

Synthesis and Properties of Oligomers Containing 3-Triethylsilyl-1-silacyclopent-3-ene and Borane Derivatives via Polyaddition Reaction

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Polyaddition reactions of 1,1-diethynyl-3-triethylsilyl-1-silacyclopent-3-ene with several organoborane derivatives have afforded the oligomeric materials containing organosilacyclic group and organoboron moiety along the oligomer main chains. All of these materials are soluble in THF as well as chloroform, and their molecular weights are in the range of 1,990/1,190-21,950/7,050 (M_w/M_n) with the polydispersity indexes of 1.67-3.43. The prepared oligomers are characterized by several spectroscopic methods such as ^1H , ^{13}C , ^{29}Si , ^{11}B NMR and FTIR spectra along with elemental analysis. FTIR spectra of all the oligomers show that the new strong C=C stretching frequencies appear at 1599-1712 cm^{-1} , in particular. The UV-vis absorption spectra of the materials in THF solution exhibit the strong absorption bands at the λ_{max} of 268-275 nm. The oligomeric materials show that the strong excitation peaks appear at the λ_{max} of 255-279 nm and the strong fluorescence emission bands at the λ_{max} of 306-370 nm. All the spectroscopic data suggest that the obtained materials contain both the organoboron π -conjugation moiety of C=C-B-C=C and the organosilacyclic group of 3-triethylsilyl-1-silacyclopent-3-ene along the oligomer main chains. The oligomers are thermally stable up to 162-200 $^\circ\text{C}$ under nitrogen.

Key Words : Boron-bearing oligocarbosilanes, 3-Triethylsilyl-1-silacyclopent-3-ene. Boration polymerization, Electronic and thermal properties

Introduction

Polycarbosilanes bearing π -conjugated groups in the polymer main chains have attracted a great deal of recent attention as their potential applications such as photonic, electronic, and ceramic materials.¹ In this sense, considerable research effort has been devoted to develop new polycarbosilanes containing conjugation moieties. For example, diacetylene-containing polycarbosilanes showed the conductivity of 10^{-5} ~ 10^{-3} S/cm when doped with FeCl_3 , and pyrolysis of the polycarbosilanes in inert atmosphere resulted in a β -SiC ceramic materials in high yield.^{2,3} Recently, a series of oligomers composed of alternating 2,5-bis(ethynylendimethylsilylene)thienylene and arylene units in the main chain have been prepared by a cross-coupling reaction.⁴ We also reported the preparation and excited-state energy dynamics of polycarbosilanes as well as polycarbogermanes containing 1,4-bis(thiophene or phenylene)buta-1,3-diyne in the polymer backbone.⁵⁻⁸

Organosilacyclic compounds such as 1-silacyclopent-3-enes have also received much concern in the field of organosilicon chemistry.⁹⁻¹¹ For instance, 1,1-dimethyl-1-silacyclopent-3-ene undergoes anionic ring-opening polymerization by reaction with alkylolithium and hexamethylphosphoramide (HMPA) at -78 $^\circ\text{C}$ to yield polycarbosilane such as poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene).¹² Recently, we also reported the preparation of polycarbosilanes containing diacetylenic and organosilacyclic groups along the polymer main chain such as poly(1,1-diethynyl-1-

silacyclopent-3-enes and -1-silacyclobutane) using oxidative coupling polymerization and their electronic properties.¹³

Organoborons are useful reagents for the preparation of a variety of functional compounds in organic synthesis.¹⁴ From this point of view, polymeric homologues of organoboron compounds may have a potential to exhibit unique properties as novel polymeric materials. Meanwhile, Chujo have reported the various preparations of organoboron polymers consisting of C-B bonds in the main chain by several polyaddition reactions between organic diynes and borane derivatives.^{15,16} Chujo have also reported that a series of π -conjugated organoboron polymer were synthesized by polyaddition using boration reaction and the extension of the π -conjugation length via the boron atom was observed in the organoboron main chain.^{17,18} However, boration polymerizations between organosilicon diynes and borane derivatives have scarcely been reported.

