

Synthesis and Properties of Poly(1,1-diethynyl-1-silacyclopent-3-enes and -1-silacyclobutane)

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Polycarbosilanes containing diacetylene and organosilacyclic groups, such as poly(1,1-diethynyl-1-silacyclopent-3-ene), poly(1,1-diethynyl-3-triethylsilyl-1-silacyclopent-3-ene), and poly(1,1-diethynyl-1-silacyclobutane), were synthesized by the Glaser oxidative coupling polymerization reactions of 1,1-diethynyl-1-silacyclopent-3-ene, 1,1-diethynyl-3-triethylsilyl-1-silacyclopent-3-ene, and 1,1-diethynyl-1-silacyclobutane, respectively. These materials are almost insoluble in usual organic solvents such as CHCl_3 and THF. The polymers were characterized by using several spectroscopic methods in solid state. FTIR spectra of all the polymeric materials show that the characteristic $\text{C}\equiv\text{C}$ stretching frequencies appear at 2146–2170 cm^{-1} , in particular. The polymers in the solid state show that the strong maximum excitation peaks appear at 255–257 nm and the strong maximum fluorescence emission bands at 401–402 nm. About 71–87% of the initial polymer weights remain at 400 °C in nitrogen according to thermogravimetric analysis.

Key Words : Polycarbosilanes, Diacetylene, 1,1-Diethynyl-1-silacyclopentenes, Excitation, Fluorescence

Introduction

Polycarbosilanes bearing π -conjugated groups in the main chain have attracted considerable attention for their potential applications as photonic, electronic, and ceramic materials.¹ For example, diacetylene-containing polycarbosilanes doped with FeCl_3 show the conductivity in the range of 10^{-5} – 10^{-3} $\text{S}\cdot\text{cm}^{-1}$ and pyrolysis of the polycarbosilane polymers in inert atmosphere results in a β -SiC ceramic material in high yield.^{2,3} Interestingly, the linear copolymers of silarylene-siloxane-diacetylene exhibit the elastomeric properties with thermal stabilities up to 330 °C in air.¹ Recently, we reported the preparation and excited-state energy dynamics of polycarbosilanes as well as polycarbogermans 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 and silacyclobutane have also received much concern in the field of organosilicon chemistry.^{9,10} For instance, 1,1-dimethyl-1-silacyclopent-3-ene undergoes anionic ring-opening polymerization reaction by treatment with alkyl-lithium and hexamethylphosphoramide (HMPA) as cocatalyst at -78 °C to yield a new type of polycarbosilanes like as poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene).^{11,12} In particular, the reaction of 1-silacyclopent-3-ene with methyl-lithium and HMPA has afforded poly(1-sila-*cis*-pent-3-ene), which gave high ceramic yield of silicon carbide upon heating to 850 °C in an argon atmosphere.¹³ The two-step synthetic method for 1,1-dichloro-1-silacyclopent-3-ene (**1a**) from readily available starting materials has been reported,^{14,15} in which chlorine atoms could be easily converted into other functional groups such as ethynyls.

We have also been interested in the preparation and their properties of polycarbosilanes containing diacetylenic conjugation group as well as organosilacyclic group along the polymer backbone. Herein, we wish to report the synthesis of novel 1,1-diethynyl-1-silacyclic compounds as new monomers such as 1,1-diethynyl-1-silacyclopent-3-ene (**2a**), 1,1-diethynyl-3-triethylsilyl-1-silacyclopent-3-ene (**2b**), and 1,1-diethynyl-1-silacyclobutane (**2c**) and their oxidative coupling polymerization reactions to give poly(1,1-diethynyl-1-silacyclopent-3-ene) (**3a**), poly(1,1-diethynyl-3-triethylsilyl-1-silacyclopent-3-ene) (**3b**), and poly(1,1-diethynyl-1-silacyclobutane) (**3c**), respectively. We also describe the electronic and thermal properties of the polymers **3a-c**.

