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Preparation of Carbosilane Dendrimers Based on Siloxane Tetramer: Silane Arborols (VII)¹

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Via hydrosilation-alkenylation approach using hydrosilanes (HSiMeCl_2 and HSiCl_3) and allylmagnesium bromide with siloxane tetramer ($\text{MeCH}_2=\text{CHSiO}$)₄ as core molecule, noble carbosilane dendrimers with 12, 24, 48 and 96 allylic end groups have been prepared. The reaction path of the repetitive alkenylation and hydrosilation was monitored by means of NMR spectroscopic measurements. Every step for the formation of dendrimer provided almost quantitative yields as pure dendrimers. Based on the observation of UV spectroscopic measurements of **G_n** ($n=1-4$) molecules containing allylic end groups, the maximal molal absorption coefficients (ϵ_{max}) at λ_{max} and the number of double bonds proved an exponentially increased correlation.

Introduction

From the beginning, due to their geometrical beauty and intriguing supramolecular properties, the interest in dendrimeric macromolecules has received increasing attention.² Since the spearhead reports on dendritic macromolecules by Vögtle,³ Denkenwalter,⁴ Newkome⁵ and Tomalia⁶ have developed several synthetic pathways. Such disclosures were pivotal for the progress toward the synthesis of cascade polymers.⁷ A literature research shows that the number of publications in this field has increased exponentially over the last decade.⁸ Currently, the development of this area is shifting from the preparation of even larger molecules to dendrimers with useful supramolecular phenomena.⁹ The application of dendrimers includes nanoscale catalysts,¹⁰ micelle mimics,¹¹ immunodiagnostics,¹² agents for delivering drugs,¹³ chemical sensors,¹⁴ high performance polymers and liquid crystals.¹⁵ The synthesis and applications of dendrimeric macromolecules spring into two basic structure

types. The first type has a globular structure in which well-defined branches radiate from a central core, becoming more branched and crowded as they extend out to the periphery. The second type of dendritic structure is observed in the hyperbranched polymer, studied by Y. H. Kim.¹⁶ This type of polymer also has random or fairly regular architectures.

Silicon chemistry offers a number of reactions with quantitative yields, which are suitable for dendrimer synthesis, such as replacement of chlorines in chlorosilanes by lithium organyls as well as Grignard reagents and hydrosilation of alkenyl- and alkynylsilanes in the presence of platinum catalyst. These properties can be the applications to the matter in dendrimeric generations. The first preparation of the carbosilane dendrimers introduced by van der Made *et al.* was performed by repetitive alkenylation-hydrosilation cycles.¹⁷ Seyferth and co-workers prepared the carbosilane dendrimers that contain ethynyl groups at its periphery with $\text{Co}_2(\text{CO})_8$.¹⁸ Polysiloxane dendrimers were prepared by Kak-

imoto by the use of a convergent process.¹⁹ To date, most of synthetic methods for silicon containing dendrimers have been demonstrated by repeat unit possessing considerable flexibilities. In the previous paper, we described a preparation of carbosilane dendrimers, based on quantitative hydrosilation-alkenylation cycles, and suggested that the dendrimeric growth has been limited.^{1a-d} For example, the reaction of **G1** with HSiCl_3 did not completely form a molecule containing 36 Si-Cl bonds but the reaction of it with HSiMeCl_2 completely formed 24 Si-Cl bonds containing dendrimeric carbosilane $(\text{MeSiCH}_2\text{CH}_2\text{MeSi}(\text{CH}_2\text{CH}_2\text{CH}_2\text{MeSiCl}_2)_3\text{O})_4$. By the use of hydrosilation-alkenylation cycles, the dendrimeric generations of hexaallylethylene-disilane $(\text{CH}_2=\text{CHCH}_2)_3\text{SiCH}_2$ as core molecules with halosilane (HSiMeCl_2) and allylmagnesium bromide was afforded **G3** with 48 allylic end groups.^{1e}

In this report, we wish to introduce reactions of 2,4,6,8-tetramethyltetra vinyltetrasiloxane $(\text{Me}(\text{CH}_2=\text{CH})\text{SiO})_4$ as core molecules with halosilane ($\text{HSiMe}_n\text{Cl}_{3-n}$; $n=0$ and 1) as hydrosilation agents and allylmagnesium bromide as alkenylating agents and characterization of products. We also report the regioselective addition of hydrosilane to vinyl groups in the presence of Pt/C as a heterogeneous catalyst. Identification of prepared cascade molecules can be obtained by ^1H and ^{13}C NMR and UV spectroscopic attachments as well as elemental analyses.

