

Articles

Synthesis and Characterization of A Carbosilane Dendrimer Containing Allylic End Groups

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Received October 10, 1995

A silane dendrimer with 48 allylic end groups has been synthesized in excellent yield, *via* repetitive alkenylation-hydrosilation cycles. Starting with hexaallylethylenedisilane ((CH₂=CHCH₂)₂SiCH₂)₂ as the core molecule (**G0**), a succession of alternate platinum catalyzed hydrosilation (Pt/C, 10% platinum content on active carbon) of all allyl groups with methyldichlorosilane and the allylation of all SiCl₂ groups with allylmagnesium bromide in THF provided 3rd generation (**G3**) as carbosilane dendrimer. All the generations of dendrimer have been characterized by ¹H and ¹³C NMR spectroscopy as well as elemental analysis.

Introduction

Much interest has been developed in a group of macromolecules known as dendrimers.¹ A literature search shows that the number of publications in this field has increased exponentially over several years.^{1a} A very extensive review of the organic dendrimer and related synthesis has appeared.^{1a-c} The preparation of the first carbosilane dendrimer introduced by Made *et al.* was performed by repetitive alkenylation and hydrosilation cycles.² More recently, Seyferth *et al.* prepared the carbosilane dendrimer with vinyl groups by the reaction of corresponding chlorosilane with vinylmagnesium bromide.³ Another type of dendrimeric polysilane was prepared and characterized by Lambert and co-workers,⁴ whose electronic properties should be as interesting as those of linear polysilane. Masamune and co-workers prepared dendrimeric polysiloxane containing SiH groups,⁵ and Sakurai *et al.* prepared polysilane dendrimer.⁶

In this paper, we wish to describe the synthesis of carbosilane dendrimer based on hexaallylethylenedisilane (*N*₁=6) as the core molecule (**G0**) and hydrosilation with methyldichlorosilane (**GnP**) in the presence of platinum catalyst (Pt/C) and allylation with allylmagnesium bromide (**Gn**) as the growth steps. The final product was a carbosilane dendrimer whose periphery contained 48 allylic end groups with a molecular weight of 5634. This model is more branched than previous syntheses^{2,3} for the preparation of the vinyl and allyl groups containing organosilane dendrimers.

Experimental

All preparations were carried out in dried solvents under nitrogen atmosphere. ¹H and ¹³C NMR spectra were recorded on a Bruker AC 200 spectrometer. The mass spectra were obtained on a HP 5280 spectrometer by EI ionization at 70 eV. HPLC was performed on a Waters Delta Prep 4000 HPLC equipped with a Bondapark C18, 125A and 25×100 mm cartridge column. Elemental analysis was carried out by

the Korean Basic Science Center in Seoul. Melting point was measured on a Buchi 510 melting point apparatus in sealed glass capillaries.

The following abbreviations are used in those experiments: **Gn** refers to each generation of dendrimeric silane with allylic end groups (*n*=0-3); **GnP** refers to each generation of dendrimeric silane with dichloromethylsilane on its terminal point (*n*=0-3); *N*₁ refers to initiator core (in our experiment, initiator core has 6 branching sites (*N*₁=6)) and *N*₂ refers to branching for each new layer (*N*₂=2 in our experiments).

G0P. A mixture of 6.38 g (39.5 mmol) of trichlorovinylsilane, 7.58 g (55.96 mmol) of trichlorosilane and 0.03 g of platinum based on hydrosilation catalyst (Pt on activated carbon, 10% Pt content) was stirred for 24 h at room temperature. When the completed reaction was checked by ¹H NMR spectroscopy, excessive HSiCl₃ was removed under vacuum. The catalyst was filtered off in pentane. The pentane was evaporated leaving a residue, which contained only Cl₃SiCH₂CH₂SiCl₃ (**G0P**) confirmed by ¹H NMR. The product was sublimated at 80 °C/10⁻¹ torr, which obtained 10.80 g (36.34 mmol, 92%) of **G0P** (Cl₃SiCH₂CH₂SiCl₃) as white crystals (mp 41 °C). The **G0P** was very sensitive to moisture. The ¹H and ¹³C NMR chemical shifts of the **G0P** are given in Table 3.