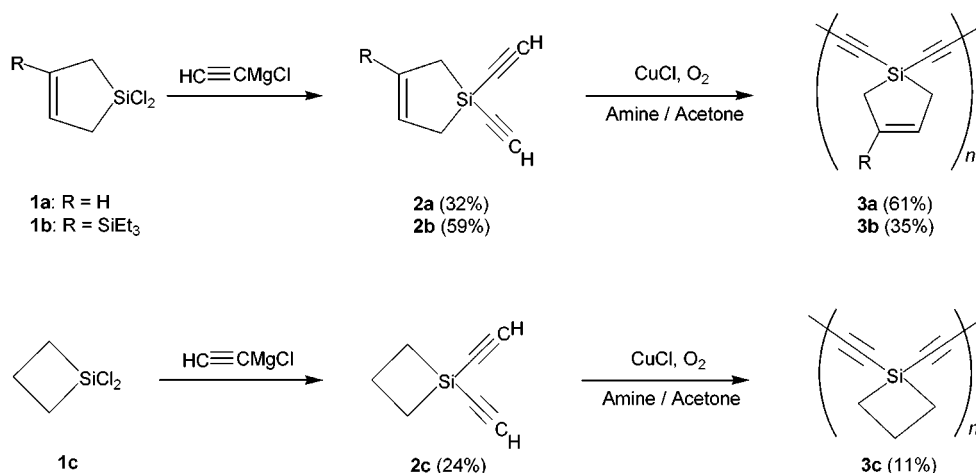
Results and Discussion

Synthesis of Monomers. The new 1,1-diethynyl-1-silacyclic monomers **2a-c** were prepared by ethynylation reactions of 1,1-dichloro-1-silacyclopent-3-ene (**1a**), 1,1-dichloro-3-triethylsilyl-1-silacyclopent-3-ene (**1b**), and 1,1-dichloro-1-silacyclobutane (**1c**) with ethynylmagnesium chloride, respectively, as shown in Scheme 1.

The compound **1a** was prepared by a two-step reaction as the previously reported method.¹¹ **1a** was treated with 2 equiv of ethynylmagnesium chloride in THF to afford **2a** as a new monomer in 32% yield. The two chlorine atoms bonded to silicon in compound **1a** were easily substituted into two ethynyl groups.

The synthesis of **1b** involves four-step reactions: a) hydrosilylation of 1,4-dichlorobut-2-yne with triethylsilane in the presence of Speier's catalyst H_2PtCl_6 , b) trichlorosilylation of 1,4-dichloro-2-triethylsilylbut-2-ene catalyzed with cuprous chloride and triethylamine, c) cyclization of 4-chloro-2-triethylsilyl-1-trichlorosilylbut-2-ene in the pre-

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Scheme 1

sence of magnesium metal,¹⁵ and then d) substitution reaction of two chlorines at **1b** with ethynyl groups by ethynylmagnesium chloride, giving **2b** as a new monomer in 59% yield. The compound **1c**, purchased commercially and used without further purification, was reacted with 2 equiv of ethynylmagnesium chloride in THF to afford **2c** in 24% yield.

All of the monomers **2a-c** were characterized using several spectroscopic methods such as ¹H, ¹³C, ²⁹Si NMR, mass, and IR spectra as well as elemental analysis. The characteristic C≡C stretching frequencies are observed at 2050 cm⁻¹ in the all IR spectra of the monomers **2a-c**. The ¹H NMR spectrum of **2a** shows that the singlet resonance appears at 2.56 ppm for ethynyl (C≡CH) protons, and the doublet at 1.65 ppm for methylene (CH₂) protons as well as the triplet at 5.90 ppm for vinyl (C=CH) protons. In the ¹H NMR of **1a**, the triplet and doublet resonances appear at 5.99 and 1.85 ppm. The comparison of these two ¹H NMR spectra indicates that ethynylation of compounds **1a-c** was completed under our reaction conditions. The ¹³C NMR spectrum of **2a** shows that four carbons peak appear at 18.11, 84.12, 96.26 and 130.14 ppm. The ethynyl carbon peaks are observed at 84.12 and 96.26 ppm. We also confirmed the molecular ion peaks *M/z* at 132, 246, and 120 in the mass spectra of **2a**, **2b**, and **2c**, respectively.

