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

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We have carried out the Glaser oxidative coupling polymerizations of diethynyl diphenylsilane, diethynyl methylphenylsilane, diethynylmethyloctylsilane, and 1,2-diethynyl-1,1,2,2-tetramethylsilane to afford polycarbosilanes containing diethynyl and organosilane groups in the main chain, such as poly(diethynyl diphenylsilane), poly(diethynyl methylphenylsilane), poly(diethynyl methyloctylsilane), and poly(1,2-diethynyl-1,1,2,2-tetramethylsilane), respectively. These obtained materials are almost insoluble in common organic solvents such as CHCl₃ 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 C≡C stretching frequencies appear at 2147-2154 cm⁻¹, in particular. The polymers in the solid state exhibit that the strong maximum excitation peaks appear at 260-283 nm and the strong maximum fluorescence emission bands at 367-412 nm, especially. Thermogravimetric analysis of the materials shows that about 55-68% of the initial polymer weights remain at 400 °C in nitrogen.

Key Words: Polycarbosilanes, Diethynylsilane derivatives, Diethynyltetramethylsilane, 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. For instance, diacetylene-containing polycarbosilanes such as poly(silylene-diyne) were reported to synthesize by polycondensation reactions of the diacetylene dilithium salt with dichlorosilanes. The prepared materials with low molecular weights of \(M_n < 5000\) g/mol exhibit the conductivities ranging from \(8 \times 10^{-5}\) to \(3 \times 10^{-3}\) S cm⁻¹ when they are doped with FeCl₃. Pyrolysis of the polycarbosilane polymers in inert atmosphere results in a \(\beta\)-SiC ceramic material in high yield. Interestingly, the linear copolymers of silarylene-siloxane-diacetylene exhibit the elastomeric properties with thermal stabilities up to 330 °C in air. 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.

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

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 C=C-B-C and organosilicacyclic group along the polymer backbone by polyaddition reactions of 1,1-diyne-1-silacyclopent-3-enes with borane derivatives. We reported also the synthesis and photoelectronic as well as thermal properties poly(1,1-diyne-1-silacyclopent-3-enes and 1,1-diyne-1-silacyclobutane) by oxidative coupling reactions of diethynyl organosilicacyclic monomers. We also have already reported the preparation and excited-state energy dynamics of polycarbosilanes as well as polycarbogermes containing 1,4-bis(thiophene or phenylene)buta-1,3-diene in the polymer backbone. 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 diethynyl diphenylsilane (2a), diethynyl methylphenylsilane (2b), diethynyl methyloctylsilane (2c), and 1,2-diethynyl-1,1,2,2-tetramethylsilane (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(diethynyl diphenylsilane) (3a), poly(diethynyl methylphenylsilane) (3b), poly(diethynyl methyloctylsilane) (3c), and poly(1,2-diethynyl-1,1,2,2-tetramethylsilane) (3d), respectively. The obtained materials were characterized by IR and \(^{29}\)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 C≡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.17

All of the monomers 2a-d were characterized using several spectroscopic methods such as 1H, 13C, 29Si 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\(^{-1}\) in the IR spectra of the monomers 2a-d, respectively.18,19 The 1H 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, 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 13C 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.20,21 We have reported recently the Glaser oxidative coupling polymerization of 1,1-diethynyl-1-silacyclic derivatives as novel monomers. 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/acetoacetic acid 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\(_3\) and THF, probably due to the presence of the long rigid diacetylene group along the polymer main chain.22 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 has been ruled out by our observing the appearance of major singlet peak in the 29Si 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](image)

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

<table>
<thead>
<tr>
<th>Polymer</th>
<th>13C CP-MAS NMR(^{e}) (\delta) (ppm)</th>
<th>29Si CP-MAS NMR(^{e}) (\delta) (ppm)</th>
<th>IR(^{f}) (\nu_{C≡C}) (cm(^{-1}))</th>
<th>Excitation(^{g}) (\lambda_{em, max}) (nm)</th>
<th>Fluorescence(^{g}) (\lambda_{em, max}) (nm)</th>
<th>TGA(^{e})</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>86.11-98.89 (br), 125.25-147.22 (br)</td>
<td>−51.84</td>
<td>2110</td>
<td>283</td>
<td>367</td>
<td>55</td>
</tr>
<tr>
<td>3b</td>
<td>80.72, 83.33-94.45 (br), 125.00-138.89 (br)</td>
<td>−35.75</td>
<td>2152</td>
<td>266</td>
<td>412</td>
<td>68</td>
</tr>
<tr>
<td>3c</td>
<td>00.29, 15.28-35.99 (br), 81.94-98.61 (br)</td>
<td>−62.51</td>
<td>2147</td>
<td>260</td>
<td>392</td>
<td>62</td>
</tr>
<tr>
<td>3d</td>
<td>1.95, 80.56-97.22 (br)</td>
<td>−62.20</td>
<td>2154</td>
<td>262</td>
<td>406</td>
<td>65</td>
</tr>
</tbody>
</table>

\(^{e}\)CP-MAS NMR, \(^{f}\)By DRIFT method. \(^{g}\)Detection wavelengths at 360, 410, 400, and 400 nm in the solid state for 3a-d, respectively. \(^{h}\)Excitation wavelengths at 260, 260, 255, and 255 nm in the solid state for 3a-d, respectively. \(^{i}\)% Weight remaining at 400°C in nitrogen.
Figure 1. Excitation (dashed line, $\lambda_{\text{ex}} = 400 \text{ nm}$) and fluorescence (solid line, $\lambda_{\text{ex}} = 255 \text{ nm}$) spectra of the polymer 3c in the solid state.