General procedure for allylation (preparation of Gn). The solution of 9.00 g (30.30 mmol) of **G0P** (Cl₃SiCH₂)₂

Table 1. Analytical Data of Dendrimeric Silanes

Compds.	Formula	Molecular mass*	No of end groups	Analysis (found/calcd., %)	
				C	H
G0	C ₂₀ H ₃₄ Si ₂	330.66	6	72.26/72.65	10.33/10.36
G1	C ₆₂ H ₁₁₈ Si ₈	1088.30	12	68.17/68.43	10.83/10.93
G2	C ₁₄₆ H ₂₈₆ Si ₂₀	2603.59	24	67.13/67.35	10.98/11.07
G3	C ₃₁₄ H ₆₂₂ Si ₄₄	5634.15	48	67.69/66.94	10.53/11.13

*: calculated mass

Table 2. NMR Spectroscopic Data of G0-G3 Dendrimeric Silanes

Comps.		MeSi	-CH ₂	=CH ₂	=CH
G0	¹ H		0.53 (s, 4H) 1.58, 1.62 (d, 12H <i>J</i> =8 Hz)	4.73-5.02(m, 12H)	5.64-5.91(m, 6H)
	¹³ C		3.29, 19.13	113.55	134.30
G1	¹ H	-0.01 (s, 18H)	0.35 (s, 4H, G0P) 0.58-0.68 (m, 24H, G0) 1.23-1.44 (m, 12H, G0) 1.53, 1.57 (d, 24H, <i>J</i> =8 Hz, G1)	4.70-4.90(m, 24H)	5.63-5.87(m, 12H)
	¹³ C	-5.71 (G1)	4.76 (G0P) 17.00, 18.14, 18.37 (G0) 21.50 (G1)	113.10	134.77
G2	¹ H	-0.06 (s, 18H, G1) -0.01 (s, 36H, G2)	0.35 (s, 4H, G0P) 0.52-0.67 (m, 72H, G1-G0) 1.20-1.45 (m, 36H, G1-G0) 1.53, 1.57 (d, 48H, <i>J</i> =8 HZ, G2)	4.81-4.90(m, 48H)	5.68-5.90(m, 24H)
	¹³ C	-5.67 (G2) -4.94 (G1)	4.79 (G0P) 17.18, 18.62, 19.18 (G0) 18.01, 18.29, 18.84 (G1) 21.50 (G2)	113.09	134.78
G3	¹ H	-0.07 (s, 54H, G2-G1) -0.01 (s, 72H, G3)	0.42 (s, 4H, G0P) 0.50-0.67 (m, 168H, G2-G0) 1.18-1.43 (m, 84H, G2-G0) 1.53, 1.57 (d, 96H, <i>J</i> =8 Hz, G3)	4.72-4.90(m, 96H)	5.66-5.91(m, 48H)
	¹³ C	-5.66 (G3) -4.92 (G2-G1)	17.16, 18.56, 19.05 (G1) 17.99, 18.29, 18.81 (G2) 21.49 (G3)	113.10	134.74

