

## Oxidative Coupling Polymerization of Diethynylsilane Derivatives and 1,2-Diethynyl-1,1,2,2-tetramethyldisilane

Ji Ho Kim and Young Tae Park\*

Department of Chemistry, Keimyung University, Daegu 704-701, Korea. \*E-mail: ytpark@kmu.ac.kr

Received February 20, 2006

We have carried out the Glaser oxidative coupling polymerizations of diethynyldiphenylsilane, diethynylmethylphenylsilane, diethynylmethyloctylsilane, and 1,2-diethynyl-1,1,2,2-tetramethyldisilane to afford polycarbosilanes containing diethynyl and organosilane groups in the main chain, such as poly(diethynyldiphenylsilane), poly(diethynylmethylphenylsilane), poly(diethynylmethyloctylsilane), and poly(1,2-diethynyl-1,1,2,2-tetramethyldisilane), respectively. These obtained materials are almost insoluble in common organic solvents such as  $\text{CHCl}_3$  and THF probably due to the presence of a rigid rod diacetylene group along the polymer main chain. Therefore, the polymers were characterized 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  $2147\text{--}2154\text{ cm}^{-1}$ , in particular. The polymers in the solid state exhibit that the strong maximum excitation peaks appear at  $260\text{--}283\text{ nm}$  and the strong maximum fluorescence emission bands at  $367\text{--}412\text{ nm}$ , especially. Thermogravimetric analysis of the materials shows that about 55–68% of the initial polymer weights remain at  $400\text{ }^\circ\text{C}$  in nitrogen.

**Key Words :** Polycarbosilanes, Diethynylsilane derivatives, Diethynyltetramethyldisilane, Excitation, Fluorescence

### Introduction

Polycarbosilanes bearing  $\pi$ -conjugated groups along the main chain have attracted considerable attention for their potential applications as photonic, electronic, and ceramic materials.<sup>1</sup> For instance, diacetylene-containing polycarbosilanes such as poly(silanylene-diethynylene)s were reported to synthesize by polycondensation reactions of the diethynylene dilithium salt with dichlorosilanes.<sup>2</sup> The prepared materials with low molecular weights of  $M_n < 5000\text{ g/mol}$  exhibit the conductivities ranging from  $8 \times 10^{-5}$  to  $3 \times 10^{-3}\text{ S cm}^{-1}$  when they are doped with  $\text{FeCl}_3$ , and pyrolysis of the polycarbosilane polymers in inert atmosphere results in a  $\beta$ -SiC ceramic material in high yield.<sup>3–6</sup> Interestingly, the linear copolymers of silarylene-siloxane-diacetylene exhibit the elastomeric properties with thermal stabilities up to  $330\text{ }^\circ\text{C}$  in air.<sup>7</sup> Some researchers have reported electronic structure of simplified organosilicon polymers containing  $\pi$ -conjugated moieties based on molecular orbital calculation in order to explain their electronic conductivity properties theoretically.<sup>8,9</sup>

Very recently, ladderlike poly(*p*-phenylenevinylene)s with silicon and carbon bridged  $\pi$ -conjugated framework have been prepared by intramolecular cyclization of mono(*o*-silylphenyl)acetylene, showing that the prepared polymers are intense fluorescent in the visible region and the emission colors vary from blue to green to yellow.<sup>10</sup> End-capped silole dendrimers on a ethenyl-phenyl carbosilane in inner shell exhibit green to greenish-blue fluorescence.<sup>11</sup>

