

Articles

Preparation of Organosilane Dendrimer Containing Allyl End Groups

Chungkyun Kim*, Eunmi Park, and Eunju Kang

Department of Chemistry, Dong-A University, Pusan 604-714, Korea

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A dendrimeric silane containing 162 allylic end groups is prepared via a divergent growing approach. The reaction process of the repetitive alkenylation and hydrosilylation cycles was monitored by NMR spectroscopic attachments. Both steps provided almost quantitative yields of pure silane dendrimers.

Introduction

The synthetic interest of dendrimer with highly controlled molecular architecture has increased lately.^{1,2} These tree-like molecules with polyfunctional groups are the result of repetitive growth starting from small core molecules in a highly controlled manner. From the core two or more identical branches emanate, each branch containing further branching points to its end. Such three dimensional emanated molecules with highly branched molecular architecture are called dendrimers.³ Two fundamentally different synthetic approaches have been developed. The divergent approach begins with a polyfunctional initiator core of which a number of branches are attached. In the next step, the ends of the branching points from which new branches are created. In a subsequent step, these reactive branch points are reacted with new branches, the ends of which can be functionalized again, and so on (Figure 1).^{1f} A second synthetic route to dendrimers was demonstrated earlier⁴ and followed the convergent strategy outlined in Figure 2. For the preparation of hyperbranched dendrimers involves convergent process in which growth begins at what will become the periphery of the final macromolecule and proceeds inward, the final

reaction being attachment to a polyfunctional core. These two approaches may provide polymers with varieties of new and improved properties.

Organic dendrimers has been actively investigated and functionalized.^{1b} However, silicon- and germanium-containing dendrimeric macromolecules and inorganic dendrimers have received limited attention.⁵ Seyferth *et al.*^{5c} carried out studies using tetravinylsilane as the core molecule and vinylmagnesium bromide in an allylation step. Dendrimers up to the fourth generation were prepared.

We report here our study of the synthesis of carbosilane dendrimer based on diallylsilane as the core molecule and hydrosilylation with HSiCl_3 and allylation with allylmagnesium bromide as the growth steps. The final product (**G4**) was the structurally well defined silane dendrimer up to the fourth generation with a molecular weight of 12,387 and 162 allylic end groups. The fifth generation of our dendrimeric silane was not structurally well defined, because the hydrosilylation process did not completely progress to **G5P**.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dry nitrogen using Schlenk techniques. Ether and THF were dried by distillation from blue solution of sodium-benzophenone ketyl, and the solvents such as pentane, benzene and toluene were dried and distilled from $\text{Na/K}_{2.8}$ amalgam. Glassware was dried under vacuum with $100^\circ\text{C}/10^{-1}$ torr. Commercially available chemicals were used as received.

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer, and the chemical shifts were referenced to internal solvent peaks. The mass spectra were obtained on a HP 5280 spectrometer by EI ionization at 70 eV. Elemental analysis was carried out by the Seoul Branch of Korean Basic Science Center.

G0. 100 mL of $\text{CH}_2=\text{CHCH}_2\text{MgBr}$ (100 mmol; 1 M solution in Et_2O) was slowly added over a period of 2 h to 8.02 g (41.90 mmol) of MePhSiCl_2 in 50 mL THF. The reaction mixture was refluxed for 6 h. After the solution had cooled to room temperature, solvent was removed under reduced pressure. The magnesium salts were precipitated in pentane

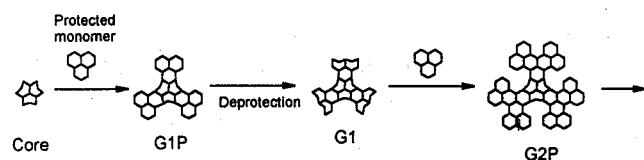


Figure 1. Divergent synthetic scheme of dendrimers.

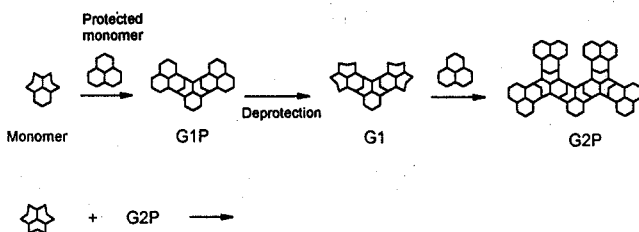


Figure 2. Convergent synthetic scheme of dendrimers.

and filtered off. The pentane was evaporated leaving a residue, which was distilled by 40 °C/10-1 torr. The product, **G0** (MePhSi(CH₂CH=CH₂)₂) was obtained as clear, colorless liquid with 6.18 g (30.58 mmol, 73%). The ¹H, ¹³C NMR data of the **G0** are given in Table 2, and the analytical data are given in Table 1.