Table 3. Spectroscopic Data of G0P-G3P Dendrimeric Silanes

Comps.		MeSi	MeSiCl ₂	CH ₂
G0P	¹ H			1.58 (s, G0P)
	¹³ C			16.29 (G0P)
G1P	¹ H		0.77 (s, 18H, G1P)	0.43 (s, 4H, G0P) 0.65-0.76 (m, 12H, G0) 1.15-1.24 (m, 12H, G0) 1.43-1.64 (m, 12H, G0)
	¹³ C		5.53	4.28 (G0P) 15.45, 17.37, 25.89 (G0)
G2P	¹ H	-0.01 (s, 18H, G1)	0.77 (s, 36H, G2P)	0.38 (s, 4H, G0P) 0.50-0.68 (m, 36H) 1.10-1.24 (m, 36H) 1.41-1.62 (m, 36H)
	¹³ C	-5.06	5.51	4.74 (G0P) 17.06, 18.57, 18.80 (G0) 17.34, 17.53, 25.92 (G1)
G3P	¹ H	-0.06 (s, 18H, G1) -0.02 (s, 36H, G2)	0.77 (s, 72H, G3P)	0.37 (s, 4H, G0P) 0.50-0.70 (m, 84H) 1.18-1.23 (m, 84H) 1.42-1.63 (m, 84H)
	¹³ C	-5.03 (G2) -4.93 (G1)	5.53	4.76 (G0P) 18.51, 18.60, 18.70 (G1-G0) 17.35, 17.51, 25.93 (G2)

CH₂SiCl₃) in 50 mL Et₂O was added slowly to 200 mL of 1.0 M allylmagnesium bromide (200 mmol). The reaction mixture was refluxed for 6 h (for the synthesis of G2 and G3 must be the reaction of the mixture refluxed in THF/Et₂O during overnight). When the completed reaction was checked by ¹H NMR spectroscopy, solvents were removed under vacuum. The magnesium salts were precipitated in pentane and filtered off (for the synthesis of G3, the reaction mixture was separated by decantation). The organic layer was washed off with distilled water, dried on MgSO₄ and concentrated to yield 7.01 g (21.21 mmol, 70%) of ((CH₂CH=CH₂)₃SiCH₂CH₂Si(CH₂CH=CH₂)₃) G0. The products G

1-G3 were obtained as clear, colorless oil whose viscosity increases with growing generations. The G3 was purified by preparative HPLC eluting with methanol. ¹H and ¹³C NMR spectroscopic measurements of each generations were shown to be pure dendrimeric silane (Table 2). All the isolated dendrimeric silane of each generation was isolated over 70% yield.

General procedure for hydrosilylation (preparation of GnP). A mixture of 2.60 g (7.80 mmol) of G0, 9.40 g (81.70 mmol) of MeSiHCl₂ and 0.03 g platinum based on hydrosilation catalyst (Pt on activated carbon, 10% Pt content) was refluxed for 24 h in THF. When the completed

reaction was checked by ^1H NMR spectroscopy, excessive HMeSiCl_2 and solvent were removed under vacuum. The catalyst was filtered off with pentane or removed by decantation (G3P). The pentane was evaporated leaving a residue, which according to NMR contained only $(\text{Cl}_2\text{SiMeCH}_2\text{CH}_2\text{CH}_2)_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMeCl}_2)_3$ G1P. The product, G1P of 7.56 g (7.41 mmol, 95%), was obtained as clear, colorless liquid. The ^1H , ^{13}C NMR chemical shifts of the G1P are given in Table 3. The product of G1P-G3P was obtained as clear, colorless and air-sensitive oil whose viscosity increases with growing generation. All the isolated dendrimeric silane of each G_nP generations produced almost quantitative yields.

