

Polyboration Reaction of 1,1-Diethynyl-1-silacyclopent-3-ene with Boranes

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Conjugated polycarbosilanes through polymer backbone have received much attention for their potential applications as electronic and ceramic materials.¹ In this sense, considerable research efforts have been devoted to develop new polycarbosilanes containing novel conjugation moieties. Poly[(silylene)diacetylene] polymers showed conductivity values in the range 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 Conjugated polycarbosilanes bearing arylethylene or acetylene-linked dithienosilole have been prepared and their electronic properties were also reported.³ Oligomeric materials composed of alternating 2,5-bis(ethynyl)dimethylsilylene)thienylene and arylene units in the main chain have been prepared by a cross-coupling reaction.⁴ We have also reported the preparation and excited-state energy dynamics of polycarbosilanes containing 1,4-bis(thiophene or phenylene)buta-1,3-diyne in the polymer backbone.⁵ Organosilacyclic compounds such as 1-silacyclopent-3-enes have received much concern in organosilicon chemistry.⁶ 1,1-Dimethyl-1-silacyclopent-3-ene undergoes anionic ring-opening reaction to give poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene).⁷ Recently, we 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 1,1-diethynyl-1-silacyclobutane) using oxidative coupling polymerization and their electronic properties.⁸ Organoborons are useful reagents for the preparation of a variety of functional compounds in organic synthesis.⁹ Chujo *et al.* have reported that various π -conjugated organoboron polymers consisting of C-B bonds in the main chain were able to be synthesized by several polyaddition reactions between organic diynes and borane derivatives.¹⁰

However, boration polymerizations between organosilicon diynes and borane derivatives have been scarcely reported. Very recently, we have demonstrated the boration polymerizations between 1,1-diethynyl-3-triethylsilyl-1-silacyclopent-3-ene and several borane derivatives.¹¹ Since we have successfully prepared 1,1-diethynyl-1-silacyclopent-3-ene as novel diyne-containing silacyclic monomer,^{8,12} we have decided to extend this polyaddition technique to the preparation of polycarbosilanes containing silacyclopentene and organoboron groups along the polymer backbone by utilizing 1,1-diethynyl-1-silacyclopent-3-ene. Furthermore, the synthesized organoborane-bearing polycarbosilanes can

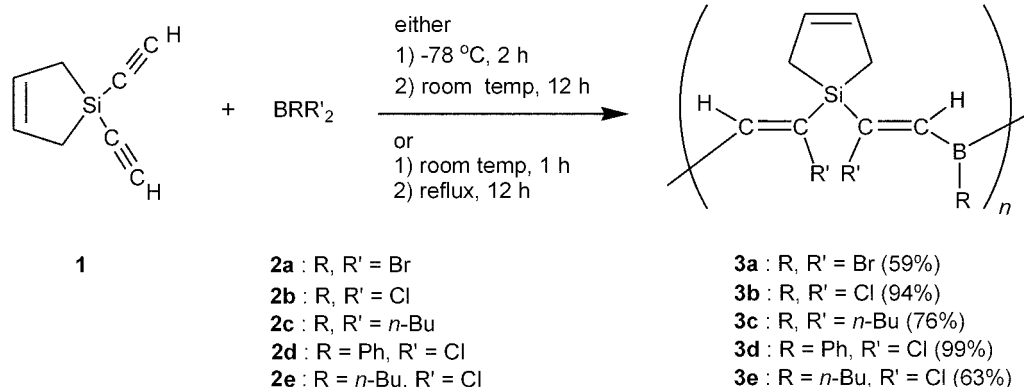
be expected to include a novel π -conjugated moiety of C=C-B-C=C and the organosilacyclic group of silacyclopent-3-ene along the polymer main chains. Here, we now report the polyboration reaction of 1,1-diethynyl-1-silacyclopent-3-ene with several organoborane derivatives along with the electronic and thermal properties of the obtained carbosilane materials. In particular, the fluorescence emission maxima of the prepared oligomers containing 1-silacyclopent-3-enes and boranes were observed at the range of 310–415 nm, whereas π -conjugated organoboron polymers containing heteroaromatic monomer such as thiophene or pyridine and mesitylborane showed those emission maxima at the visible region of 416–593 nm.^{11,13}