Mass (70 eV rel. int. %): 202 (M⁺, 4), 161 ((M-CH₂CHCH₂)⁺, 100), 145 ((M-CH₂CHCH₂, CH₃)⁺, 50), 121 ((M-2(CH₂CHCH₂))⁺, 76), 105 ((M-2(CH₂CHCH₂), CH₃)⁺, 62), 43 ((M-2(CH₂CHCH₂), Ph)⁺, 46)

Table 1. Analytical data of dendrimeric silanes

Compds.	Formula	Molecular mass	No of end groups	Analysis found/calcd(%)	
				C	H
G0	C ₁₃ H ₁₈ Si ₁	202.37	2	77.39/77.16	9.00/8.97
G1	C ₃₁ H ₅₀ Si ₃	506.99	6	72.91/73.44	9.93/9.44
G2	C ₈₅ H ₁₄₆ Si ₉	1420.86	18	70.82/71.88	10.38/10.37
G3	C ₂₄₇ H ₄₃₄ Si ₂₇	4162.47	54	69.84/71.31	10.35/10.52
G4	C ₇₃₃ H ₁₂₉₈ Si ₈₁	12387.29	162	67.69/71.11	10.53/10.57
G4P-3H	C ₂₄₇ H ₆₅₀ Si ₈₁	5896.80	54	52.80/50.31	11.14/11.11

Table 2. NMR spectroscopic data of G0-G4 dendrimeric silanes

Compds.	MeSi	-CH ₂	=CH ₂	=CH	Ph
G0	¹ H -0.04(s, 3H) ¹³ C -5.85(G0)	1.55, 1.59(d, 4H, J=8 Hz, G0) 21.57(G0)	4.75-4.85 (m, 4H) 113.83	5.62-5.83 (m, 2H) 134.17	7.38-7.51(m, 5H) 127.73(o) 129.17(p) 133.92(m) 136.87(quant)
G1	¹ H 0.28(s, 3H) ¹³ C -5.02	0.64-0.73(m, 4H, G0) 0.82-0.90(m, 4H, G0) 1.32-1.51(m, 4H, G0) 1.56, 1.60(d, 12H, J=8 Hz, G1) 16.31, 18.10, 19.01(G0), 19.70(G1)	4.80-5.00(m, 12H) 113.47	5.64-5.86(m, 6H) 134.40	7.30-7.50(m, 5H) 127.69(o) 128.77(p) 133.75(m) 138.47(quant)
G2	¹ H 0.29(s, 3H) ¹³ C 0.98	0.58-0.69(m), 0.78-0.84(m) 1.25-1.41(m), 1.58, 1.62(d, 36H, J=8 Hz, G2) 16.57(G1), 17.50(G1-G0) 18.22(G1), 18.52, 19.44(G0) 19.69(G2)	4.85-4.95(m, 36H) 113.51 133.70(m) 138.54(quant)	5.73-5.86(m, 18H) 134.38	7.32-7.45(m, 5H) 127.69(o), 128.72(p)
G3	¹ H 0.27(s, 3H) ¹³ C -5.51	0.51-0.70(m), 1.12-1.42(m) 1.56, 1.60(d, 108H, J=8 Hz, G3) 16.67, 17.53(G2-G1) 17.80, 18.81(G0) 18.32(G2-G1) 18.58(G0) 19.72(G3)	4.84-4.93(m, 108H) 113.60 128.65(p) 133.88(m)	5.71-5.85(m, 54H) 134.36	7.30-7.46(m, 5H) 127.64(o)
G4	¹ H 0.25(s, 3H) ¹³ C	0.42-0.71(m), 1.20-1.49(m) 1.56, 1.60(d, 324H, J=8 Hz, G4) 16.77, 17.56, 18.43(G3-G0) 19.73(G4)	4.84-4.92(m, 324H) 113.74	5.62-5.84(m, 162H) 134.25	7.28-7.45(m, 5H)

G1P. A mixture of 1.13 g (5.59 mmol) **G0**, 2.94 g (21.94 mmol) HSiCl₃ and 0.03 g platinum catalyst (Pt on activated carbon, 10% Pt content) in 15 mL THF was stirred for 24 h at room temperature. When the reaction was completed by ¹H NMR, excessive HSiCl₃ and THF were removed under vacuum. The catalyst was filtered off in pentane and the pentane was evaporated leaving 2.55 g (5.38 mmol, 96%) of **G1P** (MePhSi(CH₂CH₂CH₂SiCl₃)₂) as clear, colorless liquid, which are very sensitive to moisture. The ¹H, ¹³C NMR chemical shifts of the **G1P** are given in Table 3.