Since we have successfully prepared diyne-containing silacyclic monomer such as 1,1-diethynyl-3-triethylsilyl-1-silacyclopent-3-ene and applied to a coupling polymerization,^{13,19} we have also been interested in the preparation and properties of polycarbosilanes containing organoboron group along the polymer backbone by utilizing boration polymerization of 1,1-diethynyl-1-silacyclopentene derivatives. Furthermore, the organoborane-bearing polycarbosilane materials synthesized can be expected to include a novel π -conjugated moiety of C=C-B-C=C and the organosilacyclic group of 3-triethylsilyl-1-silacyclopent-3-ene along the polymer main chains. Herein, we wish to report the polyaddition reaction of 1,1-diethynyl-3-triethylsilyl-1-silacyclopent-3-ene with several organoborane derivatives.

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We also describe the electronic and thermal properties of the prepared oligocarbosilanes containing organoborane group.

Results and Discussion

Synthesis of Oligomers. 1,1-Diethynyl-3-triethylsilyl-1-silacyclopent-3-ene (**1**) was prepared by ethynylation reaction of 1,1-dichloro-3-triethylsilyl-1-silacyclopent-3-ene with ethynylmagnesium chloride as the previously reported method by our research group.¹³ The monomer **1** was characterized using several spectroscopic methods such as ¹H, ¹³C, and ²⁹Si NMR as well as IR spectra. In the IR spectrum of **1**, the characteristic acetylenic C≡C and ring vinyl C=C stretching frequencies are observed at 2050 and 1570 cm⁻¹, respectively. The ¹H NMR spectrum of **1** shows that the singlet resonance appears at 2.51 ppm for ethynyl (C≡CH) protons and the triplet at 6.15 ppm for vinyl (C=CH) proton on the ring. In the ¹³C NMR spectrum of **1**, eight carbon peaks appear at 2.63, 7.29, 20.87, 21.16, 84.08, 95.74, 139.37, and 141.34 ppm, where the resonances assigned to the ethynyl carbons are observed at 84.08 and 95.74 ppm, and ones assigned to the vinyl carbons at 139.37 and 141.34 ppm. The ²⁹Si NMR spectrum of **1** exhibits that two silicon peaks appear at 0.07 and -28.72 ppm.

Boration polymerizations between organic diynes and various borane derivatives such as haloborane, alkylborane, and phenylborane have been extensively reported to yield π -conjugated organoboron polymers by Chujo research team.¹⁵⁻¹⁸ We tried the same polymerization technique by utilizing the functionality of diethynyl-containing compound **1** as novel monomer. The polyaddition reactions of **1** with several borane derivatives **2a-f** have been carried out to afford the novel materials **3a-f** in moderate yields, respectively, which contain C=C-B-C=C moiety as well as organosilacyclic groups in the polymer main chain, as shown in Scheme 1.

The boron-bearing polycarbosilanes **3a-f** obtained as dark brown powder or yellowish viscous gel are soluble in usual organic solvents such as CHCl₃ and THF. By running gel permeation chromatography (GPC) we measured molecular weights of **3a-f** which turned out to be oligomers with

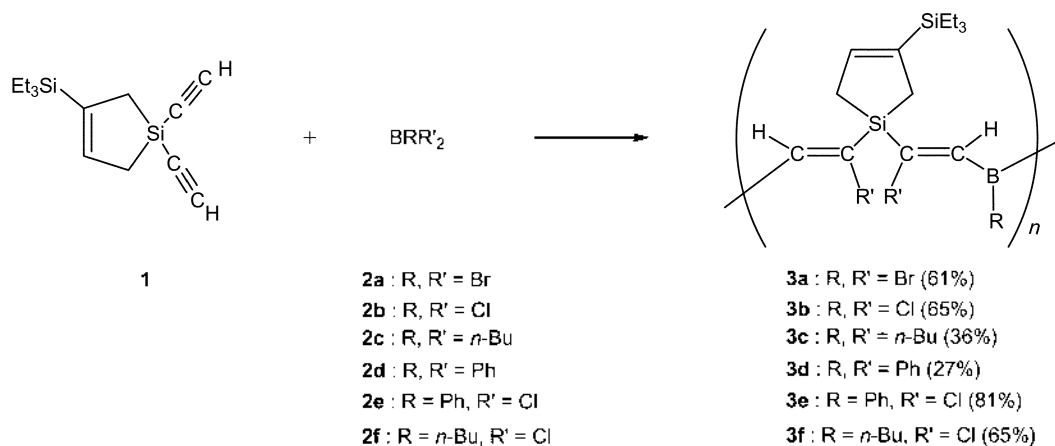
molecular weights ranging 1,990/1,190-21,950/7,050 (M_w/M_n) and to have broad molecular weight distributions with the polydispersity indexes of 1.67-3.43, as shown in Table 1. The broad molecular weights distributions might be ascribed to the copolymerization technique applied in this research by using the two different types of monomers.²⁰