However, photoelectronic properties such as excitation and fluorescence emission of diethynyl-containing polycarbosilanes have been scarcely reported up to date. Recently, we have reported the synthesis and, in particular, electronic as well as thermal properties of oligomers containing  $\pi$ -

conjugated moiety of  $\text{C}=\text{C}-\text{B}-\text{C}=\text{C}$  and organosilacyclic group along the polymer backbone by polyaddition reactions of 1,1-diethynyl-1-silacyclopent-3-enes with borane derivatives.<sup>12,13</sup> We reported also the synthesis and photoelectronic as well as thermal properties poly(1,1-diethynyl-1-silacyclopent-3-enes and 1,1-diethynyl-1-silacyclobutane) by oxidative coupling reactions of diethynyl organosilacyclic monomers.<sup>14</sup> We also have already 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.<sup>15,16</sup> With these considerations in mind, we have extended the Glaser oxidative polymerization technique to the preparation and photoelectronic properties of polymeric materials containing diethynyl silanes in the polymer main chains by utilizing functionality of diethynyl-containing silane compounds.

Herein, we now report the Glaser oxidative coupling polymerizations of diethynyldiphenylsilane (**2a**), diethynylmethylphenylsilane (**2b**), diethynylmethyloctylsilane (**2c**), and 1,2-diethynyl-1,1,2,2-tetramethyldisilane (**2d**) in the presence of cuprous chloride as catalyst and tetramethylethylenediamine/acetone as co-solvent with bubbling oxygen gas through the reaction mixture to give polycarbosilanes containing diacetylene and organosilane groups, such as poly(diethynyldiphenylsilane) (**3a**), poly(diethynylmethylphenylsilane) (**3b**), poly(diethynylmethyloctylsilane) (**3c**), and poly(1,2-diethynyl-1,1,2,2-tetramethyldisilane) (**3d**), respectively. The obtained materials were characterized by IR and  $^{13}\text{C}$  and  $^{29}\text{Si}$  CP-MAS NMR spectrophotometers in solid state as well as elemental analysis. Furthermore, the synthesized polycarbosilanes can be expected to include a novel  $\pi$ -conjugated moiety of  $\text{C}\equiv\text{C}$  and silane groups along the main chain. In particular, we focus on studying the

photoelectronic and thermogravimetric properties of the prepared polymers by using excitation and fluorescence emission spectrophotometer as well as thermogravimetric analysis (TGA).

## Results and Discussion

**Synthesis of Monomers and Polymers.** Diethynyl-containing silane monomers **2a-d** were readily prepared by ethynylation reactions of dichlorodiphenylsilane (**1a**), dichloromethylphenylsilane (**1b**), dichloromethyloctylsilane (**1c**), and 1,2-dichloro-1,1,2,2-tetramethyldisilane (**1d**) with ethynylmagnesium chloride, respectively, as shown in Scheme 1.

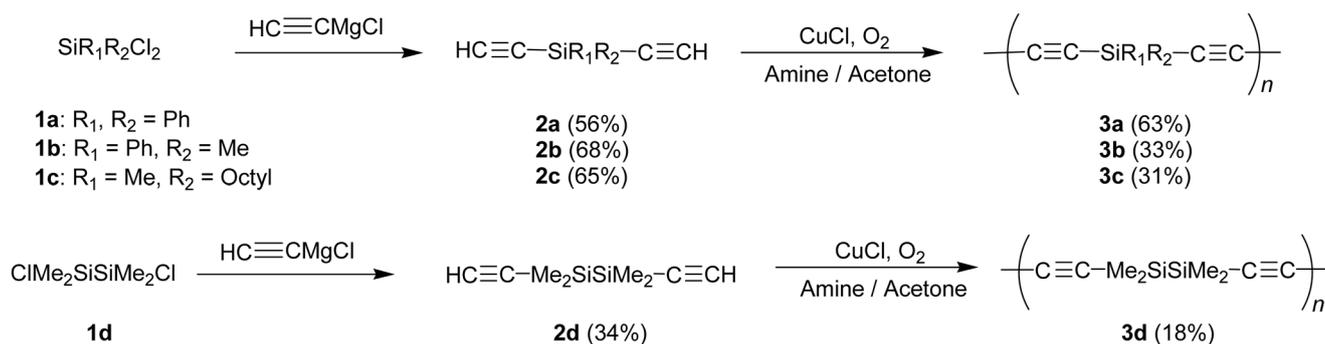
The starting materials **1a-d** were treated with 2 equivalent of ethynylmagnesium chloride in THF to afford monomers **2a-d** in moderate yields. The two chlorine atoms in compounds **1a-d** were easily substituted into two ethynyl groups.<sup>17</sup>