Synthesis of Polymers. Copper-catalyzed oxidative coupling (Glaser coupling) reaction of ethynyltrimethylsilane has been reported to yield bis(trimethylsilyl)diacetylene.¹⁶ We tried the Glaser coupling polymerization by utilizing the

functionalities of 1,1-diethynyl-1-silacyclic compounds **2a-c** as novel monomers. The Glaser oxidative coupling polymerizations of **2a-c** in the presence of cuprous chloride as catalyst and amine/acetone as co-solvent with bubbling oxygen gas through the reaction mixture have been carried out to afford polymers **3a-c**, respectively, which contain diacetylene and organosilacyclic groups in the polymer main chain, as shown in Scheme 1.

The polycarbosilanes **3a-c** as blackish powders turned out to be almost insoluble in usual organic solvents such as CHCl₃ and THF. Therefore, we cannot measure molecular weights of the polymers by running gel permeation chromatography (GPC). However, we tried to characterize the polymers by several spectroscopic methods in the solid state. Some selected spectral properties of the polycarbosilanes **3a-c** are listed in Table 1.

FTIR spectra of all the polymeric materials show that the characteristic C≡C stretching frequencies appear at 2146–2170 cm⁻¹, which indicate that the acetylene groups remain intact during polymerization reactions.¹⁷ In particular, the ²⁹Si CP MAS NMR spectra of the polymers show that the major resonances appear at -6.89 ppm for **3a**, at -0.36 and -7.57 ppm for **3b**, and at -66.27 ppm for **3c** (Figure S1, see Supporting Information), which are consistent with the backbone structures of the polymers **3a-c**.

Properties of Polymers. Due to the very low solubility of polycarbosilanes **3a-c** in usual organic solvents, we examined excitation as well as fluorescence emission spectra of the polymers in the solid state. The excitation spectrum for **3a** at

Table 1. Selected Properties of the Polycarbosilanes **3a**, **3b**, and **3c**

Polymer	¹³ C CP-MAS NMR ^a δ (ppm)	²⁹ Si CP-MAS NMR ^a δ (ppm)	IR ^b ν _(C≡C) (cm ⁻¹)	Excitation ^c λ _{max} (nm)	Fluorescence ^d λ _{max} (nm)	TGA ^e
3a	17.1, 82.1-91.1 (br), 129.2	-6.89	2146	256	401	71
3b	3.1-7.7 (br), 17.9-27.3 (br), 85.8-97.4 (br), 128.5-140.7 (br)	-0.36, -7.57	2157	257	402	71
3c	11.9-20.9 (br), 82.8-90.3 (br)	-66.27	2170	255	401	87

^aCP-MAS NMR. ^bBy DRIFT method. ^cDetection wavelength at 400 nm in the solid state. ^dExcitation wavelength at 260 nm in the solid state. ^e% Weight remaining at 400 °C in nitrogen.

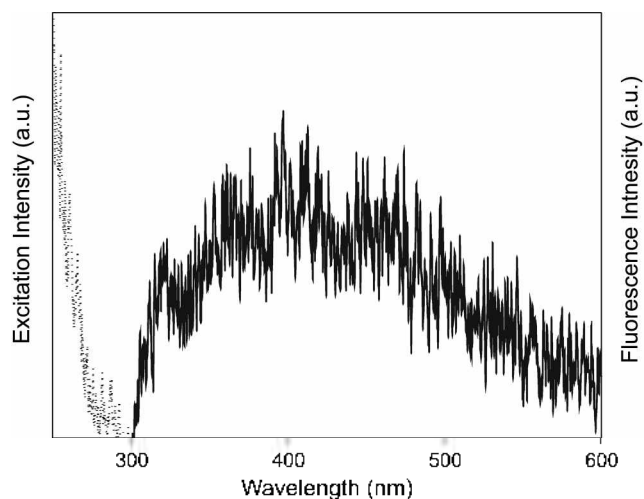


Figure 1. Excitation (dotted line, $\lambda_{det} = 400$ nm) and fluorescence (solid line, $\lambda_{ex} = 256$ nm) spectra of the polymer **3a** in the solid state.

the detection wavelength of 400 nm shows that the strong excitation peak is observed at the λ_{max} of 256 nm with the band of 250-271 nm, as indicated in Table 1. The typical excitation spectrum of the polymer **3a** in the solid state is shown in Figure 1 as the dotted line.