Results and Discussion

Synthesis of Oligomers. 1,1-Diethynyl-1-silacyclopent-3-ene (**1**) was synthesized by the reaction of 1,1-dichloro-1-silacyclopent-3-ene with ethynylmagnesium chloride according to the previous method reported by our research group.⁸ The monomer **1** was characterized using several spectroscopic methods such as ^1H , ^{13}C , and ^{29}Si NMR as well as IR spectroscopy. In the IR spectrum of **1**, the characteristic acetylenic C \equiv C and ring vinyl C=C stretching frequencies are observed at 2040 and 1606 cm^{-1} , respectively. In the ^1H NMR spectrum of **1**, the singlet resonance appears at 2.56 ppm for ethynyl (C \equiv CH) protons and the triplet at 5.91 ppm for vinyl (C=CH) proton on the ring. In the ^{13}C NMR spectrum of **1**, four carbon peaks appear at 18.11, 84.12, 96.26, and 130.14 ppm, where the resonances assigned to the ethynyl carbons are observed at 84.12 and 96.26 ppm, and one assigned to the vinyl carbons at 130.14 ppm. In the ^{29}Si NMR spectrum of **1**, silicon peak appears at -29.78 ppm.

The polyaddition reactions of **1** with several borane derivatives **2a-e** were carried out to give the novel materials **3a-e** in moderate yields, respectively, which contain C=C-B-C=C moiety and organosilacyclic group in the polymer main chain, as shown in Scheme 1. These boration reactions proceed selectively in the manner of *cis* addition.^{10a,14}

The boron-bearing polycarbosilanes **3a-e** obtained as dark brown powder or yellowish viscous gel were found to be soluble in common organic solvents such as CHCl_3 and THF. By running gel permeation chromatography (GPC) we measured average molecular weights of **3a-e** which turned out to be oligomers with average molecular weights ranging



Scheme 1

1,820/1,370-13,410/7,480 (M_w/M_n) and to have broad molecular weight distributions with the polydispersity indexes of 1.18-3.50, as summarized in Table 1. The broad molecular weights distributions might be attributed to the copolymerization technique applied in this research by using the two different types of monomers.¹⁵

The structures of **3a-e** were confirmed by ^1H , ^{13}C , ^{29}Si , ^{11}B NMR, and IR spectra along with elemental analysis. Some selected spectral properties of the oligomers **3a-e** are outlined in Table 1.

In the FTIR spectra of all the oligomers **3a-e**, the characteristic $\text{C}\equiv\text{C}$ stretching frequency of **1** at 2040 cm^{-1} almost disappeared and the $\text{C}=\text{C}$ stretching frequencies in the silacyclopentene ring of **1** remained intact at $1602\text{-}1611\text{ cm}^{-1}$, while the new strong $\text{C}=\text{C}$ stretching frequencies appeared at $1692\text{-}1714\text{ cm}^{-1}$, which indicates that the $\text{C}=\text{C}$ bonds along the oligomer backbones were newly formed during polyaddition reactions.¹⁶

In the ^1H NMR spectra of **3a-e**, the ethynyl protons of **1** at 2.56 ppm disappeared and the vinyl proton on the silacyclopentene ring of **1** remained intact at 5.61-5.94 ppm, while the new vinyl protons appeared at 4.62-5.04 ppm, which suggests that the structures of oligomers **3a-e** are consistent with the proposed ones as shown in Scheme 1. The ^{13}C NMR of **3a-e** show that the ethynyl $\text{C}\equiv\text{C}$ carbon resonances of **1** at 84.12 and 96.26 ppm disappeared and the vinyl $\text{C}=\text{C}$ carbon peaks in the silacyclopentene ring of **1** remained intact at 130.56-132.80 ppm, while the new vinyl $\text{C}=\text{C}$ carbon resonances appeared at 128.00-130.92 ppm,

which is also consistent with the proposed structure of oligomers **3a-e**. The structures of oligomers **3a-e** were also confirmed by the ^{29}Si and ^{11}B NMR spectra of all the prepared oligomers, as shown in Table 1. In the case of the polyadditions of dichlorophenylborane (**2d**) and dichlorobutylborane (**2e**), haloboration reactions occurred to yield the corresponding oligomers **3d** and **3e**, respectively, due to the higher reactivity of halogen atom such as chlorine than that of phenyl or butyl groups.¹⁷

Properties of Oligomers. All the oligomers **3a-e** were found to be soluble in common organic solvents of THF and chloroform. The solubility of **3a-e** permits us to perform studies on the properties in solution. In the UV-vis spectra of oligomers **3a-e**, the strong absorption bands are observed at the λ_{max} of 254-291 nm, as listed in Table 1, which are probably attributed to the presence of $\text{C}=\text{C}-\text{B}-\text{C}=\text{C}$ chromophore along the oligomer backbone.¹⁸ The UV-vis absorption maxima of polymer **3a-e** were not much different in comparison with the λ_{max} of 268-275 nm of the oligomers containing 3-triethylsilyl-1-silacyclopent-3-ene and boranes.¹¹