G1. 50 mL of CH₂=CHCH₂MgBr (50 mmol; 1 M solution in Et₂O) was slowly added to 3.04 g (6.42 mmol) of **G1P** in 25 mL THF. The reaction of the mixture was refluxed for 12 h. When the reaction was completed by ¹H NMR, solvents were removed under reduced pressure. The magnesium salts were precipitated in pentane and filtered off. The pentane was evaporated leaving a residue, which obtained **G1** (MePhSi(CH₂CH₂CH₂Si(CH₂CH=CH₂)₃)₂) as clear, colorless oil with 2.22 g (4.37 mmol, 68%). The ¹H, ¹³C NMR data of the **G1** are given in Table 2, and the analytical data are given in Table 1.

G2P. A mixture of 2.22 g (4.37 mmol) **G1**, 7.40 g (54.6 mmol) HSiCl₃ and 0.05 g platinum catalyst (Pt on activated

Table 3. NMR Spectroscopic Data of G1P-G4P and G4P-3H Dendrimeric Silane

Compds.	MeSi	CH ₂	Ph
G1P	¹ H 0.34(s, 3H)	0.92-1.01(m, 4H, G0)	7.39-7.58(m, 5H)
		1.43-1.51(m, 4H, G0)	
		1.63-1.67(m, 4H, G0)	
	¹³ C -5.43	17.10, 28.18(G0)	128.00(o)
			129.30(p)
G2P	¹ H 0.29(s, 3H)	0.58-0.71(m)	
		0.80-0.92(m)	
		1.35-1.80(m)	
			7.34-7.52(m, 5H)
	¹³ C -5.30	15.35(G1)	127.82(o)
		16.50(G0)	128.94(p)
		17.29(G1)	133.71(m)
		18.36, 19.14(G0)	138.10(quant)
G3P	¹ H 0.27(s, 3H)	0.48-0.74(G2-G0)	7.30-7.45(m, 5H)
		1.15-1.38(G2-G0)	
		1.41-1.70(G2-G0)	
	¹³ C -5.17	15.44(G2-G0)	127.76(o)
		17.21(G1-G0)	128.00(p)
		17.39(G2)	133.88(m)
		17.55(G1-G0)	
G4P	¹ H 0.27(s, 3H)	0.46-0.80(G3-G0)	7.28-7.51(m, 5H)
		1.18-1.40(G3-G0)	
		1.40-1.80(G3-G0)	
	¹³ C -5.86	15.40, 17.40(G3)	127.68(o)
		18.60(G2-G0)	128.67(p)
		28.45(G3)	133.95(m)
			138.17(quant)
G4P-3H	¹ H 0.28(s, 3H)	0.48-0.72(G3-G0)	7.28-7.53(m, 5H)
		0.72-0.97(G3-G0)	
		1.21-1.60(G3-G0)	
	*-SH ₃ : 3.51 (t, 162H, J=4 Hz)		
	¹³ C -5.52	10.54, 15.94(G3)	127.64(o)
		18.67, 17.62(G2-G0)	128.63(p)
		21.73(G3)	133.85(m)
			138.28(quant)

carbon, 10% Pt content) in 10 mL THF was refluxed for 12 h. When the reaction was completed by ¹H NMR, excessive HSiCl₃ and THF were removed under vacuum. The catalyst was filtered off in pentane. The pentane was evaporated leaving 5.65 g (4.27 mmol, 98%) of **G2P** MePhSi(CH₂CH₂CH₂Si(CH₂CH₂CH₂SiCl₃)₃)₂ as clear, colorless liquid. The ¹H, ¹³C NMR data of the **G2P** are given in Table 3.

