. Ohshita, D. Kanaya, M. Ishikawa, T. Koike, and T. Yamanaka, *Macromolecules*, **24**, 2106 (1991).
 3. a) P. F. van Hutten, R. E. Gill, J. K. Herrema, and G. Hadziioannou, *J. Phys. Chem.*, **99**, 3218 (1995). b) J. K. Herrema, P. F. van Hutten, R. E. Gill, J. Wildeman, R. H. Wieringa, and G. Hadziioannou, *Macromolecules*, **28**, 8102 (1995). c) M. Fang, A. Watanabe, and M. Matsuda, *Macromolecules*, **29**, 6807 (1996).
 4. M. Ishikawa, H. Z. Ni, and K. Matsusaki, *J. Polym. Sci., Polym. Lett. Ed.*, **22**, 669 (1984).
 5. M. Fang, A. Watanabe, and M. Matsuda, *J. Organomet. Chem.*, **489**, 15 (1995).
 6. K. Shiina, *J. Organomet. Chem.*, **310**, C57 (1986).
 7. a) Y. Chujo, I. Tomita, Y. Hashiguchi, H. Tanigawa, E. Ihara, and T. Saegusa, *Macromolecules*, **24**, 345 (1991). b) Y. Chujo, I. Tomita, Y. Hashiguchi, and T. Saegusa, *Macromolecules*, **25**, 33 (1992). c) Y. Chujo, I. Tomita, and T. Saegusa, *Macromolecules*, **23**, 687 (1990). (d) N. Matsumi and Y. Chujo, *Polym. Bull.*, **38**, 531 (1997).
 8. a) Y. Chujo, I. Tomita, N. Murata, H. Mauermann, and T. Saegusa, *Macromolecules*, **25**, 27 (1992). b) Y. Chujo, *ACS Symp. Ser.*, **572**, 398 (1994).
 9. N. Matsumi, K. Naka, and Y. Chujo, *J. Am. Chem. Soc.*, **120**, 5112 (1998).
 10. N. Matsumi, K. Kotera, K. Naka, and Y. Chujo, *Macromolecules*, **31**, 3155 (1998). As reported in ref 11, haloboration toward aromatic acetylene takes place under mild conditions, while the phenylboration requires severe reaction conditions. The high degree of the unit alternation was confirmed by ¹¹B NMR measurements.
 11. M. F. Lappert and B. Prokai, *J. Organomet. Chem.*, **1**, 384 (1964).
 12. The peak at 315 nm disappeared after air-oxidation of the disilanylene unit. After the air-oxidation, PL intensity was fairly decreased.
 13. W. Haubold, J. Herdlte, W. Gollinger, and W. Einholz, *J. Organomet. Chem.*, **315**, 1 (1986).
 14. S. Takahashi, Y. Kuroyama, K. Sonogashira, and N. Hagihara, *Synthesis*, 627 (1980).
 15. T. Iwahara, S. Hayase, and R. West, *Macromolecules*, **23**, 1298 (1990).