The excitation spectra of **3b** and **3c** also exhibit the strong excitation peaks at the λ_{max} of 257 nm with the band of 253-269 nm and at the λ_{max} of 255 nm with the band of 252-273 nm, respectively, as shown in Table 1 (Figure S2, see Supporting Information). These strong excitation bands in the excitation spectra of the polymers may be attributed to the chromophore of diethynyl groups along the polymer backbone.

The fluorescence emission spectrum for **3a** at the excitation wavelength of 260 nm in the solid state reveals that the strong emission peak appears at the λ_{max} of 401 nm with the broad band of 316-547 nm, as shown in Table 1. The typical fluorescence spectrum of the polymer **3a** in the solid state is shown in Figure 1 as the solid line. The fluorescence spectra of **3b** and **3c** also show the strong emission peaks at the λ_{max} of 402 nm with the broad band of 308-556 nm and at the λ_{max} of 401 nm with the broad band of 317-552 nm, respectively, as indicated in Table 1 (Figure S2, see Supporting Information). These strong emission bands in the fluorescence spectra of the polymers may be ascribed to the fluorophore of diethynyl groups along the polymer backbone.¹⁸ Both excitation and fluorescence emission spectra of the polymers imply that the polycarbosilanes **3a**, **3b**, and **3c** have the chromophores containing the diethynyl functional groups along the polymer main chains.

The thermal stabilities of polymers **3a-c** in a nitrogen atmosphere were determined by thermogravimetric analysis (TGA) with a heating rate of 10 °C/min. The weight loss of polymer **3a** occurs slowly upon heating from room temperature. Rapid weight loss of 29% of the initial weight occurs between 200 and 600 °C. When **3a** is heated to 900 °C, 48% of the initial weight of **3a** is lost, and about 52%

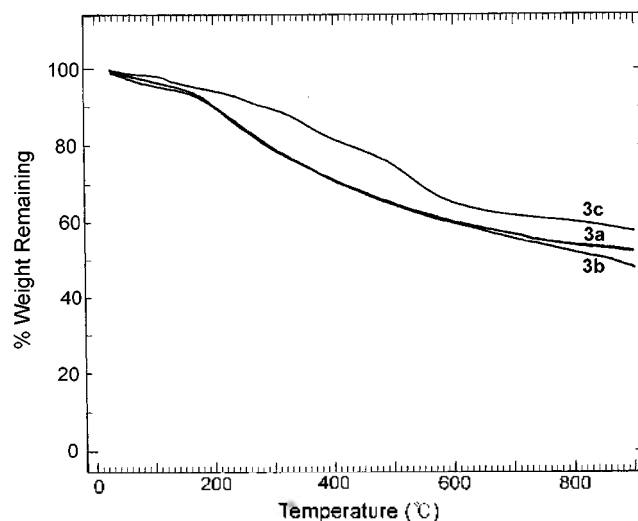


Figure 2. TGA thermograms of the polymers **3a**, **3b**, and **3c** in nitrogen.

char yield is observed. The weight loss of polymer **3b** occurs slowly upon heating from room temperature. Rapid weight loss of 30% of the initial weight occurs between 200 and 600 °C. When **3b** is heated to 900 °C, 52% of the initial weight of **3b** is lost, and about 48% char yield is observed. The weight loss of polymer **3c** occurs slowly upon heating from room temperature. Rapid weight loss of 29% of the initial weight occurs between 200 and 600 °C. When **3c** is heated to 900 °C, 42% of the initial weight of **3c** is lost, and about 58% char yield is observed. Usually, about 71-87% of the initial polymer weights remain at 400 °C in nitrogen as indicated in Table 1 and Figure 2.