The typical excitation spectrum for **3e** at the detection wavelength of 339 nm in THF exhibits the strong excitation band at the λ_{max} of 287 nm, as shown in Figure 1. As outlined in Table 1, the excitation spectra of **3a-d** at the detection wavelengths of 300-410 nm in THF show that the strong excitation peaks appear at the λ_{max} of 273-334 nm, which are probably attributable to $\text{C}=\text{C}-\text{B}-\text{C}=\text{C}$ group along the oligomer chain. The excitation maxima of polymer **3a-e** were observed at longer wavelengths in comparison with

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

Oligomer	M_w, PDI^a	^{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	1820, 1.32	-33.86	-2.56	1714	268	273	330	59
3b	7970, 3.50	-17.23	-2.00	1699	274	334	415	82
3c	13410, 1.79	-21.93	-0.82	1699	291	321	390	92
3d	4050, 1.18	-14.70	-1.24	1692	254	285	346	78
3e	13430, 2.45	-15.75	-2.25	1702	269	287	336	70

^aDetermined by GPC in THF relative to polystyrene standards. M_w/M_n = Polydispersity index (PDI). ^bTaken in CDCl_3 . ^c $\text{C}=\text{C}$ bond stretching in the oligomer main chain and measured by neat or DRIFT method. ^dUV-vis absorption in THF. ^eDetection wavelengths at 300-410 nm in THF. ^fExcitation wavelengths at 280-340 nm in THF. ^g% Weight remaining at 400 °C under nitrogen.

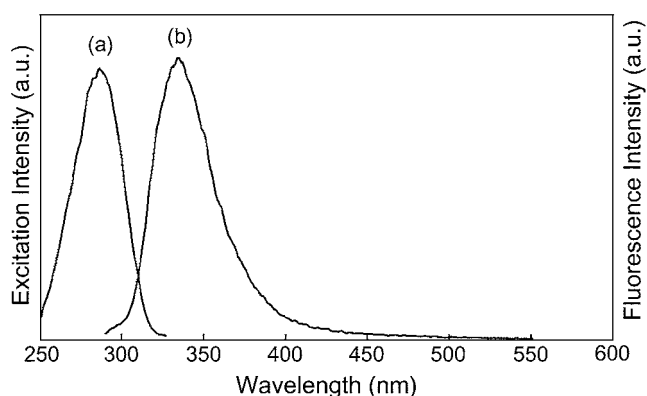


Figure 1. Excitation (line (a), $\lambda_{\text{det}} = 339$ nm) and fluorescence (line (b), $\lambda_{\text{ex}} = 285$ nm) spectra of the oligomer **3e** in THF.

those of 255–279 nm of the oligomers containing 3-triethylsilyl-1-silacyclopent-3-ene and boranes.¹¹

The typical fluorescence emission spectrum of **3e** at the excitation wavelength of 285 nm exhibits the strong emission peak at the λ_{max} of 336 nm with the broad emission band of 300–520 nm, as shown in Figure 1. As indicated in Table 1, the fluorescence emission spectra of **3a–d** at the excitation wavelengths of 280–340 nm in THF reveal that the strong fluorescence emission peaks appear at the λ_{max} of 330–415 nm, which are probably ascribed to the fluorophore of C=C-B-C=C along the oligomer chain.¹⁸ The emission maxima of polymer **3a–e** were observed relatively at longer wavelengths as compared with those of 310–370 nm of the oligomers containing 3-triethylsilyl-1-silacyclopent-3-ene and boranes.¹¹

Those strong absorption, excitation, and fluorescence bands of **3a–e** 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 moiety through the oligomer main chains.

The thermal stabilities of oligomers **3a–e** under nitrogen atmosphere were examined by thermogravimetric analysis (TGA) with a program heating rate of 10 °C/min. The typical TGA thermogram of **3c** was shown in Figure 2. **3c** is stable up to 200 °C with weight loss of 1% only. Rapid weight loss of 38% of the initial weight occurs between 300 and 600 °C. When **3c** is heated to 900 °C, 48% of the initial weight of **3c** is lost, and about 52% of TGA char yield is observed.

Normally, the oligomers **3a–e** are thermally stable up to 182–200 °C with weight loss of 1–10% only. Rapid weight loss of 18–38% 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 23–59% remain. Usually, about 59–92% of the initial polymer weights remain at 400 °C under nitrogen atmosphere, as indicated in Table 1.

In conclusion, we have successfully prepared the oligomeric carborane 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-1-silacyclopent-3-ene with several organoborane derivatives.