Experimental

General Procedures. All reactions were carried out under a static pressure of N_2 atmosphere that has been dried by passage through three columns (4.0×100 cm) of a molecular sieve (3 Å), CaCl_2 and KOH. Ether and THF were dried by distillation from the blue solution of sodium-benzophenone ketyl, while solvents, such as pentane, toluene and benzene, were dried and distilled from $\text{Na/K}_{2,8}$ amalgam. Glassware was dried under vacuum with ca $100^\circ\text{C}/10^{-2}$ torr. 2,4,6,8-tetramethyltetra vinyltetrasiloxane were dried by molecular sieve (3 Å). Hydrosilanes (HSiMeCl_2 and HSiCl_3) were used by vacuum distillation before the experiment. A platinum catalyst (Pt on activated carbon, 10% Pt content) was used after vacuum dry at room temperature. Grignard reagent were prepared by literature.²⁰ NMR spectra were measured using samples in CDCl_3 solution. ^1H NMR spectra at 200.13 MHz and ^{13}C NMR spectra at 50.32 MHz by Bruker AC-200 Spectrometer. FT-IR spectra were measured by IFS 55 (Bruker). UV spectra were measured by HP 8452A Diode Array UV/Vis. Spectrophotometer (HP). Elemental analyses were performed by the Seoul Branch of the Korean Basic Science Institute. Molecular simulation can be obtained by ChemSite 2.2.²¹

G1P. A mixture of 2.25 g (6.52 mmol) $(\text{MeSi}(\text{CH}=\text{CH}_2)\text{O})_4$, **G0**, 3.35 g (26.11 mmol) HSiCl_3 and 0.03 g of a dried platinum catalyst (Pt on activated carbon, 10% Pt content) in 15 mL THF was stirred for 12 h at room temperature. After completion of the reaction was monitored by ^1H NMR, excessive HSiCl_3 and THF were removed under vacuum. The catalyst was filtered off in pentane and the pentane was evaporated leaving 5.53 g (6.24 mmol; 96%) of **G1P** $(\text{MeSiCH}_2\text{CH}_2\text{SiCl}_2\text{O})_4$ as a clear, colorless oil, which was very sensitive to moisture. ^1H and ^{13}C NMR spec-

troscopic data are given in Table 2.

G1. 75 mmol of allylmagnesium bromide (55 mL of 1.36 M solution in ether) was slowly added to 5.53 g (6.24 mmol) of **G1P** in 25 mL Et_2O at room temperature. After the addition was completed, the reaction mixture was refluxed for 2 h. After completion of the reaction was monitored by ^1H NMR, solvents were removed under reduced pressure. The magnesium salt was precipitated in pentane and filtered off. The volatile components were removed under reduced pressure, leaving 5.17 g of a colorless liquid. All portions of yielded compounds were chromatographed on silica gel with chloroform as an eluent. The product, **G1** $(\text{MeSiCH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_3\text{O})_4$ was obtained as a clear, colorless oil (5.00 g; 5.24 mmol, 61%). ^1H and ^{13}C NMR spectroscopic data are given in Table 1, UV spectroscopic data Table 4, analytical data Table 3 and IR spectroscopic data Table 5.