Conclusion

We have successfully prepared the polycarbosilanes containing both diacetylene and organosilacyclic groups such as poly(1,1-diethynyl-1-silacyclopent-3-ene), poly(1,1-diethynyl-3-triethylsilyl-1-silacyclopent-3-ene), and poly(1,1-diethynyl-1-silacyclobutane) by the Glaser oxidative coupling polymerizations of 1,1-diethynyl-1-silacyclopent-3-ene, 1,1-diethynyl-3-triethylsilyl-1-silacyclopent-3-ene, and 1,1-diethynyl-1-silacyclobutane, respectively. The materials are not soluble in usual organic solvents such as CHCl_3 and THF. Therefore, we cannot measure molecular weights of the polymers by GPC. The polymers were characterized by using several spectroscopic methods in the solid states. In particular, FTIR spectra of all the polymeric materials show that the characteristic $\text{C}\equiv\text{C}$ stretching frequencies appear at 2146-2170 cm^{-1} . The materials in the solid state show that the strong maximum excitation peaks appear at 255-257 nm and the strong maximum emission bands at 401-402 nm. Both the strong excitation and emission spectra imply that the obtained polycarbosilanes contain the diethynyl groups in the polymer main chain. Usually, about 71-87% of the initial polymer weights remain at 400 °C in nitrogen according to TGA. Ultrafast kinetic

studies are planned to investigate further the electronic properties of the prepared organosilicon materials.

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.¹⁹ 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, ¹³C, and ²⁹Si nuclear magnetic resonance (NMR) spectroscopy were performed on a Bruker ARX-300 or a Bruker DRX Avance 400 MHz FT-NMR spectrometers or a Varian Unity INOVA 500 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. CP-MAS solid state NMR spectroscopy was performed on a Bruker DSX 400 MHz FT-NMR spectrometer 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. Low-resolution mass spectra were recorded by GC/MS, using a Hewlett Packard 5890II gas chromatography equipped with a Hewlett Packard 5971A mass selective detector by EI ionization at 70 eV. Excitation and fluorescence emission spectra were obtained on a Hitachi F-4500 fluorescence spectrophotometer. 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 $^{\circ}$ C/min from room temperature to 900 $^{\circ}$ C with nitrogen flow rate of 20 mL/min. Elemental analyses were performed by a Fisons EA 1108 elemental analyzer.

1a and **1b** were prepared by the previously reported methods,^{14,15} and **1c** was purchased from Gelest, Inc.

1,1-Diethynyl-1-silacyclopent-3-ene (2a). A 1 L three-necked, round bottomed flask was equipped with a reflux condenser, a pressure equalizing addition funnel, and a Teflon covered magnetic stirring bar. The flask was charged with 0.5 M ethynylmagnesium chloride (300 mL, 150 mmol) and THF (70 mL) under an argon atmosphere. Compound **1a** (10.0 g, 65.4 mmol) and THF (50 mL) were placed into the addition funnel and added drop-wise to the well stirred reaction mixture over 1h. It was quenched by addition of saturated aqueous ammonium chloride (10 mL), and THF (30 mL) was added. The organic layer was washed with water, dried with anhydrous MgSO₄, filtered, and concentrated at reduced pressure. The residue was then fractionally distilled to give **2a**, 4.20 g (32%); bp 20 $^{\circ}$ C/0.65 mmHg; ¹H-NMR (300 MHz, CDCl₃) δ 1.65 (d, 4H, *J* = 1.0 Hz), 2.56 (s, 2H), 5.90 (t, 2H, *J* = 1.0 Hz); ¹³C-NMR (75 MHz, CDCl₃) δ

18.11, 84.12, 96.26, 130.14; ²⁹Si-NMR (99 MHz, CDCl₃) δ -29.74; IR (neat) ν : 3290, 3010, 2900, 2050 (C=C), 1600, 1390, 1205, 1105, 945, 825, 810, 740, 680, 640 cm⁻¹; MS *m/z* (relative intensity): 132 (M⁺, 46.6), 131 (91.7), 130 (22.6), 107 (6.9), 106 (36.2), 105 (51.9), 79 (36.2), 78 (29.3), 77 (56.0), 53 (100); Elem. Anal. Calcd for C₈H₈Si: C, 72.67; H, 6.10. Found: C, 72.21; H, 6.11.