All of the monomers **2a-d** were characterized using several spectroscopic methods such as <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR, and IR spectra as well as mass data. The characteristic C≡C stretching frequencies are clearly observed at 2034, 2039, 2040, and 2254 cm<sup>-1</sup> in the IR spectra of the monomers **2a-d**, respectively.<sup>18,19</sup> The <sup>1</sup>H NMR spectra of **2a-d** show that the singlet resonances appear newly at 2.72, 2.69, 2.48, and 2.51 ppm for the ethynyl (C≡CH) protons, respectively,<sup>19</sup> and which indicates that ethynylation reaction in the compounds **1a-d**, such as the substitution reaction of two chlorine atoms with ethynyl groups, was completed under our reaction condition by using ethynylmagnesium Grignard reagent. In the <sup>13</sup>C NMR spectra of **2a-d**, the two carbon peaks of ethynyl groups are observed at 83.3-87.65 and 94.80-97.4 ppm.<sup>19</sup> In the <sup>29</sup>Si NMR spectra of **2a-d**, the

silicon resonances are observed at 0.00, 4.49, -35.94, and -35.72 ppm, respectively. We also confirmed the molecular ion peaks of each monomer in the mass spectra of **2a-d**.

Copper-catalyzed oxidative coupling (Glaser coupling) reaction of ethynyltrimethylsilane has been reported to yield bis(trimethylsilyl)diacetylene.<sup>20,21</sup> We have reported recently the Glaser oxidative coupling polymerization of 1,1-diethynyl-1-silacyclic derivatives as novel monomers.<sup>14</sup> Here, we tried the Glaser coupling polymerization by utilizing the functionalities of diethynylsilane derivatives **2a-c** and 1,2-diethynyl-1,1,2,2-tetramethyldisilane compounds **2d** as novel monomers. The Glaser oxidative coupling polymerizations of **2a-d** in the presence of cuprous chloride as catalyst and tetramethylethylenediamine/acetone as co-solvent with bubbling oxygen gas through the reaction mixture have been carried out to afford polycarbosilane materials **3a-d**, respectively, which contain diacetylene and organosilyl groups in the polymer main chain, as shown in Scheme 1.

The polycarbosilanes **3a-d** as dark brownish powders turned out to be almost insoluble in common organic solvents such as CHCl<sub>3</sub> and THF, probably due to the presence of the long rigid diacetylene group along the polymer main chain.<sup>22</sup> In a possible explanation of the reason for low solubilities of the obtained materials in common organic solvents, the partially cross-linking of diacetylene groups in polymer main chain<sup>23</sup> has been ruled out by our observing the appearance of major singlet peak in the <sup>29</sup>Si CP-MAS NMR spectral data (*vide infra*). 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-d** are listed in Table 1.