Figure 2. TGA thermograms of the polymers 3a-d in nitrogen.
initial weight occurs between 200 and 600 °C. When 3e is heated to 900 °C, 68% of the initial weight of 3e 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 polyorganosilanes containing both diethynyl and organosilane groups such as poly(diethynylidendiphenylsilane), poly(diethynylmethyldiphenylsilane), poly(diethynylmethylhexyldisilane), and poly(1,2-diethynyl-1,1,2,2-tetramethyldisilane), by the Glaser oxidative coupling polymerizations of diethynylidendiphenylsilane, diethynylmethylphenylsilane, diethynylmethylhexyldisilane, and 1,2-diethynyl-1,1,2,2-tetramethyldisilane, respectively. The materials are not soluble in common organic solvents such as CHCl₃ 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 C≡C stretching frequencies appear at 2147-2154 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 strong maximum excitation peaks appear at 260-283 nm and that the obtained polyorganosilanes 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. 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 (0.32 mm × 30 m) coated with cross-linked methyl silicone gum and with flame ionization detector (FID). The column was deactivated immediately before use by injection of 10 µL of hexamethyldisilazane. ¹H, ¹³C, and ²⁸Si 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 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 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.

**Diethynylidendiphenylsilane (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 1 h. 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. 8.90 g (56.0%); bp 124-125 °C/0.05 mmHg. ¹H-NMR (400 MHz, CDCl₃): δ 7.79 (m, 10H, C=H), 7.36-7.79 (m, 10H, C=H); ¹³C-NMR (100 MHz, CDCl₃): δ 158.9, 142.9, 125.7, 111.7, 110.8, 100.8; IR (neat): ν 3274 (CH≡CH), 3072, 3060, 2970, 2935, 1674 (CH≡CH), 1589, 1429, 1310, 1234, 795 (Si-C), 551 (Si-C); δ 8.49; MS: m/z (relative intensity) 232 (M⁺, 51), 231 (100), 230 (21), 155 (M⁺-Ph, 31), 154 (22), 130 (16), 129 (42), 79 (6), 78 (4), 77 (14), 53 (34), 51 (14), 50 (7).
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1,2-Diethynyl-1,1,2,2-tetramethylsilane (2d) was prepared in the similar manner to that for the synthesis of 3a, using 2c (1.0 g, 15.0 mmol). Polymeric material 3e, 0.17 g, 18%, was obtained as a dark brownish solid state and almost insoluble in usual organic solvents such as THF and CHCl3.

1C CP-MAS NMR (100 MHz): δ = -0.29, 85.33-94.45 (br), 125.00-138.89 (br); 29Si CP-MAS NMR (80 MHz): δ = -35.75; IR (KBr): ν = 3072, 2960, 2152 (C≡C), 1577, 1420, 1188, 1109, 787 (Si-C) cm⁻¹; Elem. Anal. Calcd for C30H43Si: 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(diethynylmethylolotrisilane) (3c) was prepared in the similar manner to that for the synthesis of 3a, using 2c (3.10 g, 15.0 mmol). Polymeric material 3e, 0.95 g, 31%, was obtained as a dark brownish solid state and almost insoluble in usual organic solvents such as THF and CHCl3.

1C CP-MAS NMR (100 MHz): δ = -0.29, 15.28-35.99 (br), 81.94-98.61 (br); 29Si CP-MAS NMR (80 MHz): δ = -62.51; IR (KBr): ν = 2956, 2925, 2855, 2147 (C≡C), 1625, 1461, 1144, 1263, 705, 660 cm⁻¹; Elem. Anal. Calcd for C29H40Si3: 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-tetramethylsilane) (3d) was prepared in the similar manner to that for the synthesis of 3a, using 2c (1.0 g, 6.02 mmol). Polymeric material 3e, 0.17 g, 18%, was obtained as a dark brownish solid state and almost insoluble in usual organic solvents such as THF and CHCl3.

1C CP-MAS NMR (100 MHz): δ = 1.95, 80.56-97.22 (br); 29Si CP-MAS NMR (80 MHz): δ = -62.20; IR (KBr): ν = 2957, 2154 (C≡C), 1617, 1403, 1253, 1052, 793 cm⁻¹; Elem. Anal. Calcd for C29H40Si3: 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.

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References