Results and Discussion

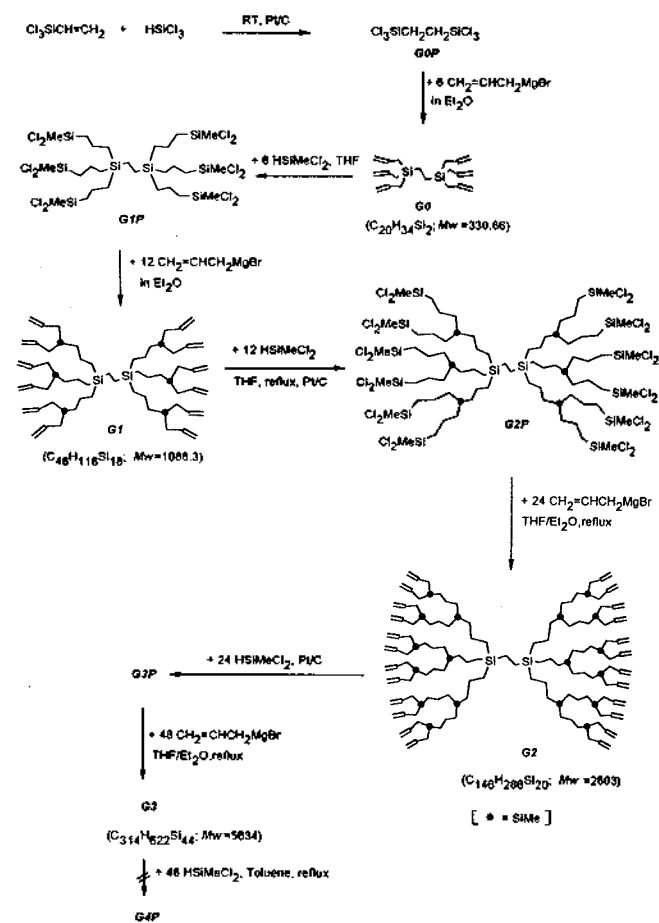
The synthesis of our silane dendrimers starts with exhaustive allylation of hexachloroethylenedisilane ($\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{SiCl}_3$) with allylmagnesium bromide to produce hexaallylethylenedisilane ($(\text{CH}_2\text{CHCH}_2)_3\text{SiCH}_2\text{CH}_2$). This six-fold initiator molecule has been attached to six functional core point (N_1), the so called G0 generation. In the next step, the 6 allyl groups of G0 are hydrosilylated by methylchlorosilane in the presence of platinum catalyst (Pt/C, 10% content of Pt on activated carbon) for hydrosilylation with quantitative yield which is a molecule contained in 12 terminal Si-Cl bonds (Scheme 2). But a reaction of G0 with trichlorosilane was not completely formed by a molecule containing 6 SiCl_3 groups from room temperature and 200 °C in toluene. The products observed by ^1H NMR were the half-reacted compounds of G0 (Scheme 1).

The G1P molecule containing 12 growth cores ($N_B=2$) was produced by the reaction of 12 equiv allylmagnesium bromide with a dendrimeric silane having 12 allylic end groups (G1) via overnight refluxing in THF. The complete reaction of G1P to G1 was confirmed by ^1H NMR spectroscopy. The G1 generation of silane dendrimer was produced with 12 equiv allylmagnesium bromide in quantitative yield. The G1 dendrimeric molecule is converted into G2P via the same hydrosilylation process, and G2P generation containing 24 Si-Cl bonds was produced via alkenylating G2 containing 24 allylic end groups via alkenylation process. By the repetition of the alkenylation and hydrosilylation cycle, the third generation could be produced to G3. The G3 is purified by HPLC eluting with methanol. All the preparation of each generation dendrimer was made on the basis of the exhaustive yields that can be obtained for the formation of G_n from G_nP and G_{n+1}P from G_n . However G3 with excess of HSiMeCl_2 did not completely progress to G4P with 48 SiCl_2 groups. The major product shown by ^1H NMR was the half-reacted product of previous generation. The reason for this failure is not entirely clear, but possibly due to steric hindrance.

The third generation of our silane dendrimer (G3) has 48 allylic end groups. The prepared silane dendrimers (G_n and G_nP) are dramatically provided by the pure substance of NMR spectroscopic views as well as HPLC. By ^{13}C NMR spectroscopic attachments, the growth of molecule through repeated hydrosilylation and alkenylation cycle could be demonstrated. The novel carbosilane dendrimers (G_n) have been characterized by ^1H and ^{13}C NMR spectroscopy as well as elemental analysis. The ^1H NMR spectra for G0-G3 show



Scheme 1.