Scheme 1

Table 1. Selected Properties of the Polycarbosilanes **3a-d**

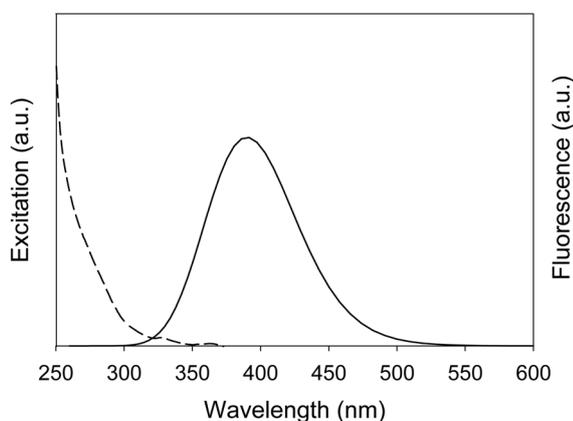
Polymer	<sup>13</sup> C CP-MAS NMR <sup>a</sup> δ(ppm)	<sup>29</sup> Si CP-MAS NMR <sup>a</sup> δ(ppm)	IR <sup>b</sup> ν(C=C) (cm <sup>-1</sup> )	Excitation <sup>c</sup> λ <sub>ex,max</sub> (nm)	Fluorescence <sup>d</sup> λ <sub>em,max</sub> (nm)	TGA <sup>e</sup>
<b>3a</b>	86.11-98.89 (br), 125.28-147.22 (br)	-51.84	2150	283	367	55
<b>3b</b>	-0.28, 83.33-94.45 (br), 125.00-138.89 (br)	-35.75	2152	266	412	68
<b>3c</b>	00.29, 15.28-35.99 (br), 81.94-98.61 (br)	-62.51	2147	260	392	62
<b>3d</b>	1.95, 80.56-97.22 (br)	-62.20	2154	262	406	65

<sup>a</sup>CP-MAS NMR. <sup>b</sup>By DRIFT method. <sup>c</sup>Detection wavelengths at 360, 410, 400, and 400 nm in the solid state for **3a-d**, respectively. <sup>d</sup>Excitation wavelengths at 260, 260, 255, and 255 nm in the solid state for **3a-d**, respectively. <sup>e</sup>% Weight remaining at 400 °C in nitrogen.

FTIR spectra of all the polymeric materials **3a-d** show that the characteristic C≡C stretching frequencies appear at 2150, 2152, 2147, and 2154  $\text{cm}^{-1}$ , respectively, which indicate that the acetylene groups remain intact during polymerization reactions.<sup>18,19</sup> In particular, the  $^{29}\text{Si}$  CP-MAS NMR spectra of the polymers **3a-d** show that the major singlet resonance peaks appear at  $-51.84$ ,  $-35.75$ ,  $-62.51$ , and  $-62.20$  ppm, respectively, which indicating that the silicon atoms in polymer main chain might have one kind of major structural environment, and suggesting that the polymeric structure are consistent with the backbone structures of the polymers **3a-d**.

**Properties of Polymers.** We examined excitation as well as fluorescence emission spectra of the polymers in the solid state, due to the very low solubility of polycarbosilanes **3a-d** in usual organic solvents. The excitation spectrum for **3a** at the detection wavelength of 360 nm in the solid state shows that the strong excitation peak is observed at the  $\lambda_{\text{ex, max}}$  of 283 nm with the band of 258-300 nm, as indicated in Table 1. The excitation spectra of **3b** and **3c** at the detection wavelength of 410 and 400 nm also exhibit that the strong excitation peaks are observed at the  $\lambda_{\text{ex, max}}$  of 266 nm with the band of 252-299 nm and at the  $\lambda_{\text{ex, max}}$  of 260 nm with the band of 252-296 nm, respectively, as shown in Table 1. Typical excitation spectrum of the polymer **3c** in the solid state is shown in Figure 1 as the dashed line. The excitation spectrum for **3d** at the detection wavelength of 400 nm reveals that the strong excitation peak is observed at the  $\lambda_{\text{ex, max}}$  of 262 nm with the band of 252-292 nm (Table 1). These strong excitation bands in the excitation spectra of the polymers **3a-d** may be attributed to the chromophore of diethynyl groups along the polymer backbone.<sup>24</sup> The maximum excitation wavelength of **3a** is longer than those of other polycarbosilanes **3b-c** probably due to the presence of phenyl groups in silicon atom.