We tried to characterize the oligomers **3a-f** by several spectroscopic methods. The structures of **3a-f** were supported by ¹H, ¹³C, ²⁹Si, ¹¹B NMR, and IR spectra as well as elemental analysis. Some selected spectral properties of the oligomers **3a-f** are summarized in Table 1.

In the FTIR spectra of all the oligomers **3a-f**, the characteristic C≡C stretching frequency of **1** at 2050 cm⁻¹ almost disappeared and the C=C stretching frequencies in the silacyclopentene ring of **1** remained intact at 1570-1602 cm⁻¹, while the new strong C=C stretching frequencies appeared at 1599-1712 cm⁻¹, indicating that the C=C bonds along the oligomer backbones were newly formed during polyaddition reactions.^{21,22}

In the ¹H NMR spectra of **3a-f** in CDCl₃, ethynyl protons of **1** at 2.51 ppm disappeared and the vinyl proton on the silacyclopentene ring of **1** remained intact at 6.14-6.50 ppm, while the new vinyl protons appeared at 5.28-5.90 ppm, which is consistent with the proposed structure of oligomers **3a-f**. The ¹³C NMR of **3a-f** show that the ethynyl C≡C carbon resonances of **1** at 84.08 and 95.74 ppm disappeared and the vinyl C=C carbon peaks in the silacyclopentene ring of **1** remained intact at 130.87-141.71 ppm, while the new vinyl C=C carbon resonances appeared at 128.77-140.00 ppm, which is also consistent with the proposed structure of oligomers **3a-f**. The structures of oligomers **3a-f** were also confirmed by the ²⁹Si and ¹¹B NMR spectra of all the prepared oligomers, as shown in Table 1. In the case of the polyadditions of dichlorophenylborane (**2e**) and dichlorobutylborane (**2f**), haloboration reactions occurred to yield corresponding oligomers **3e** and **3f**, respectively, due to the higher reactivity of halogen atom such as chlorine than that of phenyl or butyl groups.²³

Properties of Oligomers. All oligomers **3a-f** were soluble in common organic solvents such as THF and chloroform.