1,1-Diethynyl-3-triethylsilyl-1-silacyclopent-3-ene (2b) was prepared in the similar manner to that for the synthesis of **2a**, using **1b** (10.3 g, 38.0 mmol) and 0.5 M ethynylmagnesium chloride (170 mL, 85.0 mmol). Compound **2b**, 5.50 g, 59%, was obtained as a liquid; bp 105-106 $^{\circ}$ C/2.7 mmHg; ¹H-NMR (300 MHz, CDCl₃) δ 0.60 (q, 6H, *J* = 7.9 Hz), 0.91 (t, 9H, *J* = 7.9 Hz), 1.65 (s, 2H), 1.75 (d, 2H, *J* = 2.0 Hz), 2.51 (s, 2H), 6.15 (t, 1H, *J* = 2.0 Hz); ¹³C-NMR (75 MHz, CDCl₃) δ 2.63, 7.29, 20.87, 21.16, 84.08, 95.74, 139.37, 141.34; ²⁹Si-NMR (99 MHz, CDCl₃) δ 0.072, -28.79; IR (neat) ν : 3300, 2960, 2890, 2050 (C=C), 1570, 1460, 1410, 1390, 1240, 1145, 1090, 1005, 735, 715, 680 cm⁻¹; MS *m/z* (relative intensity): 248 (0.6), 247 (1.6), 246 (M⁺, 6.2), 219 (9.1), 218 (25.0), 217 (M⁺-Et, 100), 189 (62.0), 163 (8.8), 162 (8.5), 161 (42.7), 145 (3.9), 135 (7.8), 133 (6.1), 131 (4.3), 111 (3.6), 109 (5.1), 107 (8.8), 105 (8.8), 95 (4.3), 93 (9.6), 83 (9.2), 81 (12.5), 79 (9.4), 69 (4.5), 67 (5.7), 59 (14.1), 58 (4.2), 57 (7.7), 53 (15.4). Elem. Anal. Calcd for C₁₄H₂₂Si₂: C, 68.21; H, 9.00. Found: C, 67.34; H, 9.14.

1,1-Diethynyl-1-silacyclobutane (2c) was prepared in the similar manner to that for the synthesis of **2a**, using **1c** (15.0 g, 106 mmol) and 0.5 M ethynylmagnesium chloride (468 mL, 233 mmol).²⁰ Compound **2c**, 3.00 g, 24%, was obtained as a liquid; bp 31 $^{\circ}$ C/100 mmHg; ¹H-NMR (400 MHz, CDCl₃) δ 1.28 (t, 4H, *J* = 8.0 Hz), 2.15 (m, 2H), 2.64 (s, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ 15.64, 18.35, 84.16, 96.35; ²⁹Si-NMR (99 MHz, CDCl₃) δ -35.87; IR (neat) ν : 3290, 2990, 2910, 2890, 2050 (C=C), 1425, 1380, 1360, 1180, 1120, 1060, 900, 860, 820, 700 cm⁻¹; MS *m/z* (relative intensity): 121 (1.2), 120 (M⁺, 5.0), 119 (M⁺-H, 20.5), 105 (10.0), 94 (8.8), 93 (14.4), 92 (100.0), 89 (1.3), 79 (7.4), 78 (4.7), 77 (13.8), 76 (1.3), 68 (1.8), 67 (6.1), 66 (31.3), 65 (5.9), 55 (3.1), 54 (6.1), 53 (71.3).