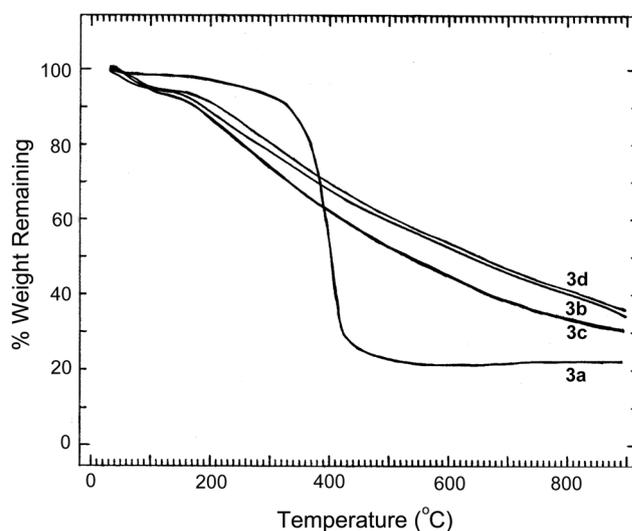
The fluorescence emission spectrum for **3a** at the excitation wavelength of 260 nm in the solid state reveals that the strong emission peak appears at the  $\lambda_{\text{em, max}}$  of 367 nm with the band of 298-466 nm, as shown in Table 1. The



**Figure 1.** Excitation (dashed line,  $\lambda_{\text{det}} = 400$  nm) and fluorescence (solid line,  $\lambda_{\text{ex}} = 255$  nm) spectra of the polymer **3c** in the solid state.

fluorescence spectra of **3b** and **3c** at the excitation wavelength of 260 and 255 nm also show that the strong emission peaks are observed at the  $\lambda_{\text{em, max}}$  of 412 nm with the band of 344-498 nm, and at the  $\lambda_{\text{em, max}}$  of 392 nm with the band of 336-470 nm, respectively, as indicated in Table 1. The typical fluorescence spectrum of the polymer **3c** in the solid state is shown in Figure 1 as the solid line. The fluorescence emission spectrum for **3d** at the excitation wavelength of 255 nm reveals that the strong emission peak appears at the  $\lambda_{\text{em, max}}$  of 406 nm with the band of 338-490 nm (Table 1). These strong emission bands in the fluorescence spectra of the polymers may be ascribed to the fluorophore of diethynyl groups along the polymer backbone.<sup>24</sup> The maximum fluorescence emission wavelengths of **3b** and **3d** are longer than those of other polycarbosilanes **3a** and **3c**. Both excitation and fluorescence emission spectra of the polymers imply that the polycarbosilanes **3a-d** have the chromophores containing the diethynyl functional groups along the polymer main chains.<sup>24</sup> Ultrafast time-resolved kinetic study might be required in order to furthermore investigate the electronic conjugation properties of the prepared materials.

The thermal stabilities of polymers **3a-d** in a nitrogen atmosphere were determined by thermogravimetric analysis (TGA) with a heating rate of 10  $^{\circ}\text{C}/\text{min}$  as shown in Figure 2. The polymer **3a** is stable up to 200  $^{\circ}\text{C}$  with the only 2% weight loss of the initial weight in nitrogen. The weight loss of polymer **3a** occurs slowly upon heating from room temperature. Rapid weight loss of 76% of the initial weight occurs between 200 and 600  $^{\circ}\text{C}$ . When **3a** is heated to 900  $^{\circ}\text{C}$ , 78% of the initial weight of **3a** is lost, and about 22% char yield is observed. The weight loss of polymer **3b** occurs slowly upon heating from room temperature. Rapid weight loss of 36% of the initial weight occurs between 200 and 600  $^{\circ}\text{C}$ . When **3b** is heated to 900  $^{\circ}\text{C}$ , 66% of the initial weight of **3b** is lost, and about 34% char yield is observed. The weight loss of polymer **3c** occurs slowly upon heating from room temperature. Rapid weight loss of 42% of the



