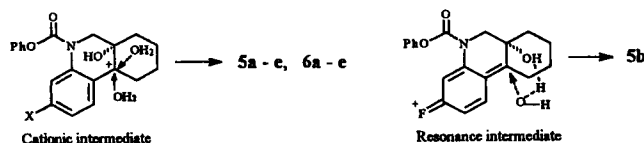


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7. A cationic intermediate is suggested to give epoxide opened products as below. Water near cation will randomly attack the positive carbon center to generate

the *cis* diols **5a-e** and allylic alcohols **6a-e** derived from *trans* diols. On the other hand, compound **2b** with fluorine at C3 can make a resonance intermediate. The hydrogen bonding between hydroxy group and water will place water at the same side with hydroxy group and predominantly induce the *cis* diol **5b**.



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Synthesis and Properties of Novel Poly[3,4-(silylisopropyl)benzo-1-silapentene]

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Received October 15, 1996

Introduction

Chlorosilane derivatives have received considerable academic and industrial attention since the direct synthesis process was developed.¹⁻³ Recently, novel chlorosilane derivatives such as 3,4-benzo-1,1-dichloro-1-silacyclopentene and allyldichlorosilane have been prepared by direct synthesis method.^{4,5} 3,4-Benzo-1,1-dimethyl-1-silacyclopentene undergoes anionic ring opening polymerization to give a thermally stable polycarbosilane.⁶ Friedel-Crafts reaction of aromatic compounds with allyldichlorosilane has also reported.^{7,8} We have previously reported the regioselective Friedel-Crafts reaction of allyldichlorosilane with 3,4-benzo-1,1-dichloro-1-silacyclopentene.⁹

Here we wish to report the synthesis of poly[3,4-(silylisopropyl)benzo-1-silapentene] by anionic ring opening polymerization of 3,4-[(silyl)isopropyl]benzo-1-silacyclopentene, which was prepared by the regioselective Friedel-Crafts reaction of allyldichlorosilane with 3,4-benzo-1,1-dichloro-1-silacyclopentene followed by reduction with LiAlH₄.

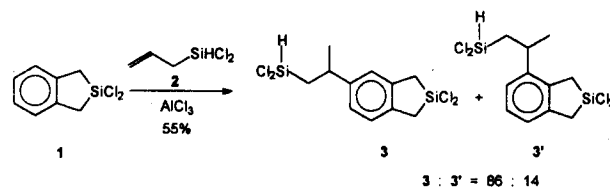
Results and Discussion

3,4-Benzo-1,1-dichloro-1-silacyclopentene (**1**) has the two reactive functional groups: the aromatic benzene ring and the chlorine atoms bonded to silacyclopentene ring. We previously reported that the Friedel-Crafts reaction of **1** with allyldichlorosilane (**2**) in the presence of AlCl₃ gave an 86:14 isomeric mixture of 3,4-[3'-(dichlorosilyl)isopropyl]benzo-1,

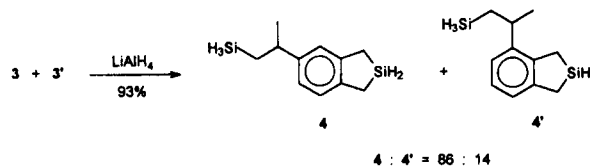
1-dichloro-1-silacyclopentene (**3**) and 3,4-[2'-(dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene (**3'**) in 55% yield (Scheme 1).⁹

The chlorine atoms bonded to silicon in the mixture of **3** and **3'** were easily converted in high yield into SiH groups by reduction with LiAlH₄ (Scheme 2).

The structure of the reduced product was determined by ¹H, ¹³C NMR spectra, IR spectrum, and mass spectrum analysis. The IR spectrum of the product shows the characteristic strong Si-H stretching at 2150 cm⁻¹.¹⁰ The isomeric ratio of the products **3** and **3'** was again confirmed. Based on the integration of ¹H NMR spectrum, the distilled product of 3,4-[3'-(silyl)isopropyl]benzo-1-silacyclopentene (**4**) contains the isomer of 3,4-[2'-(silyl)isopropyl]benzo-1-sila-



Scheme 1.



Scheme 2.