G2. 130 mL of CH₂=CHCH₂MgBr (130 mmol; 1 M solution in Et₂O) was slowly added to 6.30 g (4.77 mmol) of **G2P** in 25 mL Et₂O. The reaction mixture was refluxed for 12 h. When the reaction was completed by ¹H NMR, solvent was removed under vacuum. The magnesium salts were pre-

cipitated in pentane and filtered off. The solvent portion was evaporated, leaving a clear, colorless oil of 4.10 g (2.88 mmol, 61%) of **G2** (MePhSi(CH₂CH₂CH₂Si(CH₂CH₂CH₂Si(CH₂CH=CH₂)₃)₃)₂). The ¹H, ¹³C NMR data of the **G2** are given in Table 2, and the analytical data are given in Table 1.

G3P. A mixture of 4.10 g (2.88 mmol) **G2**, 10.0 g (73.8 mmol) HSiCl₃ and 0.03 g platinum catalyst (Pt on activated carbon, 10% Pt content) in 10 mL THF was refluxed over night. When the reaction was completed by ¹H NMR, excessive HSiCl₃ and THF were removed under vacuum. The catalyst was filtered off in pentane. The pentane was evaporated leaving 10.20 g (2.64 mmol, 92%) **G3P** (MePhSi(CH₂CH₂CH₂Si(CH₂CH₂CH₂SiCl₃)₃)₃)₂ as clear, colorless oil. The ¹H, ¹³C NMR data of the **G3P** are given in Table 3.

G3. 175 mL of CH₂=CHCH₂MgBr (175 mmol; 1 M solution in Et₂O) was slowly added to 10.20 g (2.64 mmol) of **G3P** in 25 mL Et₂O. The reaction mixture was refluxed over night. When the reaction was completed by ¹H NMR, solvent was removed under vacuum. The magnesium salts were precipitated in pentane and decanted. The solvent was evaporated leaving a clear, colorless oil. This material was chromatographed on silicagel using chloroform, as eluant. **G3** (MePhSi(CH₂CH₂CH₂Si(CH₂CH₂CH₂Si(CH₂CH₂CH₂Si(CH₂CH=CH₂)₃)₃)₃)₂) was obtained as clear, colorless oil (9.51 g, 2.28 mmol, 87%). The ¹H, ¹³C NMR data of the **G3** are given in Table 2, and the analytical data are given in Table 1.

G4P. A mixture of 3.27 g (0.78 mmol) **G3**, 8.02 g (59.2 mmol) HSiCl₃ and 0.05 g platinum based on hydrosilylation catalyst (Pt on activated carbon, 10% Pt content) in 10 mL THF was refluxed over night. When the reaction was completed by ¹H NMR, excessive HSiCl₃ and THF were removed under vacuum. The catalyst was filtered off in pentane. Removal of volatiles by vacuum left **G4P** (MePhSi(CH₂CH₂CH₂Si(CH₂CH₂CH₂Si(CH₂CH₂CH₂SiCl₃)₃)₃)₃)₂ as clear, colorless oil (8.50 g, 0.74 mmol, 95%). The ¹H, ¹³C NMR data of the **G4P** are given in Table 3.

G4. 26 mL of CH₂=CHCH₂MgBr (26 mmol; 1 M solution in Et₂O) was slowly added to 1.80 g (0.156 mmol) of **G4P** in 25 mL Et₂O. The reaction mixture was refluxed over night. When the reaction was completed by ¹H NMR, solvent was removed under vacuum. The magnesium salts were precipitated in pentane and decanted. The solvent was evaporated leaving colorless glass-type solid. This material was chromatographed on silicagel using chloroform as an eluant. **G4** (MePhSi(CH₂CH₂CH₂Si(CH₂CH₂CH₂Si(CH₂CH₂CH₂Si(CH₂CH₂CH₂Si(CH₂CH=CH₂)₃)₃)₃)₃)₂) was obtained as clear, colorless glass type material (0.61 g, 0.049 mmol, 32%). IR (KBr) 1628 cm⁻¹ for C=C stretching. Mol. wt (GPC) Mw=9862 (calcd 12387).