Scheme 2. Schematic View of Synthetic Routes for Dendrimeric Silane.

three main regions: resonances with 4.5-6.0 ppm refers to allylic proton, 0.5-1.5 ppm refer to CH_2 protons, and -0.3-0.0 ppm with single signal refer to MeSi protons. They have also different resonance region between end groups (new generation) and inner core groups (old generation). ^1H NMR spectroscopy allows each different building block to be determined and it also allows subtle structure change for G_n and G_nP type to be clearly detected (Table 2 and 3). For example, a great difference between allylic end group containing generation (G0-G3) and hydrosilylated group containing generation (G1P-G3P) is also observed by ^1H NMR spectroscopy. In all cases, the intergration of resonance was employed to further confirm the generation number and to ascertain whether the reaction of G_n with HSiMeCl_2 (or G_nP with allylmagnesium bromide) reached to completion. More complete information can be gathered from the analysis of the ^{13}C NMR spectra of G_n and G_nP generations. A greater difference between G_n and G_nP generator is observed between 25 to -10 ppm. The core groups (old generation) show unique resonance about -5 ppm for MeSi signal and

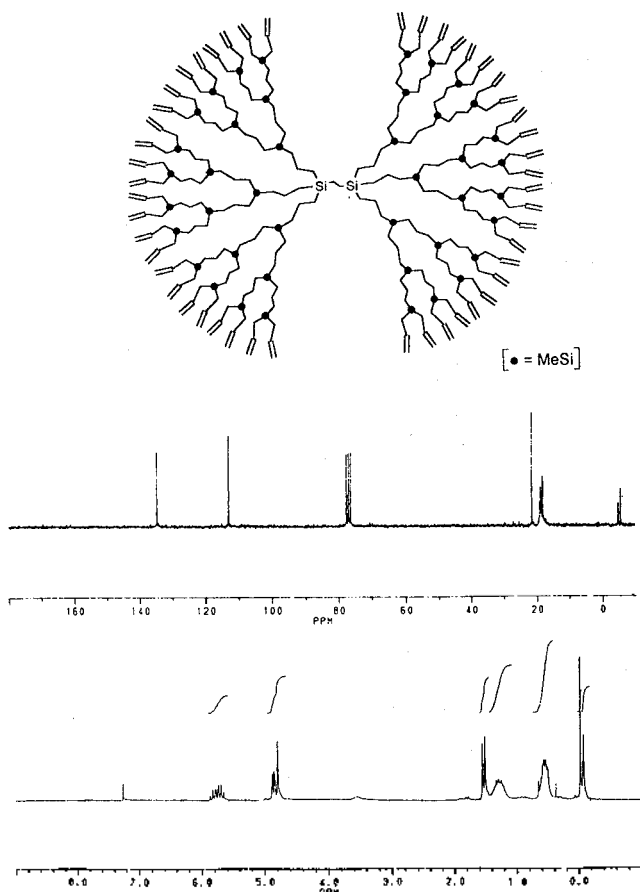


Figure 1. The Schematic View of 3rd Generation of Dendrimeric Silane with 48 Allylic End Groups and its ^{13}C (up) and ^1H (down) NMR Spectra.

17-19 ppm for CH_2 signals to assist in controlling the reaction and detecting the existing small amounts of impurities

which exist in the reaction mixture. Elemental composition of the dendrimers (Gn generation) determined by combustion is very close to the expected value (Table 1).

Acknowledgment. This work was supported by the Korea Sanhak Foundation (1995).

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Reaction of Nitrile Oxides with 3(2H)- and 2(5H)-Furanones

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Received January 18, 1996

1,3-Dipolar cyclization of various nitrile oxides with 3(2H)- and 2(5H)-furanones regioselectively furnished the corresponding syn-addition products of 3-oxotetrahydro-furano[4,5-d]isoxazolines and 2-oxotetrahydrofurano[3,4-d]isoxazolines.

Introduction

Nitrile oxides are reactive 1,3-dipoles, which add to ethylenic and acetylenic dipolarophiles with high regioselectivity

to furnish Δ^2 -isoxazolines and isoxazoles, respectively. These stereoselectively controlled reaction intermediates serve as useful building blocks that lead to various compounds through chemical modification and ring cleavage. For exam-