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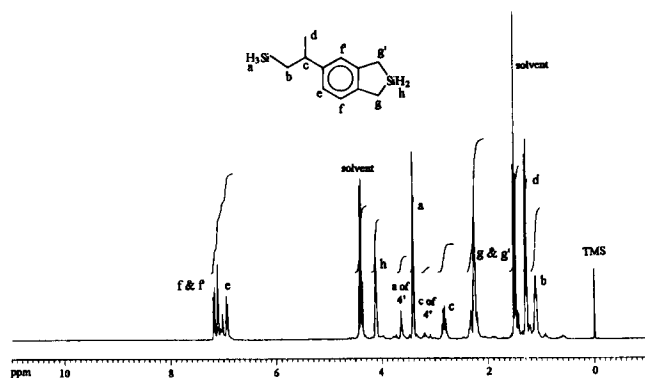
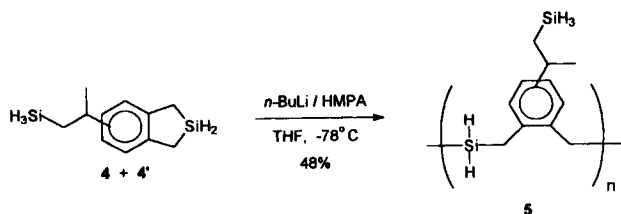


Figure 1. ^1H NMR spectrum of mixture of **4** and **4'**.



Scheme 3.

cyclopentene (**4'**) in the same ratio of 86:14 (*vide infra*) (Figure 1).

The triplet resonances appear at 3.33 ppm and 2.16 ppm for the SiH_3 group (H^a) and two methylene groups (H^g and H^h) of silacyclopentene ring, respectively. The multiplet resonances are observed at 0.77–0.82 ppm and 2.66–2.81 ppm for protons H^b and H^c , respectively. The doublet peak is observed at 1.20 ppm for methyl group (H^d). The quintet peak is observed at 4.03 ppm for SiH_2 in the silacyclopentene ring (H^e). The phenylene resonances appear at 6.79–6.89 ppm for H^f and at 6.99–7.22 ppm for H^f and H^f . The area ratio of the tertiary isopropyl proton (H^c of **4** and H^c of **4'**) in the ^1H NMR spectrum shows that an 86:14 isomeric mixture of **4** and **4'** has been formed. Moreover, the integrated ratio of the silyl proton (H^a of **4** and H^a of **4'**) in the ^1H NMR spectrum indicates the formation of isomeric mixture of **4** and **4'** in the same ratio of 86:14. Those facts are consistent with the structural conformation of **3** and **3'** by their derivatization reactions such as methylation or methoxylation.⁹

The obtained isomeric mixture of **4** and **4'** undergoes anionic ring opening oligomerization on treatment with a catalytic amount of *n*-butyllithium and hexamethylphosphoramide (HMPA) in THF at -78°C to yield poly[3,4-(silylisopropyl)benzo-1-silapentene] (**5**) (Scheme 3). The molecular weight is 920/530 ($\overline{M}_w/\overline{M}_n$).

After drying in vacuum, the oligomer **5** was slightly soluble in THF and CHCl_3 , probably due to the partial cross-linking of the reactive Si-H functional groups. IR spectrum of polymer **5** shows that characteristic Si-H stretching frequency appears again at 2148 cm^{-1} .¹⁰ We believe this polymerization process is initiated by nucleophilic attack of *n*-butyllithium at the silyl center of **4** or **4'** to form a pentacoordinate cyclic siliconate intermediate.¹¹ Ring opening of this intermediate leads to a *cis*-allyl anion which reacts rapidly with another monomer to form a new anionic sil-

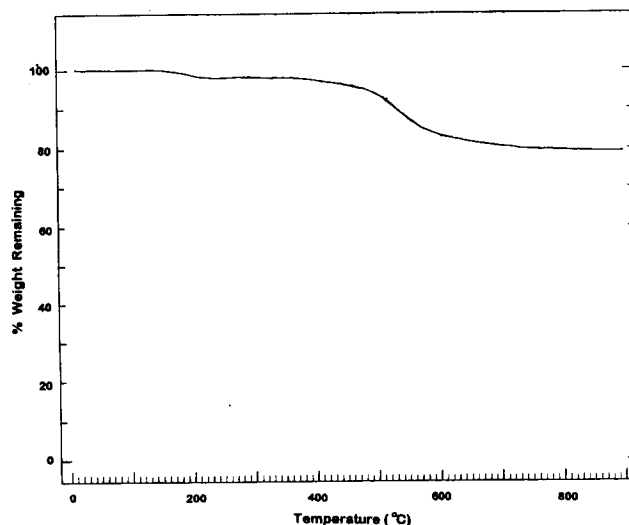


Figure 2. TGA thermogram of polymer **5** under N_2 .

iconate species.¹¹

The TGA of **5** is particularly unusual, even though the molecular weight is rather low (Figure 2).