G4P-3H. A solution of 3.58 g (0.312 mmol) **G4P** in 25 mL Et₂O was added slowly to an ice-cooled suspension of LiAlH₄ (1 g, 26.35 mmol) in 50 mL Et₂O. The mixture was stirred at room temperature for 24 h and then the solvent was evaporated. The salts were precipitated in pentane and decanted. The reaction mixture was added slowly to 75 mL of an ice-cooled 1 N HCl solution. The layers were separated. The organic layers were washed out twice with distilled water and then were dried over anhydrous MgSO₄. The pentane solution was filtered. Removal of solvent left **G4P-3H**

(1.20 g, 0.20 mmol, 65%, $\text{MePhSi}(\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_3)_3)_3)_3)_2$) as colorless clear glass type solid.

Results and Discussion

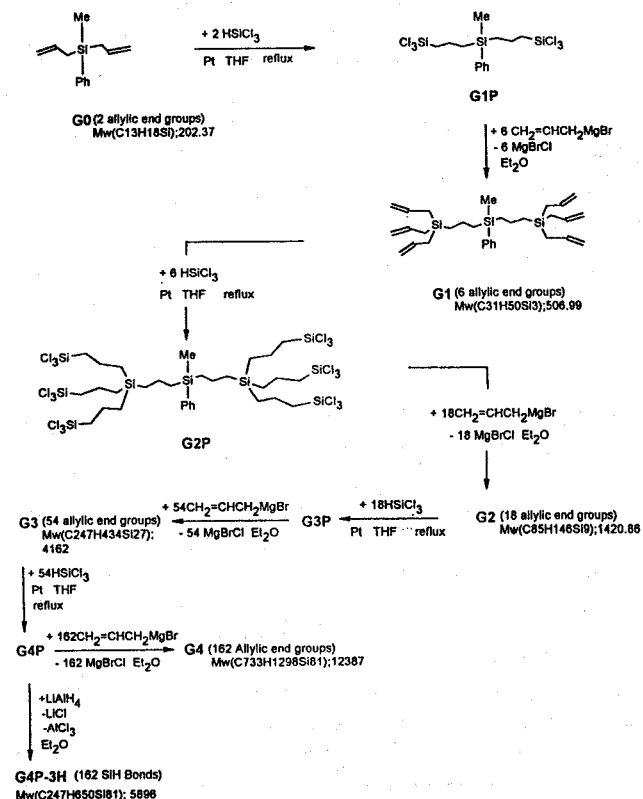
The synthetic method of our dendrimeric carbosilane is outlined in Scheme 1. Diallylsilane (**G0**) was the initiator core which was quantitatively prepared from exhaustive allylation of dichlorosilane with allylmagnesium bromide. The preparation of **G0** via exhaustive allylation gave a pure product, as observed by ^1H NMR spectrum of the reaction mixture was obtained. The work-up gave **G0** in 73% isolated yield. Then the allyl groups of **G0** were hydrosilylated with an excess of trichloromethylsilane in THF solution by a hydrosilylation catalyst (Pt on activated carbon with 10% content; 10^{-4} – 10^{-5} mol per double bond) giving **G1P** with two SiCl_3 functional groups each end branches. The ^1H NMR spectrum of the reaction mixture showed a quantitative yield of **G1P**. After purification of the reaction mixture, **G1P** was obtained in 96% yield. (see Table 3).

Next, all the active functional groups (6 Si-Cl bonds) of **G1P** were reacted with allylmagnesium bromide in THF refluxing condition over night to produce a dendrimeric silane with 6 allylic end groups (**G1**), which were formed in quantitative yields and confirmed by ^1H NMR spectrum. Its ^1H NMR spectrum clearly showed three multiplet at δ 0.64–0.73, 0.82–0.90, and 1.32–1.51 ppm for old generation (**G0**) and 1.56, 1.16 ppm ($-\text{CH}_2-$), 4.80–5.00 ($\text{CH}_2=$), and 5.64–5.86 ($\text{CH}=\text{}$)

ppm of characteristic allylic end groups for new generation (**G1**; see Figure 1, 2 and Table 2).

This first generation (**G1**) can be converted into a protected second generation (**G2P**) with 18 active functional groups by the hydrosilylation process. The **G2P** generation can be converted into a **G2** generation by the alkenylation process by reacting with allylmagnesium bromide. By repetition of the hydrosilylation-alkenylation cycles, third (**G3**) and fourth (**G4**) generations were obtained.