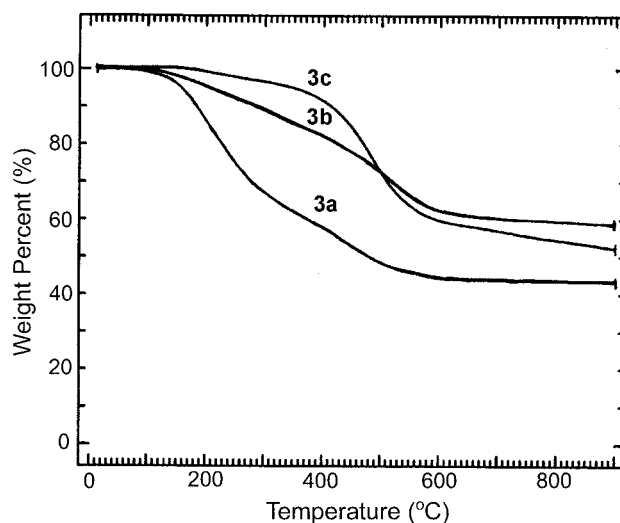


Figure 2. TGA thermogram of the oligomers **3a**, **3b**, and **3c** under nitrogen.

Experimental Section

General Procedures. All chemicals were purchased from Aldrich Chemicals Inc. All solvents were purified prior to use according to standard literature methods.¹⁹ All glasswares were assembled and then flame-dried while being swept with dry 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). ¹H (operating at 400 MHz) and ¹³C (operating at 100 MHz) nuclear magnetic resonance (NMR) spectroscopy were performed on a Bruker DRX Avance 400 MHz FT-NMR spectrometer using CDCl₃ as solvent. Chemical shifts were measured using tetramethylsilane as internal standard or the residual proton signal of the solvent as standard. ²⁹Si (operating at 99 MHz) and ¹¹B (operating at 160 MHz) NMR spectroscopy were performed on a Varian Unity INOVA 500 MHz FT-NMR spectrometer at the Korea Basic Science Institute. IR spectra were recorded by 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 1525 pump and Breeze software system with a Waters Styragel HR 3 column and refractive index detector at 40 °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 a heating rate of 10 °C/min from room temperature to 900 °C with a nitrogen flow rate of 20 mL/min. Elemental analyses were performed on a Fisons EA 1108 elemental analyzer.

1,1-Diethynyl-1-silacyclopent-3-ene (1) was prepared by the previously reported method.^{8,12}

Polyboration 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, 7.58 mL, 7.58 mmol) was placed using a syringe under argon atmosphere. The flask was cooled to $-78\text{ }^{\circ}\text{C}$ using a dry ice/acetone bath, and then **1** (1.00 g, 7.58 mmol) was added with vigorous stirring. The reaction mixture was stirred for 2 hrs and allowed to warm to room temperature with well stirring for overnight. The crude oligomer was precipitated by addition of dry *n*-pentane or methanol and dried under reduced pressure. The oligomeric material **3a**, 1.71 g, 59% was obtained as a dark brown solid with M_w/M_n of 1,820/1,370 (polydispersity index, PDI = 1.32). ^1H NMR (DMSO- d_6 , 400 MHz): δ 1.79 (m, 4H), 4.62 (br s, 2H), 5.61 (m, 2H); ^{13}C NMR (CDCl₃, 100 MHz): δ 17.50, 128.44, 129.72, 130.56; ^{29}Si NMR (CDCl₃, 99 MHz): δ -33.86; ^{11}B NMR (CDCl₃, 160 MHz): δ -2.56; IR (KBr, DRIFTS): ν 3212, 3059, 2956, 2041 (w), 1714 (C=C), 1611, 1434, 1196, 1073, 809 cm^{-1} ; UV-vis (THF): λ_{max} nm (ϵ) 268 (3.36×10^3). Anal. Calcd for (C₈H₈SiBBr₃)_n: C, 25.10; H, 2.11. Found: C, 24.84; H, 2.10. All 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** (1.77g, 94%) was obtained from **1** (1.00 g, 7.58 mmol) and boron trichloride (**2b**) (1.0 M/dichloromethane, 7.58 mL, 7.58 mmol): $M_w/M_n = 7,970/2,270$ (PDI = 3.50); ^1H NMR (CDCl₃, 400 MHz): δ 1.55 (m, 4H), 4.85 (br s, 2H), 5.94 (m, 2H); ^{13}C NMR (CDCl₃, 100 MHz): δ 20.41, 128.93, 130.92, 132.15; ^{29}Si NMR (CDCl₃, 99 MHz): δ -17.23; ^{11}B NMR (CDCl₃, 160 MHz): δ -2.00; IR (KBr, DRIFTS): ν 3213, 3038, 2962, 2042 (w), 1699 (C=C), 1606, 1457, 1196, 1044, 808 cm^{-1} ; UV-vis (THF): λ_{max} nm (ϵ) 274 (1.02×10^4). Anal. Calcd for (C₈H₈SiBCl₃)_n: C, 38.53; H, 3.23. Found: C, 37.87; H, 3.13.