Polymer **5** is stable in a nitrogen atmosphere to 150°C . When **5** is heated above this temperature, weight loss occurs in two stages. Between 150 and 250°C two percent of the initial weight of the sample is lost. Between 400 and 600°C an additional fifteen percent weight is lost. When the sample is heated to 900°C , a grayish black residue is obtained which amounts to about eighty percent of the initial weight of the polymer. This high 80% char yield is striking since poly(3,4-benzo-1,1-dimethyl-1-silapentene) and poly(3,4-benzo-1-phenyl-1-silapentene) undergo almost complete weight loss above 530°C .^{6,12} This char has been analyzed by ESCA (Figure 3).

The surface of the remained char was composed of silicon and carbon atoms. The analysis of C 1s high-resolution ESCA spectrum in Figure 3 shows that the binding energy peak at 282.7 eV may be attributed to carbidic carbon of the bulk $\beta\text{-SiC}$.¹³ This high char yield may result from both the reactive Si-H groups and aromatic C-C double bonds of polymer **5**.¹⁴

In conclusion, the regioselective Friedel-Crafts reaction of 3,4-benzo-1,1-dichloro-1-silacyclopentene with allyldichlorosilane catalyzed by Lewis acid AlCl_3 gave an 86:14 isomeric mixture of 3,4-[3'-(dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene and 3,4-[2'-(dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene, respectively. The isomeric ratio was confirmed by reduction reaction with LiAlH_4 . In addition, anionic ring opening polymerization of 3,4-[(silyl)isopropyl]benzo-1-silacyclopentene catalyzed by *n*-butyllithium/HMPA in THF at -78°C yielded oligo[3,4-(silylisopropyl)benzo-1-silapentene]. Pyrolysis of this material afforded a high 80% char yield at 900°C in nitrogen. This char was composed of silicon and carbon by ESCA analysis.

Experimental Section

All chemicals were purchased from Aldrich Chemicals

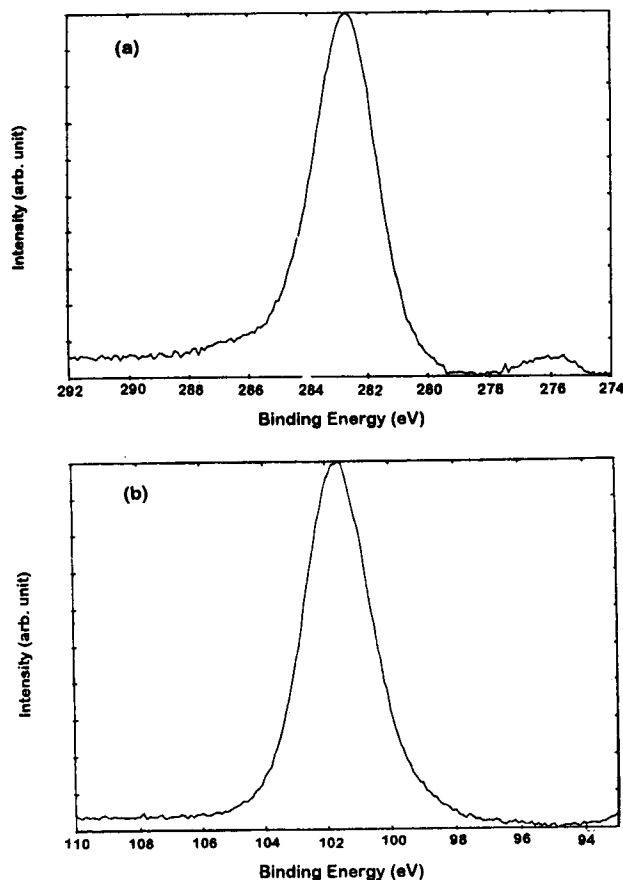


Figure 3. High-resolution ESCA spectra of C 1s (a) and Si 2p (b) of TGA residue.

Inc. Tetrahydrofuran (THF), *n*-hexane, and diethylether were distilled from sodium metal and benzophenone ketyl prior to use. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride and stored over 4 Å molecular sieves. All glassware was dried overnight in an oven at 120 °C. The apparatus was assembled and was then flame-dried while being swept with argon.