**Figure 2.** TGA thermograms of the polymers **3a-d** in nitrogen.

initial weight occurs between 200 and 600 °C. When **3c** is heated to 900 °C, 68% of the initial weight of **3c** is lost, and about 32% char yield is observed. The weight loss of polymer **3d** occurs slowly upon heating from room temperature. Rapid weight loss of 41% of the initial weight occurs between 200 and 600 °C. When **3d** is heated to 900 °C, 64% of the initial weight of **3d** is lost, and about 36% char yield is observed. Usually, about 55-68% 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 diethynyl and organosilane groups such as poly(diethynyldiphenylsilane), poly(diethynylmethylphenylsilane), poly(diethynylmethyloctylsilane), and poly(1,2-diethynyl-1,1,2,2-tetramethyldisilane), by the Glaser oxidative coupling polymerizations of diethynyldiphenylsilane, diethynylmethylphenylsilane, diethynylmethyloctylsilane, and 1,2-diethynyl-1,1,2,2-tetramethyldisilane, respectively. The materials are not soluble in common organic solvents such as  $\text{CHCl}_3$  and THF probably due to the presence of the long rigid diacetylene group along the polymer main chain. 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 2147-2154  $\text{cm}^{-1}$ . The materials in the solid state show that the strong maximum excitation peaks appear at 260-283 nm and the strong maximum emission bands at 367-412 nm. Both the strong excitation and emission spectra imply that the obtained polycarbosilanes contain the diethynyl groups in the polymer main chain. Usually, about 55-68% of the initial polymer weights remain at 400 °C in nitrogen according to TGA. Ultrafast time-resolved kinetic studies are planned to further investigate the electronic conjugation properties of the prepared 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) and *n*-hexane were distilled from sodium benzophenone ketyl.<sup>25</sup> 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 10  $\mu\text{L}$  of hexamethyldisilazane.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  nuclear magnetic resonance (NMR) spectroscopy were performed on a Bruker ARX-400 or a Bruker DRX Avance 400 MHz FT-NMR spectrometers or a Varian Unity INOVA 500 MHz FT-NMR spectrometer

using  $\text{CDCl}_3$  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 Daegu Branch of 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 taken on a Spex Fluorolog-3-11 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 °C/min from room temperature to 900 °C with nitrogen flow rate of 20 mL/min. Elemental analyses were performed by a Fisons EA 1108 elemental analyzer.

**Diethynyldiphenylsilane (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  $\text{MgSO}_4$ , filtered, and concentrated at reduced pressure. The residue was then fractionally distilled to give **2a**, 8.90 g (56.0%); bp 124-125 °C/0.45 mmHg;<sup>26</sup>  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.72 (s, 2H,  $\text{C}\equiv\text{CH}$ ), 7.36-7.79 (m, 10H,  $\text{C}_6\text{H}_5$ );  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  83.3, 97.4, 128.2, 130.6, 131.2, 134.7;  $^{29}\text{Si}$ -NMR (99 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.00; IR (neat):  $\nu$  3267 ( $\equiv\text{CH}$ ), 3063, 3046, 3000, 2034 ( $\text{C}\equiv\text{C}$ ), 1424, 1115, 640  $\text{cm}^{-1}$ ; MS: *m/z* (relative intensity) 232 ( $\text{M}^+$ , 51), 231 (100), 230 (21), 155 ( $\text{M}^+$ -Ph, 31), 154 (22), 130 (16), 129 (42), 79 (6), 78 (4), 77 (14), 53 (34), 51 (14), 50 (7).

**Diethynylmethylphenylsilane (2b)** was prepared in the similar manner to that for the synthesis of **2a**, using **1b** (12.0 g, 65.0 mmol) and 0.5 M ethynylmagnesium chloride (300 mL, 0.150 mol). Compound **2b**, 8.20 g, 68.0%, was obtained as a liquid; bp 73 °C/0.7 mmHg;<sup>27</sup>  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.72 (s, 3H,  $\text{CH}_3$ ), 2.69 (s, 2H,  $\text{C}\equiv\text{CH}$ ), 7.46-7.87 (m, 5H,  $\text{C}_6\text{H}_5$ );  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.8, 84.5, 96.1, 128.1, 130.3, 132.3, 133.8;  $^{29}\text{Si}$ -NMR (99 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.49; IR (neat):  $\nu$  3274 ( $\equiv\text{CH}$ ), 3072, 3060, 2970, 2039 ( $\text{C}\equiv\text{C}$ ), 1589, 1429, 1255, 1117, 795 (Si-C), 731, 695  $\text{cm}^{-1}$ ; MS: *m/z* (relative intensity) 170 ( $\text{M}^+$ , 23), 169 (32), 156 (16), 155 ( $\text{M}^+$ - $\text{CH}_3$ , 100), 130 (3), 129 (17), 53 (34), 51 (8).