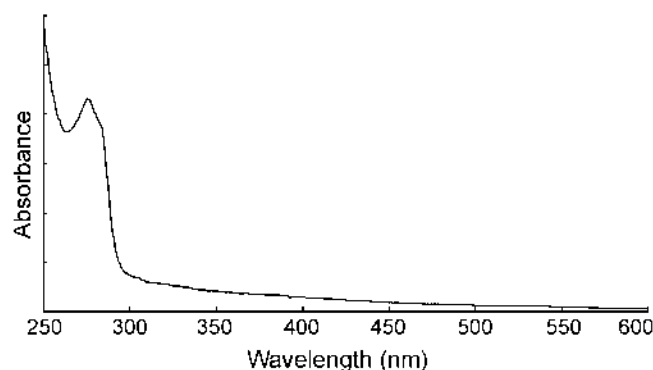


Scheme 1

Table 1. Selected Properties of the Oligomers **3a-f**

| Oligomer | M_w/M_n^a (PDI) | ^{29}Si NMR ^b δ (ppm) | ^{11}B NMR ^b δ (ppm) | IR ^c $\nu_{\text{C}=\text{C}}$ (cm^{-1}) | Absorption ^d λ_{max} (nm) | Excitation ^e λ_{max} (nm) | Fluorescence ^f λ_{max} (nm) | TGA ^g |
|-----------|------------------------|---|--|---|--|--|--|------------------|
| 3a | 4.290/1.250 (3.43) | 0.03, 19.09 | 4.04 | 1712 | 271 | 277 | 310 | 68 |
| 3b | 4.140/1.260 (3.29) | 0.01, 23.12 | -3.78 | 1710 | 269 | 277 | 311 | 83 |
| 3c | 7.180/2.100 (3.42) | -0.45, -21.95 | -3.80 | 1711 | 269 | 276 | 306 | 87 |
| 3d | 21.950/7.050 (3.11) | -0.45, -5.85 | 12.29 | 1599 | 275 | 279 | 326 | 66 |
| 3e | 1.990/1.190 (1.67) | 0.00, 8.87 | -3.96 | 1711 | 269 | 272 | 344 | 76 |
| 3f | 3.720/1.920 (1.93) | 0.00, 19.74 | -2.49 | 1709 | 268 | 255 | 370 | 64 |

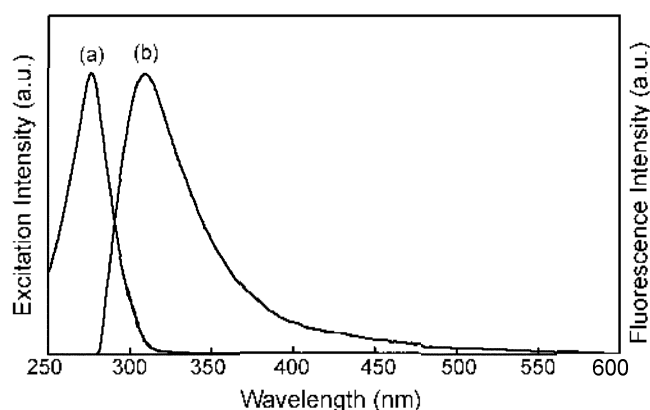
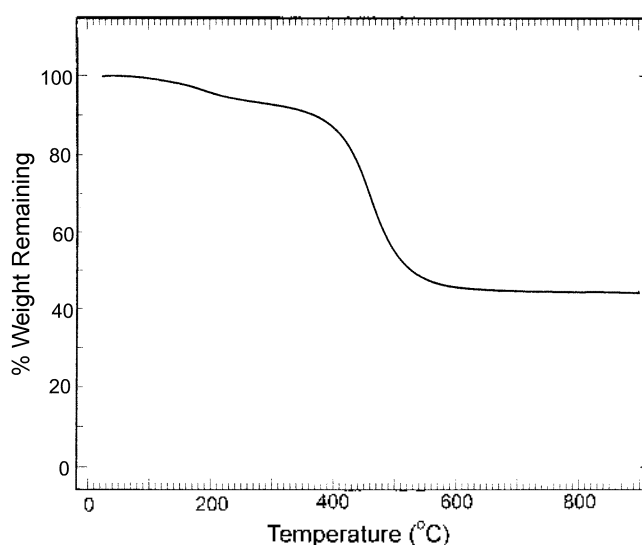
^aDetermined by GPC in THF relative to polystyrene standards. M_w/M_n = Polydispersity index (PDI). ^bIn CDCl_3 . ^cC=C bond stretching in the oligomer main chain and measured by neat or DRIFT method. ^dUV-vis absorption in THF. ^eDetection wavelength at 310 or 340 nm in THF. ^fExcitation wavelength at 275 nm in THF. ^g% Weight remaining at 400 °C under nitrogen.