Reactions were monitored by a Hewlett Packard 5890II analytical GLC equipped with HP-1 capillary column (0.53 mm × 30 m) coated with cross-linked methyl silicone gum and with FID detector. The column was deactivated immediately before use by injection of 50 μL of hexamethyldisilazane.

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM-300 spectrometer. Chemical shifts were measured using tetramethylsilane as internal standard or the solvents as standard. IR spectra were recorded by a Shimadzu IR 430 spectrometer or a Bruker IFS-48 FTIR spectrometer.

Low resolution mass spectra were measured on a Hewlett Packard 5971A instrument by EI ionization at 70 eV. High-resolution mass spectra were obtained at the Korea Basic Science Institute Mass Spectrometry Facility on a JEOL JMS-SX102A mass spectrometer. Exact masses were determined by peak matching against known masses of perfluorokerosene.

Gel permeation chromatography (GPC) analyses were per-

formed on a Waters Model 510 system equipped with a Waters Styragel HR 3 column and a refractive index detector. The eluting solvent was HPLC grade THF at a flow rate of 1.0 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: M_p 580, 3250, 10100, and 28500 whose $\overline{M}_w/\overline{M}_n$ are less than 1.2.

Thermogravimetric analysis (TGA) of polymer samples was performed on a TGA-50 Shimadzu thermal analysis system. The temperature program for the analysis was from room temperature with a heating rate of 10 °C/min to 900 °C with nitrogen flow rate of 20 mL/min. ESCA spectra were measured on a VG ESCALAB MK II spectrometer.

3,4-Benzo-1,1-dichloro-1-silacyclopentene (1) and **allyldichlorosilane (2)** were generously provided by Dr. Il Nam Jung, Korea Institute of Science and Technology.

3,4-[3'-(Dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene (3)⁹. In a 250 mL 3-neck round bottom flask equipped with reflux condenser, pressure equalizing addition funnel, and a Teflon covered magnetic stirring bar was placed **1** (10.8 g, 0.05 mol) and AlCl₃ (0.67 g, 5.0 mmol) under argon atmosphere. The flask and its contents were immersed in an ice-water bath. **2** (6.20 g, 0.04 mol) was placed in the dropping funnel, and added dropwise to the well stirred mixture over 1 h. The reaction was exothermic and the mixture was stirred for 1 h after cooling. The reaction mixture was stirred vigorously with heating at 50 °C for 1 h and treated with NaCl (1.0 g). 20 mL of hexane was added, filtered and the volatile solvent removed by evaporation under reduced pressure. The residue was fractionally distilled. A fraction, bp 105-106 °C/5 mmHg, 7.5 g, 55% yield, was obtained. ¹H NMR (CDCl₃) δ: 1.36 (d, 3H, *J*=7 Hz), 1.55-1.61 (m, 2H), 2.57 (d, 4H, *J*=5 Hz), 3.07-3.14 (m, 1H), 5.33 (t, 1H, *J*=2 Hz), 7.02-7.05 (m, 1H), 7.11-7.20 (m, 2H). ¹³C NMR (CDCl₃) δ: 24.85, 24.89, 25.37, 30.34, 34.60, 125.37, 127.08, 129.32, 135.39, 137.51, 145.67. IR (KBr) ν: 3070, 3020, 2960, 2930, 2870, 2200 (Si-H), 1600, 1565, 1500, 1490, 1480, 1450, 1440, 1420, 1380, 1330, 1265, 1235, 1210, 1190, 1130, 1100-1000, 900-750, 600-500 cm⁻¹. MS *m/e* (relative intensity): 344 [M⁺, 63], 329 [(M-CH₃)⁺, 40], 301 [41], 265 [29], 229 [(M-SiHCl₂CH₂)⁺, 71], 193 [23], 129 [29], 115 [22], 83 [100]. Elemental Anal. Calcd. for C₁₁H₁₄Cl₄Si₂: C, 38.37; H, 4.10. Found: C, 37.80; H, 4.22. Compound **3** was containing 3,4-[2'-(dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene **3'** in 14% based on the ¹H NMR spectrum.