G2P. A mixture of 1.45 g (1.52 mmol) **G1**, 2.09 g (18.24 mmol) HSiMeCl_2 and 0.09 g of a dried platinum catalyst (Pt on activated carbon, 10% Pt content) in 25 mL THF was stirred for 24 h at room temperature. After completion of the reaction was monitored by ^1H NMR, excessive HSiMeCl_2 and THF were removed under vacuum. The catalyst was filtered off in pentane and all of the volatile components were evaporated leaving 3.27 g (1.40 mmol, 92%) of **G2P** $(\text{MeSiCH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMeCl}_2)_3\text{O})_4$ as a clear, colorless oil, which was very sensitive to moisture. ^1H and ^{13}C NMR spectroscopic data are shown in Table 2.

G2. 33 mmol of allylmagnesium bromide (25 mL of 1.36 M solution in ether) was slowly added to 3.27 g (1.40 mmol) of **G2P** in 25 mL THF. After the addition was completed, the reaction mixture was refluxed for 2 h. After completion of the reaction was monitored by ^1H NMR, solvents were removed under reduced pressure. The magnesium salt was precipitated in pentane and filtered off. The volatile components were removed under reduced pressure, leaving 3.20 g of colorless liquid. All portion of yielded compounds were chromatographed on silica gel with chloroform as an eluent. The product, **G2** $(\text{MeSiCH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}(\text{CH}_2\text{CH}=\text{CH}_2)_2)_3\text{O})_4$ was obtained as a clear, colorless oil (2.42 g; 0.98 mmol, 71%). ^1H and ^{13}C NMR spectroscopic data are given in Table 1, UV spectroscopic data Table 4, analytical data Table 3 and IR spectroscopic data Table 5.

G3P. A mixture of 1.50 g (0.60 mmol) **G2**, 1.65 g (14.40 mmol) HSiMeCl_2 and 0.10 g of dried a platinum catalyst (Pt on activated carbon, 10% Pt content) in 15 mL THF was stirred for 12 h at room temperature. After completion of the reaction was monitored by ^1H NMR, excessive HSiMeCl_2 and THF were removed under vacuum. The catalyst was filtered off in pentane and the pentane was evaporated leaving 2.95 g (0.56 mmol; 93%) of **G3P** $(\text{MeSiCH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMeCl}_2)_2)_3\text{O})_4$ as clear, colorless liquid, which was very sensitive to moisture. ^1H and ^{13}C NMR spectroscopic data are given in Table 2.

G3. 27 mmol of allylmagnesium bromide (20 mL of 1.36 M solution in ether) was slowly added to 2.95 g (0.56 mmol) of **G3P** in 25 mL Et_2O . After the addition, the reaction mixture was refluxed for 3 h. After completion of the reaction was monitored by ^1H NMR, solvents were re-

Table 1. ^1H and ^{13}C NMR Spectroscopic Data of G_n Type Dendrimers measured in CDCl_3

Compds.		MeSi	CH_2	$\text{CH}_2=$	$\text{CH}=\text{(ppm)}$
G0	^1H	0.24 (q, 3H)		5.99 (m, 8H)	6.01 (m, 4H)
	^{13}C	-0.80		133.50	136.12
G1	^1H	0.08 (s, 12H)	0.15 (m, 16H) 1.62 (d, 24H, $J=8.0$ Hz) 2.62, 8.89 (G0)	4.84 (m, 24H)	5.80 (m, 12H)
	^{13}C	-1.51 (G0)	19.15 (G1)	113.56	134.33
G2	^1H	0.01 (s, 36H, G2) 0.09 (s, 12H, G0)	0.41 (m, 16H) 0.63 (m, 48H) 1.35 (m, 24H) 1.59 (d, 48H, $J=8.0$ Hz)	4.82 (m, 40H)	5.79 (m, 24H)
	^{13}C	-5.67 (G2) -1.34 (G0)	3.73, 8.62 (G0) 16.96, 18.19, 18.38 (G1), 21.50 (G2)	113.14	134.74
G3	^1H	-0.06 (s, 36H, G2) -0.01 (s, 72H, G3) 0.06 (s, 12H, G0)	0.40 (m, 16H, G0) 0.58 (m, 144H, G1-G2) 1.34 (m, 72H, G1-G2) 1.56 (d, 96H, $J=8.0$ Hz)	4.80 (m, 96H)	5.79 (m, 48H)
	^{13}C	-5.62 (G3), -4.86 (G2) -3.85 (G0)	17.54 (G1), 18.04 (G2) 18.33 (G2), 18.34 (G2) 18.55 (G1)	113.15	134.74
G4	^1H	-0.06 (s, 72H) -0.01 (s, 144H) 0.07 (s, 36H)	0.38 (m, 16H) 0.58 (m, 336H) 1.35 (m, 168H) 1.36 (d, 192H, $J=8.0$ Hz)	4.80 (m, 192H)	5.78 (m, 96H)
	^{13}C	-5.62 (G4) -4.86 (G0, G3) 1.98 (G2)	18.02, 18.32, 18.61, 18.33, 19.15, 19.57, (G0-G3), 21.50 (G4)	113.15	134.70