**Diethynylmethyloctylsilane (2c)** was prepared in the similar manner to that for the synthesis of **2a**, using **1c** (15.0 g, 66.0 mmol) and 0.5 M ethynylmagnesium chloride (270

mL, 140 mmol). Compound **2c**, 8.79 g, 65.0%, was obtained as a liquid; bp 58 °C/100 mmHg; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 0.35 (s, 3H, CH<sub>3</sub>), 0.75-1.62 (m, 17H, C<sub>8</sub>H<sub>17</sub>), 2.48 (s, 2H, C≡CH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ -1.88, 14.07, 15.39, 22.62, 23.23, 29.15, 31.86, 32.84, 85.47, 94.80; <sup>29</sup>Si-NMR (99 MHz, CDCl<sub>3</sub>): δ -35.94; IR (KBr): ν 3292 (≡CH), 2924, 2855, 2040 (C≡C), 1465, 1255, 790, 729, 668 cm<sup>-1</sup>; MS: *m/z* (relative intensity) 191 (M<sup>+</sup>-CH<sub>3</sub>, 0.062), 137 (12), 121 (13), 93 (M<sup>+</sup>-C<sub>8</sub>H<sub>17</sub>, 100), 79 (11), 67 (9.8), 53 (33).

**1,2-Diethynyl-1,1,2,2-tetramethyldisilane (2d)** was prepared in the similar manner to that for the synthesis of **2d**, using **1d** (5.0 g, 27.0 mmol) and 0.5 M ethynylmagnesium chloride (108 mL, 54 mmol). Compound **2d**, 1.50 g, 33.5%, was obtained as a liquid; bp 82 °C/100 mmHg; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 0.34 (s, 12H, CH<sub>3</sub>), 2.51 (s, 2H, C≡CH); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ -3.46, 87.65, 95.68; <sup>29</sup>Si-NMR (99 MHz, CDCl<sub>3</sub>): δ -35.72; IR (KBr disk): ν 3158 (≡CH), 2943, 2880, 2254 (C≡C), 1721, 1479, 1383, 1261, 1100, 769, 722 cm<sup>-1</sup>; MS: *m/z* (relative intensity) 166 (M<sup>+</sup>, 6), 165 (M<sup>+</sup>-H, 4), 152 (14), 151 (M<sup>+</sup>-CH<sub>3</sub>, 81), 93 (10), 83 (M<sup>+</sup>-C<sub>4</sub>H<sub>7</sub>Si, 100), 73 (65), 67 (19), 53 (29), 43 (42).

**Poly(diethynyldiphenylsilane) (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 (80 mL) and cuprous chloride (0.10 g, 1.0 mmol) under an argon atmosphere. The well stirred suspension was slowly heated to 30 °C. The solution of acetone (10 mL) and tetramethylethylenediamine (10 mL) was placed into the addition funnel and 10 mL of this solution was added to the flask. The dark green mixture was stirred for 10 min, and **2a** (2.32 g, 10.0 mmol) was added to the flask. The remaining 10 mL of acetone/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 dark brownish solid state and almost insoluble in usual organic solvents such as THF and CHCl<sub>3</sub>. In this way, 1.45 g, 63.1% yield of **3a** was prepared. <sup>13</sup>C CP-MAS NMR (100 MHz): δ 86.11-98.89 (br), 125.28-147.22 (br); <sup>29</sup>Si CP-MAS NMR (80 MHz): δ -51.84; IR (KBr): ν 3069, 3043, 3029, 2150 (C≡C), 1591, 1429, 1120, 699 (Si-C) cm<sup>-1</sup>. Elem. Anal. Calcd for (C<sub>16</sub>H<sub>10</sub>Si)<sub>n</sub>: C, 83.43; H, 4.38. Found: C, 82.56; H, 4.31. The excitation and fluorescence emission spectra in the solid state as well as TGA thermogram are described in Result and Discussion.