The fifth generation (**G5** contained 486 allylic end groups and M_w ; 37,061) of dendrimeric silane could not be prepared by general preparative cycle applied to the 4th generation due to the phenomenon of surface congestion.^{2a,b} Most likely, steric congestion in the periphery hindered a complete reaction and therefore, more forcing reaction conditions had to be applied. When THF solution of **G4**, with an excess of HSiCl_3 and platinum catalyst was sealed in a thick-walled glass tube and heated at 100 °C for 12 h, hydrosilylation of allyl groups of **G4** was incompletely progressed to **G5P** ($\text{MePhSi}(\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_3)_3)_3)_3)_3)_2$) according to the ^1H NMR spectrum of the reaction mixture. But both steps (alkenylation and hydrosilylation) applied to **G4P** produced **G4** in almost quantitative yields after a simple chromatographic pu-



Scheme 1. Schematic view of synthetic routes for dendrimeric silane.

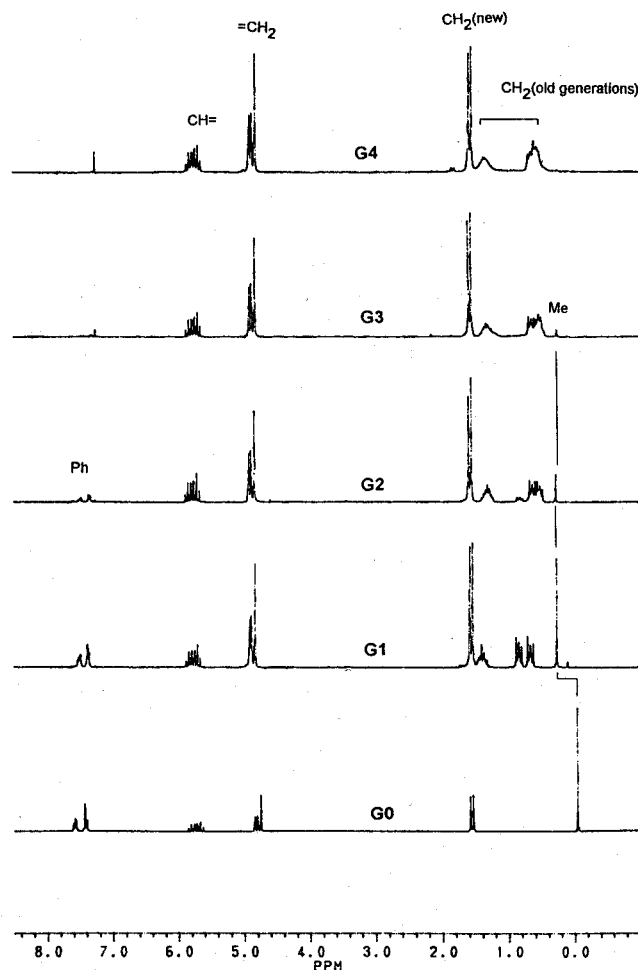


Figure 3. ^1H NMR spectroscopic view of each generation of dendrimeric silanes.

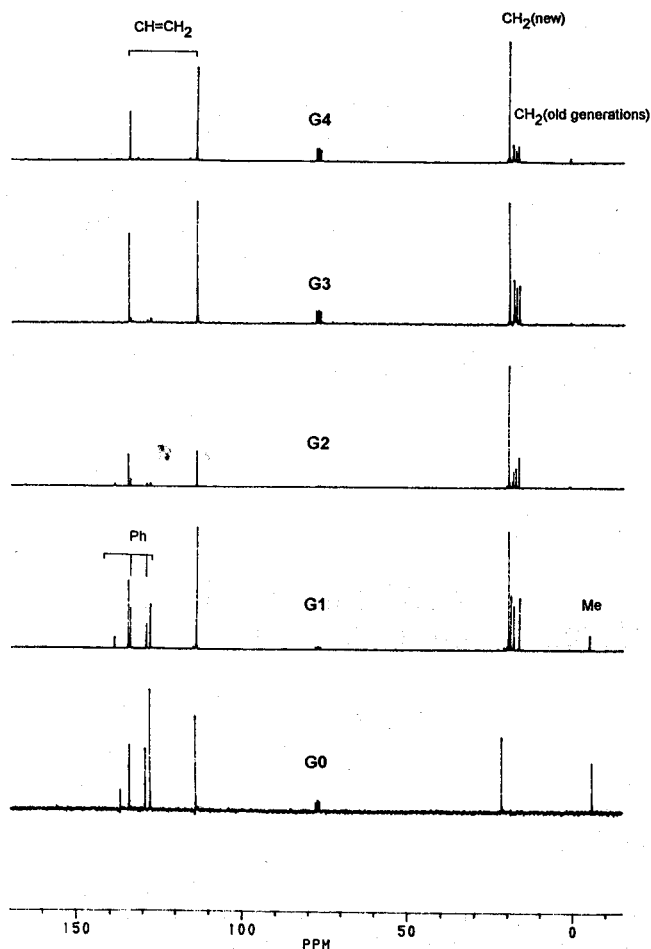


Figure 4. ^{13}C NMR spectroscopic view of each generation of dendrimeric silanes.