A reddish yellow viscous gel **3c** (1.80 g, 76%) was obtained from **1** (1.00 g, 7.58 mmol) and tributylborane (**2c**) (1.0 M/diethyl ether, 7.58 mL, 7.58 mmol). The reaction mixture was stirred at room temperature for 1 h and then warmed to reflux for overnight. For oligomer **3c**: $M_w/M_n = 13,410/7,480$ (PDI = 1.79); ^1H NMR (CDCl₃, 400 MHz): δ 0.92-0.97 (m, 9H), 1.23-1.70 (br m, 18H), 1.87 (m, 4H), 4.94 (br s, 2H), 5.94 (m, 2H); ^{13}C NMR (CDCl₃, 100 MHz): δ 13.63, 13.84, 18.86, 19.02, 22.60, 26.73, 29.70, 30.49, 34.80, 128.58, 130.44, 131.56; ^{29}Si NMR (CDCl₃, 99 MHz): δ -21.93; ^{11}B NMR (CDCl₃, 160 MHz): δ -0.82; IR (neat): ν 3015, 2959, 2929, 2871, 2035 (w), 1699 (C=C), 1607, 1559, 1457, 1377, 1326, 1262, 1098, 1021, 802 cm^{-1} ; UV-vis (THF): λ_{max} nm (ϵ) 291 (1.54×10^4). Anal. Calcd for (C₂₀H₃₅SiB)_n: C, 76.41; H, 11.22. Found: C, 75.72; H, 11.16.

A dark brown powder **3d** (2.2 g, 99%) was obtained from **1** (1.00 g, 7.58 mmol) and dichlorophenylborane (**2d**) (0.98 g, 7.58 mmol) by the same manner to that described for **3c**: $M_w/M_n = 4,050/3,430$ (PDI = 1.18); ^1H NMR (DMSO- d_6 , 400 MHz): δ 1.89(m, 4H), 4.84 (br s, 2H), 5.83 (m, 2H),

7.13-7.77 (m, 5H); ^{13}C NMR (CDCl₃, 100 MHz): δ 19.26, 128.32, 128.50, 128.60, 129.64, 130.13, 130.80, 132.80; ^{29}Si NMR (CDCl₃, 99 MHz): δ -14.70; ^{11}B NMR (CDCl₃, 160 MHz): δ -1.24; IR (KBr, DRIFTS): ν 3076, 3059, 2988, 2882, 1692 (C=C), 1602, 1345, 1101, 759, 700, 614 cm^{-1} ; UV-vis (THF): λ_{max} nm (ϵ) 254 (5.71×10^4). Anal. Calcd for (C₁₄H₁₃SiBCl₂)_n: C, 57.78; H, 4.50. Found: C, 57.69; H, 4.55.

A pale yellowish viscous gel **3e** (1.3 g, 63%) was obtained from **1** (1.00 g, 7.58 mmol) and butyldichloroborane (**2e**) (1.0 M/hexane, 7.58 mL, 7.58 mmol) by the same manner to that described for **3c**: $M_w/M_n = 13,430/5,470$ (PDI = 2.45); ^1H NMR (THF- d_8 , 400 MHz): δ 0.85-0.91 (m, 3H), 1.28-1.70 (m, 6H), 1.56 (m, 4H), 4.73 (br s, 2H), 5.77 (br s, 2H); ^{13}C NMR (CDCl₃, 100 MHz): δ 13.77, 18.87, 19.43, 29.70, 35.09, 128.00, 129.40, 132.80; ^{29}Si NMR (CDCl₃, 99 MHz): δ -15.75; ^{11}B NMR (CDCl₃, 160 MHz): δ -2.25; IR (neat): ν 3031, 2929, 2941, 2862, 2025 (w), 1702 (C=C), 1602, 1370, 1103, 831, 663 cm^{-1} ; UV-vis (THF): λ_{max} nm (ϵ) 269 (2.24×10^4). Anal. Calcd for (C₁₂H₁₇SiBCl₂)_n: C, 53.17; H, 6.32. Found: C, 53.42; H, 6.31.

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