**Poly(diethynylmethylphenylsilane) (3b)** was prepared in the similar manner to that for the synthesis of **3a**, using **2b** (1.70 g, 10.0 mmol). Polymeric material **3b**, 0.55 g, 33%,

was obtained as a dark brownish solid state and almost insoluble in usual organic solvents such as THF and CHCl<sub>3</sub>. <sup>13</sup>C CP-MAS NMR (100 MHz): δ -0.28, 83.33-94.45 (br), 125.00-138.89 (br); <sup>29</sup>Si CP-MAS NMR (80 MHz): δ -35.75; IR (KBr): ν 3072, 2960, 2152 (C≡C), 1577, 1420, 1188, 1109, 787 (Si-C) cm<sup>-1</sup>; Elem. Anal. Calcd for (C<sub>11</sub>H<sub>8</sub>Si)<sub>n</sub>: C, 78.52; H, 4.79. Found: C, 78.45; H, 4.74. The excitation and fluorescence emission spectra in the solid state as well as TGA thermogram are described in Result and Discussion.

**Poly(diethynylmethyloctylsilane) (3c)** was prepared in the similar manner to that for the synthesis of **3a**, using **2c** (3.10 g, 15.0 mmol). Polymeric material **3c**, 0.95 g, 31%, was obtained as a dark brownish solid state and almost insoluble in usual organic solvents such as THF and CHCl<sub>3</sub>. <sup>13</sup>C CP-MAS NMR (100 MHz): δ -0.29, 15.28-35.99 (br), 81.94-98.61 (br); <sup>29</sup>Si CP-MAS NMR (80 MHz): δ -62.51; IR (KBr): ν 2956, 2925, 2855, 2147 (C≡C), 1625, 1461, 1414, 1263, 1059, 773, 660 cm<sup>-1</sup>. Elem. Anal. Calcd for (C<sub>13</sub>H<sub>20</sub>Si)<sub>n</sub>: C, 76.39; H, 9.86. Found: C, 76.44; H, 9.76. The excitation and fluorescence emission spectra in the solid state as well as TGA thermogram are described in Result and Discussion.

**Poly(1,2-diethynyl-1,1,2,2-tetramethyldisilane) (3d)** was prepared in the similar manner to that for the synthesis of **3a**, using **2c** (1.00 g, 6.02 mmol). Polymeric material **3d**, 0.17 g, 18%, was obtained as a dark brownish solid state and almost insoluble in usual organic solvents such as THF and CHCl<sub>3</sub>. <sup>13</sup>C CP-MAS NMR (100 MHz): δ 1.95, 80.56-97.22 (br); <sup>29</sup>Si CP-MAS NMR (80 MHz): δ -62.20; IR (KBr): ν 2957, 2154 (C≡C), 1617, 1403, 1253, 1052, 793 cm<sup>-1</sup>. Elem. Anal. Calcd for (C<sub>8</sub>H<sub>12</sub>Si<sub>2</sub>)<sub>n</sub>: C, 58.47; H, 7.36. Found: C, 58.55; H, 7.12. The excitation and fluorescence emission spectra in the solid state as well as TGA thermogram are described in Result and Discussion.

**Acknowledgment.** This work was supported by the Bisa Research Grant of Keimyung University in 2005 and partly by the Program for the Training of Graduate Students in Regional Innovation which was conducted by the Ministry of Commerce Industry and Energy of the Korean Government.

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