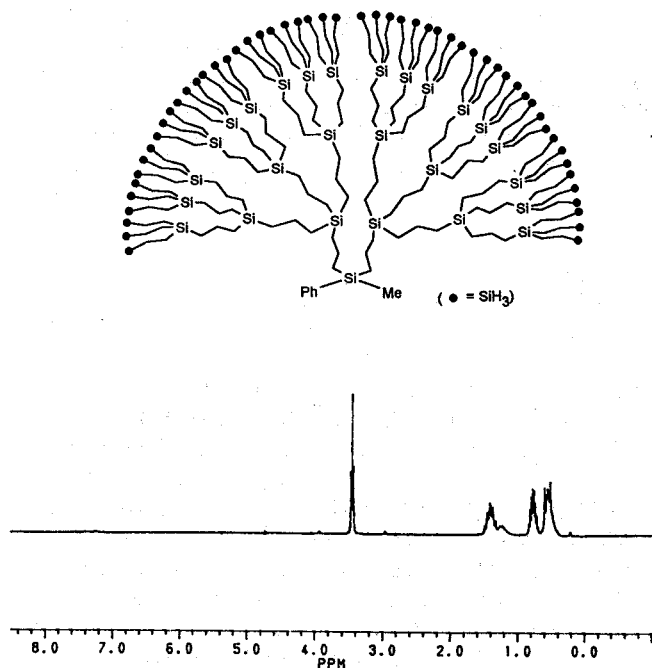


Figure 5. ^1H NMR spectrum of the G4P-3H generation of dendrimeric Silane with 162 Si-H bonds.

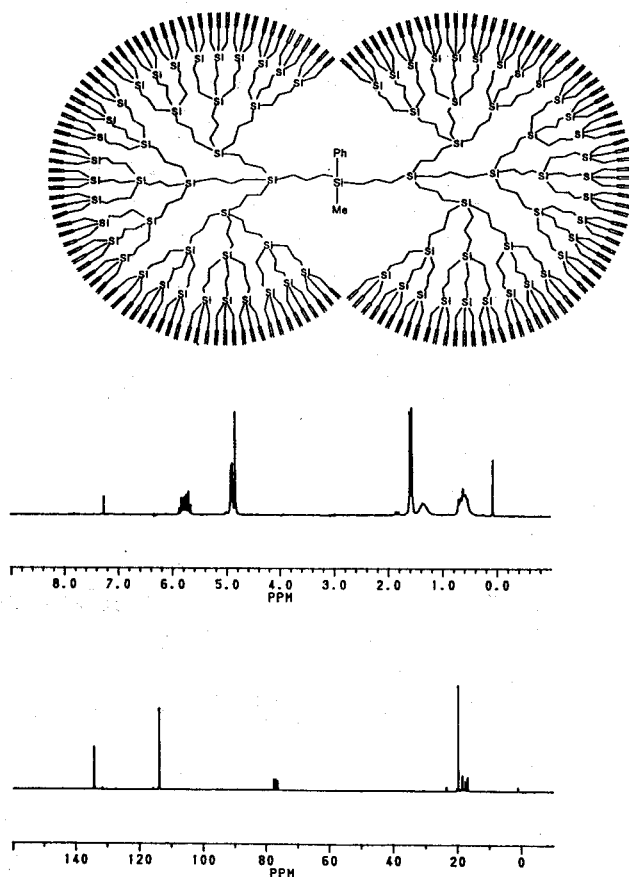


Figure 6. The schematic view of 4th generation of dendrimeric silane with 162 allylic end groups and its ^1H and ^{13}C NMR spectra.

rification of the dendrimers, as is evident from ^1H , ^{13}C NMR spectra, gel-permeation chromatography (GPC) trace and elemental analysis (C, H).