**Figure 1.** UV-vis absorption spectrum of the oligomer **3a** in THF.

The solubility of **3a-f** allows us to perform studies on the properties in solution. The typical UV-vis absorption spectrum of **3a** in THF has been shown in Figure 1, where the maximum absorption band at 271 nm ($\epsilon = 1.43 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) with broad and weak tailing between 264 and 571 nm is observed. For oligomers **3a-f** the strong absorption bands are observed at the λ_{max} of 268–275 nm, as listed in Table 1, which are probably due to the presence of C=C-B-C=C chromophore along the oligomer backbone.²³

The typical excitation spectrum for **3a** at the detection wavelength of 310 nm in THF exhibits the strong excitation band at the λ_{max} of 277 nm, as shown in Figure 2. As outlined in Table 1, the excitation spectra of **3b-f** at the detection wavelength of 310 or 340 nm in THF show that the strong excitation peaks appear at the λ_{max} of 255–279 nm, which are probably attributable to C=C-B-C=C group along the oligomer chain.

The typical fluorescence emission spectrum of **3a** at the excitation wavelength of 275 nm also exhibits the strong emission peak at the λ_{max} of 310 nm with the broad emission band of 281–556 nm, as shown in Figure 2. As indicated in Table 1, the fluorescence emission spectra of **3b-f** at the excitation wavelength of 275 nm in THF reveal that the

**Figure 2.** Excitation (line (a), $\lambda_{\text{det}} = 310 \text{ nm}$) and fluorescence (line (b), $\lambda_{\text{ex}} = 275 \text{ nm}$) spectra of the oligomer **3a** in THF.**Figure 3.** TGA thermogram of the oligomer **3c** under nitrogen.

strong fluorescence emission peaks appear at the λ_{max} of 306–370 nm, which are probably ascribed to the fluorophore

of C=C-B-C=C along the oligomer chain.²⁴

Those strong absorption, excitation, and fluorescence bands of **3a-f** in their corresponding spectra imply that all the prepared oligomers contain the partially delocalized π -conjugation groups of C=C-B-C=C as well as organosilacyclic group through the oligomer main chains.

The thermal stabilities of oligomers **3a-f** under nitrogen atmosphere were determined by thermogravimetric analysis (TGA) with a heating rate of 10 °C/min. The typical TGA thermogram of **3c** was shown in Figure 3. **3c** is stable up to 200 °C with weight loss of 4% only. Rapid weight loss of 46% of the initial weight occurs between 300 and 600 °C. When **3c** is heated to 900 °C, 55% of the initial weight of **3c** is lost, and about 45% char yield is observed.

Normally, the oligomers **3a-f** are thermally stable up to 162-200 °C with weight loss of only 2-10%. Rapid weight loss of 16-68% of the initial weight occurs between 300 and 600 °C. When the oligomers are heated to 900 °C by the heating rate of 10 °C/min, residues of 21-62% remain. Usually, about 64-87% of the initial polymer weights remain at 400 °C under nitrogen atmosphere, as indicated in Table 1.

Conclusion

We have successfully prepared the oligomeric materials which contain the partially delocalized π -conjugation moiety of C=C-B-C=C as well as organosilacyclic group along the oligomer main chains by the polyaddition reaction of 1,1-diethynyl-3-triethylsilyl-1-silacyclopent-3-ene with several organoborane derivatives. All of these materials are soluble in THF and chloroform, and turned out to be oligomers with molecular weights in the range of 1,990/1,190-21,950/7,050 (M_w/M_n) with the polydispersity indexes of 1.67-3.43. The FTIR spectra of all the oligomers indicate that C=C bonds along the oligomer backbones were newly formed during the polymerization. Structures of the oligomers were also confirmed by several other spectroscopic methods such as ¹H, ¹³C, ²⁹Si, and ¹¹B NMR spectra as well as elemental analysis. The oligomers are thermally stable up to 162-200 °C under nitrogen. The UV-vis absorption spectra exhibit the strong absorption bands at the λ_{max} of 268-275 nm. The excitation spectra show that the strong excitation peaks appear at the λ_{max} of 255-279 nm. The fluorescence emission spectra show that the strong emission peaks are observed at the λ_{max} in the range of 306-370 nm. All the spectroscopic data strongly suggest that the obtained oligomeric materials contain both the organoboron-bearing π -conjugated moiety of C=C-B-C=C and the organosilacyclic group of 3-triethylsilyl-1-silacyclopent-3-ene along the oligomer main chains.