3,4-[3'-(Silyl)isopropyl]benzo-1-silacyclopentene (4). In a 250 mL 3-neck round bottom flask equipped with reflux condenser, pressure equalizing addition funnel, and a Teflon covered magnetic stirring bar were placed LiAlH₄ (2.40 g, 0.063 mol) and diethylether (100 mL) under argon atmosphere. A mixture of **3** and **3'** (14.58 g, 0.042 mol) and diethylether (100 mL) were placed in the addition funnel. This solution was added to the vigorously stirred suspension of LiAlH₄ over 2 h on the ice-water bath. After addition of a mixture of **3** and **3'**, the ice-water bath was then removed and the reaction mixture was stirred at room temperature overnight. Excess LiAlH₄ and salts were removed by filtration through a sintered glass filter. The salts were washed several times with pentane. The volatile solvent was removed by evaporation under reduced pressure. The residue was then fractionally distilled. A fraction, bp 86

$^{\circ}\text{C}/0.95\text{ mmHg}$, 8.01 g, 93% yield, was obtained. ^1H NMR (CDCl_3 , 300 MHz) δ : 0.77-0.82 (m, 2H), 1.20 (d, 3H, $J=6.8$ Hz), 2.16 (t, 4H, $J=3.6$ Hz), 2.66-2.81 (m, 1H), 3.33 (t, 3H, $J=3.6$ Hz), 4.03 (qui, 2H, $J=3.6$ Hz), 6.79-6.89 (m, 1H), 6.99-7.22 (m, 2H). ^{13}C NMR (CDCl_3 , 75 MHz) δ : 14.34, 14.90, 16.21, 24.61, 37.48, 124.31, 127.03, 128.98, 139.01, 141.44, 146.08. IR (neat) ν : 2990, 2940, 2150 (Si-H), 1530, 1440, 1385, 1190, 1145, 1090, 990, 950, 920, 870, 830, 770 cm^{-1} . MS m/e (relative intensity): 206 (M^+ , 58), 163 (58), 161 (100), 145 (15), 133 (47), 132 (67). HRMS calcd. for $\text{C}_{11}\text{H}_{18}\text{Si}_2$ 206.0947, found 206.0941.

Compound **4** was containing 3,4-[2'-(silyl)isopropyl]benzo-1-silacyclopentene **4'** in 14% on the base of ^1H NMR spectrum.

Poly[3,4-(silylisopropyl)benzo-1-silapentene] (**5**).

In a flame-dried 100 mL Schlenk flask equipped with a Teflon covered magnetic stirring bar under argon were placed a mixture of **4** and **4'** (3.0 g, 14.5 mmol), dry THF (40 mL) and five drops of HMPA. The flask was sealed with a rubber septum and was cooled to $-78\text{ }^{\circ}\text{C}$ in a dry ice/acetone bath. To the well stirred reaction mixture was slowly added *n*-butyllithium (0.12 mL, 0.19 mmol) via a syringe. The reaction was allowed to stir at $-78\text{ }^{\circ}\text{C}$ for 3 h. It was then quenched by addition of saturated aqueous ammonium chloride (10 mL). 50 mL of THF was then added, and the organic layer was washed with water, dried over anhydrous magnesium sulfate, filtered, and the solvents were removed by evaporation under reduced pressure. The residue was taken up in THF. The oligomeric material **5** was precipitated by addition of methanol ($\overline{M}_w/\overline{M}_n=920/530$), and was dried under high vacuum for 12 h. After drying in vacuum, the obtained material **5** was slightly soluble in THF or CHCl_3 . In this way, 1.43 g, 48% yield of **5** was obtained. ^1H NMR (CDCl_3 , 300 MHz) δ : 0.86 (m, 2H), 1.19 (d, 3H, $J=7.0$ Hz), 1.93 (m, 4H), 2.66 (m, 1H), 3.34 (m, 3H), 3.50 (m, 2H), 6.80-7.12 (m, 3H). IR (KBr) ν : 2958, 2918, 2148 (Si-H), 1606, 1486, 1456, 1138, 1145, 1076, 923, 874, 827, 788 cm^{-1} . TGA data are described in Results and Discussion.

Acknowledgment. We thank Dr. Il Nam Jung, Korea Institute of Science and Technology, for generous gifts of 3,

4-benzo-1,1-dichloro-1-silacyclopentene along with allyldichlorosilane and helpful discussions. We thank also Dr. Yunsoo Kim, Korea Research Institute of Chemical Technology for ESCA experiment and helpful discussions. This work was supported by the Korea Science and Engineering Foundation (941-0300-043-2) and partly by the Basic Science Research Institute Program, Ministry of Education (Project No. BSRI-95-3424) as well as the Center for Inorganic Materials Chemistry.

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