The LAH reduction of **G4P** with 162 Si-Cl bonds gave **G4P-3H** dendrimer ($M_w=5890$) in good yield. The dendrimeric carbosilanes, **G0** (M_w ; 202.37), **G1** (506.99), and **G2** (1420.86) are clear colorless liquids whose viscosity increases with the growing generation while **G3** (4162) and **G4** (12387) are colorless wax-like compounds.

All generations exhibit reasonable solubility in a wide range of solvents including, toluene, diethyl ether, chloroform and THF.

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Synthesis and Characterization of Thallium (III) Complexes with Tetracyanoquinodimethane, $\text{Ti}(\text{TCNQ})_3$ and $\text{TlCl}_2(\text{TCNQ})_{2.5}$

Mi-Kyung Kim, Young-Inn Kim*, Seong Bae Moon, and Sung-Nak Choi†

Department of Chemistry Education, Pusan National University, Pusan 609-735, Korea

*Department of Chemistry, Pusan National University, Pusan 609-735, Korea

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$\text{TlCl}_2(\text{TCNQ})_{2.5}$ and $\text{Ti}(\text{TCNQ})_3$ were obtained from the reaction of LiTCNQ (TCNQ =tetracyanoquinodimethane) and TiX_3 ($\text{X}=\text{Cl}$ and NO_3). These compounds were characterized by spectroscopic (IR, UV, EPR), electrochemical methods, and electrical conductivity measurements. Thermal analysis (TG, DSC) was also conducted. The room temperature electrical conductivities of these compounds are in the range of semiconductors. Spectroscopic studies indicate that $\text{Ti}(\text{TCNQ})_3$ has fully ionized TCNQ^- ions in a form of simple salt, whereas $\text{TlCl}_2(\text{TCNQ})_{2.5}$ is consisted of TCNQ^- and TCNQ^0 as a complex salt. EPR $\langle g \rangle$ values of TCNQ^- radical anion are 1.999 in both compounds and the signal attributable to metal ion is not observed, suggesting that any unpaired electrons are localized on TCNQ radicals, and metal atoms have diamagnetic state. Ligand decomposition and reduction process are simultaneously progressed in both compounds above at 200 °C. The endothermic activation energy of $\text{TlCl}_2(\text{TCNQ})_{2.5}$ is shown somewhat larger than that of $\text{Ti}(\text{TCNQ})_3$, it may be due to Ti-Cl bond strength. The mid-peak potentials of these compounds are very similar to those of TCNQ and the values of E_{pa} and E_{pc} are almost equal to 1. The wave of thallium ion is not detected in cyclic voltammogram, hence the redox processes of the complexes might be mainly localized to the TCNQ ligand rather than thallium ion.

Introduction

The understanding of the electrical properties of purely organic compounds has been focused over past fifteen years. While most of known organic materials are electrical insulators, some of those exhibit high electrical conductivity comparable to metals.¹ Conducting organic compounds have been called as "organic metals" or "synmetals". Many researchers have performed in the studies of their designs, syntheses and physical properties as well as their potential technological applications.¹⁻⁹ Two paths of conducting organic charge transfer complexes are proposed as follows: One is the combination of various organic cations with TCNQ .²⁻⁶ But, the conductivities of these complexes are lower than that of tetrathiafulvalene-tetracyanoquinodimethane (TTF- TCNQ) com-

pound.² The others are focused on the electrical properties of TTF- TCNQ and their relationship to the metallic state.

We have interested in incorporating inorganic materials with TCNQ . Shchegolov and coworkers⁶ first reported a 1:1 and a 1:2 complex between bis(benzene)-chromium and TCNQ . Siedle and coworkers⁷ also reported $\text{V}(\text{TCNQ})_2$, $\text{Cr}(\text{TCNQ})_2(\text{CH}_3\text{CN})_2$, $\text{Mo}(\text{TCNQ})(\text{CO})_2$, $\text{W}(\text{TCNQ})(\text{CH}_3\text{CN})_2$, $\text{Co}(\text{TCNQ})(\text{CH}_3\text{CN})_2$, and $\text{Ni}(\text{TCNQ})_2$. All of these complexes exhibited interesting properties, but none of them were conducting. TCNQ molecule is a very interesting ligand;¹⁰ (i) stacking ligand to form aggregates *via* π/π interaction (ii) ambidentate and bridging ligand through one or more nitrile N lone pairs (iii) non-innocent ligand to be reduced to anionic radical and further to dianionic form exhibiting unusual conducting, optical, and magnetic properties.