Experimental Section

General Procedures. All chemicals were purchased from Aldrich Chemicals Inc. All solvents were purified prior to use according to standard literature methods: tetrahydrofuran (THF), *n*-hexane, and diethyl ether were distilled from

sodium benzophenone ketyl.²⁵ All glassware was assembled and was then flame-dried while being swept with argon. Reactions were monitored by Hewlett Packard 5890II analytical GLC equipped with HP-1 capillary column (0.53 mm \times 30 m) coated with cross-linked methyl silicon gum and with flame ionization detector (FID). The column was deactivated immediately before use by injection of 50 μ L of hexamethyldisilazane. ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy were performed on a Bruker DRX Avance 400 MHz FT-NMR spectrometers using CDCl₃ as solvent. Chemical shifts were measured using tetramethylsilane as internal standard or the residual proton signal of the solvent as standard. ²⁹Si and ¹¹B nuclear magnetic resonance (NMR) spectroscopy were performed on a Varian Unity INOVA 500 MHz FT-NMR spectrometer using CDCl₃ as solvent at the Korea Basic Science Institute. IR spectra were recorded by a Shimadzu IR 430 spectrometer or a Bruker IFS-48 FT-IR spectrometer using DRIFT method. UV-vis absorption spectra were obtained on a Hewlett Packard 8453 spectrophotometer. Excitation and fluorescence emission spectra were obtained on a Hitachi F-4500 fluorescence spectrophotometer. Gel permeation chromatography (GPC) analyses were performed on a Waters model 510 system with a Waters Styragel HR 3 column and refractive index detector at 25 °C. The eluent was THF at a flow rate of 1.0 mL/min. The calibration was made with a series of monodispersed polystyrene standards: M_p 580, 3250, 10100, and 28500 whose M_w/M_n are less than 1.2. Thermogravimetric analysis (TGA) of polymer samples was performed on a TGA-50 Shimadzu thermal analysis system. The temperature was increased at the heating rate of 10 °C/min from room temperature to 900 °C with nitrogen flow rate of 20 mL/min. Elemental analyses were performed on a Fisons EA 1108 elemental analyzer.

1,1-Diethynyl-3-triethylsilyl-1-silacyclopent-3-ene (1) was prepared by the previously reported methods.^{13,19}

Polyaddition Reactions of 1 with Borane Derivatives (2). A general procedure for polyaddition reactions of **1** with **2** is described as follows: In a flame dried 50 mL Schlenk flask with rubber septum, boron tribromide (**2a**) (1.0 M/dichloromethane, 3.73 mL, 3.73 mmol) was placed using a syringe under argon atmosphere. The flask was cooled to -78 °C using a dry ice/acetone bath, and then **1** (0.92 g, 3.37 mmol) was added with vigorous stirring. The reaction mixture was stirred for 2 h and allowed to warm to room temperature with well stirring. The crude oligomer was precipitated by addition of dry *n*-pentane or methanol and dried under reduced pressure. The oligomeric material **3a**, 1.15 g, 61% was obtained as a dark brown solid with M_w/M_n of 4.290/1,250 (polydispersity index, PDI = 3.43). ¹H NMR (THF-*d*₆, 400 MHz): δ 0.62 (m, 6H), 0.95 (m, 9H), 1.29 (s, 4H), 5.77 (s, 2H), 6.50 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 2.63, 6.77, 22.96, 23.60, 128.77, 129.18, 130.87, 132.35; ²⁹Si NMR (CDCl₃, 99 MHz): δ 0.03, 19.09; ¹¹B NMR (CDCl₃, 160 MHz): δ 4.04; IR (KBr, DRIFTS): ν 3219, 2965, 2911, 2877, 2261, 2043, 1712 (C=C), 1602, 1413, 1368, 1235, 1195, 1086, 1008, 882, 846, 812, 743,

669 cm^{-1} ; UV-vis (THF): λ_{max} nm (ϵ) 271 (1.43×10^5). Anal. Calcd for $(\text{C}_{14}\text{H}_{22}\text{Si}_2\text{BBr}_3)_n$: C, 33.83; H, 4.46. Found: C, 33.33; H, 4.49. The excitation and fluorescence emission spectra in THF solution as well as TGA thermogram are described in Result and Discussion.