Poly(1,1-diethynyl-1-silacyclopent-3-ene) (3a). A 500 mL three-necked, round bottomed flask was equipped with a heating mantle, a reflux condenser, a pressure equalizing addition funnel, and a Teflon covered magnetic stirring bar. The flask was charged with acetone (200 mL) and cuprous chloride (0.13 g, 1.3 mmol) under an argon atmosphere. The well stirred suspension was slowly heated to 30 $^{\circ}$ C. The solution of acetone (20 mL) and pyridine or tetramethylethylenediamine (20 mL) was placed into the addition funnel and 20 mL of this solution was added to the flask. The dark green mixture was stirred for 10 min, and **2a** (1.60 g, 12.1 mmol) was added to the flask. The remaining 20 mL of acetone/pyridine or tetramethylethylenediamine mixture was then added. After a further stirring for 10 min, oxygen gas was bubbled through the reaction mixture during all the reaction. The reaction mixture was stirred vigorously with

heating at 35–40 °C for an additional 6 h. The reaction mixture was allowed to cool to room temperature and filtered by using sintered glass. The crude solid product was poured into THF (100 mL), and washed with 10% HCl solution (3 × 50 mL), water (3 × 50 mL), and finally methanol (50 mL). After separated by filtration and dried under vacuum, the polymeric material **3a** was obtained as a blackish solid state and almost insoluble in usual organic solvents such as THF and CHCl₃. In this way, 1.01 g, 61% yield of **3a** was prepared. ¹³C CP-MAS NMR (100 MHz) δ 17.1, 82.1–91.1 (br), 129.2; ²⁹Si CP-MAS NMR (80 MHz) δ –6.89; IR (KBr) ν: 3421, 3091, 2958, 2146 (C≡C), 1625, 1209, 1063, 750 cm⁻¹. Elem. Anal. Calcd for (C₈H₆Si)_n: C, 73.78; H, 4.65. Found: C, 72.76; H, 4.83. The excitation and fluorescence emission spectra in the solid state as well as TGA thermogram are described in Result and Discussion.

Poly(1,1-diethynyl-3-triethylsilyl-1-silacyclopent-3-ene) (3b) was prepared in the similar manner to that for the synthesis of **3a**, using **2b** (1.50 g, 6.09 mmol). Polymeric material **3b**, 0.52 g, 35%, was obtained as a blackish solid state and almost insoluble in usual organic solvents such as THF and CHCl₃. ¹³C CP-MAS NMR (100 MHz) δ 3.1–7.7 (br), 17.9–27.3 (br), 85.8–97.4 (br), 128.5–140.7 (br); ²⁹Si CP-MAS NMR (80 MHz) δ –0.36, –7.57; IR (KBr) ν: 3072, 2954, 2157 (C≡C), 1711, 1630, 1580, 1478, 1421, 1365, 1237, 1150, 1103, 1013, 830, 762, 717, 682 cm⁻¹. Elem. Anal. Calcd for (C₁₄H₂₀Si)_n: C, 68.82; H, 8.26. Found: C, 68.94; H, 8.65. The excitation and fluorescence emission spectra in the solid state as well as TGA thermogram are described in Result and Discussion.

Poly(1,1-diethynyl-1-silacyclobutane) (3c) was prepared in the similar manner to that for the synthesis of **3a**, using **2c** (1.00 g, 8.40 mmol). Polymeric material **3c**, 0.10 g, 11%, was obtained as a blackish solid state and almost insoluble in usual organic solvents such as THF and CHCl₃. ¹³C CP-MAS NMR (100 MHz) δ 11.9–20.9 (br), 82.8–90.3 (br); ²⁹Si CP-MAS NMR (80 MHz) δ –66.27; IR (KBr) ν: 2950, 2910, 2890, 2170 (C≡C), 1120, 1040, 900, 760, 680 cm⁻¹. Elem. Anal. Calcd for (C₇H₆Si)_n: C, 71.12; H, 5.13. Found: C, 72.10; H, 5.17. The excitation and fluorescence emission spectra in the solid state as well as TGA thermogram are described in Result and Discussion.

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Supporting Information Available: ²⁹Si CP-MAS NMR spectra of the polymers **3a**, **3b**, and **3c** (Figure S1) and excitation (dotted line, λ_{det} = 400 nm) and fluorescence (solid line, λ_{ex} = 260 nm) spectra of the polymers **3b** and **3c** in the solid state (Figure S2) will be given upon your request to the correspondence author.

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