A dark brown solid **3b** (0.95 g, 65%) was obtained from **1** (1.00 g, 4.06 mmol) and boron trichloride (**2b**) (1.0 M/dichloromethane, 4.06 mL, 4.06 mmol): $M_w/M_n = 4.140/1,260$ (PDI = 3.29); ^1H NMR (CDCl_3 , 400 MHz): δ 0.59-0.61 (m, 6H), 0.86-0.99 (m, 9H), 1.57 (s, 2H), 1.85-1.87 (m, 2H), 5.28 (s, 2H), 6.25 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 2.68, 6.79, 22.68, 25.59, 129.25, 130.63, 131.38, 133.13; ^{29}Si NMR (CDCl_3 , 99 MHz): δ 0.01, 23.12; ^{11}B NMR (CDCl_3 , 160 MHz): δ -3.78; IR (KBr, DRIFTS): ν 3286, 2953, 2909, 2876, 2732, 2367, 2042, 1710 (C=C), 1573, 1413, 1357, 1236, 1147, 1089, 1006, 867, 830, 719 cm^{-1} ; UV-vis (THF): λ_{max} nm (ϵ) 269 (7.72×10^4). Anal. Calcd for $(\text{C}_{14}\text{H}_{22}\text{Si}_2\text{BCl}_3)_n$: C, 46.23; H, 6.10. Found: C, 45.31; H, 6.16. The excitation and fluorescence emission spectra in THF solution as well as TGA thermogram are described in Result and Discussion.

Oligomeric Materials 3c-f were prepared in the similar manner to that described for **3a**, except that the reaction mixture was stirred at room temperature for 1h and then warmed to reflux for overnight. A reddish yellow viscous gel **3c** (0.63 g, 36%) was obtained from **1** (1.00 g, 4.06 mmol) and tributylborane (**2c**) (1.0 M/diethyl ether, 4.06 mL, 4.06 mmol): $M_w/M_n = 7,180/2,100$ (PDI = 3.42); ^1H NMR (CDCl_3 , 400 MHz): δ 0.59 (m, 8H), 0.88 (m, 19H), 1.21-1.25 (m, 9H), 1.45-1.70 (br, 8H), 1.86 (m, 2H), 5.30 (s, 2H), 6.14 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 2.74, 5.87, 6.74, 7.43, 14.00, 20.41, 22.56, 25.53, 26.88, 29.65, 31.88, 140.35, 140.52, 141.50, 141.71; ^{29}Si NMR (CDCl_3 , 99 MHz): δ -0.45, 21.95; ^{11}B NMR (CDCl_3 , 160 MHz): δ -3.80; IR (neat): ν 3291, 2955, 2874, 2732, 2037, 1711 (C=C), 1574, 1461, 1414, 1377, 1262, 1237, 1092, 1016, 861, 801, 716 cm^{-1} ; UV-vis (THF): λ_{max} nm (ϵ) 269 (1.62×10^5). Anal. Calcd for $(\text{C}_{26}\text{H}_{40}\text{Si}_2\text{B})_n$: C, 72.85; H, 11.52. Found: C, 71.66; H, 11.40. The excitation and fluorescence emission spectra in THF solution as well as TGA thermogram are described in Result and Discussion.

A pale yellow viscous gel **3d** (0.55 g, 27%) was obtained from **1** (1.00 g, 4.06 mmol) and triphenylborane (**2d**) (0.25 M/THF, 16.26 mL, 4.06 mmol): $M_w/M_n = 21,950/7,050$ (PDI = 3.11); ^1H NMR (CDCl_3 , 400 MHz): δ 0.88 (q, 6H), 1.26 (t, 9H), 1.68 (s, 2H), 2.04 (s, 2H), 5.28 (s, 2H), 6.21 (m, 1H), 7.48-7.72 (m, 15H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 2.93, 7.32, 20.55, 21.06, 122.28, 122.47, 125.50, 135.68, 139.42, 139.78, 140.22, 140.98, 141.48, 141.61, 141.78; ^{29}Si NMR (CDCl_3 , 99 MHz): δ -0.45, -5.85; ^{11}B NMR (CDCl_3 , 160 MHz): δ 12.29; IR (neat): ν 3300, 2900, 2050, 1599 (C=C), 1570, 1460, 1440, 1410, 1390, 1380, 1340, 1280, 1240, 1150, 1050, 970, 950, 850, 830, 780, 720, 670 cm^{-1} ; UV-vis (THF): λ_{max} nm (ϵ) 275 (1.12×10^4). Anal. Calcd for $(\text{C}_{32}\text{H}_{37}\text{Si}_2\text{B})_n$: C, 78.66; H, 7.63. Found: C, 79.21; H, 7.65. The excitation and fluorescence emission spectra in THF solution as well as TGA thermogram are described in Result

and Discussion.

A dark brown powder **3e** (1.33 g, 81%) was obtained from **1** (1.00 g, 4.06 mmol) and dichlorophenylborane (**2e**) (0.65 g, 4.06 mmol): $M_w/M_n = 1,990/1,190$ (PDI = 1.67); ^1H NMR (CDCl_3 , 400 MHz): δ 0.55 (m, 6H), 0.90-0.99 (m, 9H), 1.58 (s, 2H), 1.88 (s, 2H), 5.90 (br, 2H), 6.20 (m, 1H), 7.42-7.78 (m, 5H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 2.81, 6.80, 21.25, 26.95, 125.51, 127.97, 128.31, 129.61, 130.14, 130.27, 132.70, 135.63; ^{29}Si NMR (CDCl_3 , 99 MHz): δ 0.00, 8.87; ^{11}B NMR (CDCl_3 , 160 MHz): δ -3.96; IR (KBr, DRIFTS): ν 3213, 2953, 2909, 2876, 2359, 2261, 2039, 1948, 1894, 1710 (C=C), 1601, 1573, 1461, 1414, 1335, 1237, 1237, 1196, 1148, 1098, 1071, 1007, 818, 719 cm^{-1} ; UV-vis (THF): λ_{max} nm (ϵ) 269 (1.04×10^5). Anal. Calcd for $(\text{C}_{20}\text{H}_{27}\text{Si}_2\text{BCl}_2)_n$: C, 59.27; H, 6.71. Found: C, 60.18; H, 6.87. The excitation and fluorescence emission spectra in THF solution as well as TGA thermogram are described in Result and Discussion.

A dark brown viscous gel **3f** (1.01 g, 65%) was obtained from **1** (1.00 g, 4.06 mmol) and butyldichloroborane (**2f**) (1.0 M/hexane, 4.06 mL, 4.06 mmol): $M_w/M_n = 3,720/1,910$ (PDI = 1.95); ^1H NMR (CDCl_3 , 400 MHz): δ 0.59 (q, 6H), 0.88 (t, 9H), 1.20-1.25 (m, 9H), 1.55 (d, 2H), 1.86 (t, 2H), 5.30 (s, 2H), 6.16 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 2.66, 6.61, 7.46, 13.97, 22.68, 26.96, 29.70, 30.29, 139.63, 140.00, 141.04, 141.42; ^{29}Si NMR (CDCl_3 , 99 MHz): δ 0.00, 19.74; ^{11}B NMR (CDCl_3 , 160 MHz): δ -2.49; IR (neat): ν 3290, 2953, 2911, 2875, 2733, 2359, 2150, 2041, 1709 (C=C), 1574, 1460, 1415, 1364, 1260, 1089, 1008, 859, 805, 722 cm^{-1} ; UV-vis (THF): λ_{max} nm (ϵ) 268 (7.65×10^4). Anal. Calcd for $(\text{C}_{18}\text{H}_{31}\text{Si}_2\text{BCl}_2)_n$: C, 56.11; H, 8.11. Found: C, 57.20; H, 8.36. The excitation and fluorescence emission spectra in THF solution as well as TGA thermogram are described in Result and Discussion.

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