Table 2. ^1H and ^{13}C NMR Spectroscopic Data of G_nP Type Dendrimers measured in CDCl_3

Compds.		MeSi	MeSiCl ₂	CH_2 (ppm)
G1P	^1H	0.18 (s, 12H)		0.74 (m, 8H) 1.31 (m, 8H) 8.05, 16.76
		-1.37		
G2P	^1H	0.09 (s, 12H, G0)	0.77 (s, 36H)	0.45 (m, 16H) 0.72 (m, 24H) 1.22 (m, 24H) 1.55 (m, 24H)
		3.30 (G0)	5.53	-1.33, 9.08 (G0), 15.45, 17.34, 25.93 (G1)
G3P	^1H	-0.01 (s, 36H, G2) 0.10 (s, 12H, G0)	0.77 (s, 72H)	0.41 (m, 16H) 0.64 (m, 72H) 1.21 (m, 48H) 1.32 (m, 48H) 1.54 (m, 48H)
		-5.04 (G2) -1.53 (G0)	5.51	4.02 (G0) 17.04, 18.56, 18.87 (G1), 17.33, 1.50, 25.91(G2)
G4P	^1H	-0.05 (s, 36H, G2) -0.01 (s, 72H, G3) 0.06 (s, 12H, G0) -10.72 (G0-G3),	0.76 (s, 144H)	0.39 (m, 16H) 0.63 (m, 216) 1.21, 1.34, 1.54 (m, 96H, G4P)
			5.55	18.53, 18.76, 18.94 (G1-G2), 19.35, 17.51, 25.94(G3)

Table 3. Elemental Analysis Data of G_n Type Dendrimers

Compds.	Mw	Analysis (Found/Calcd)	
		C	H (%)
G1 ($\text{C}_{48}\text{H}_{88}\text{Si}_8\text{O}_4$)	953.91	60.70/60.44	9.50/9.30
G2 ($\text{C}_{132}\text{H}_{256}\text{Si}_{20}\text{O}_4$)	2469.19	64.87/64.21	10.36/10.45
G3 ($\text{C}_{300}\text{H}_{592}\text{Si}_{44}\text{O}_4$)	5499.76	63.57/65.52	10.78/10.85
G4 ($\text{C}_{636}\text{H}_{1264}\text{Si}_{92}\text{O}_4$)	11560.90	64.87/66.08	11.01/11.02

moved under reduced pressure. The magnesium salt was precipitated in pentane and filtered off. The volatile components were removed under reduced pressure, leaving 5.17 g of a colorless liquid. All portion of yielded compounds were chromatographed on silica gel with chloroform as eluent. The product, G3 ($\text{MeSiCH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}(\text{CH}_2\text{CH}=\text{CH}_2)_2)_2)_2\text{O}_4$) was obtained as a clear, colorless oil (2.25 g; 0.41 mmol, 73%). ^1H and ^{13}C NMR spectroscopic data are given in Table 1, UV spectroscopic data Table 4, analytical data Table 3 and IR spectroscopic data Table 5.

G4P. A mixture of 1.45 g (1.52 mmol) G3, 2.09 g (18.24 mmol) HSiMeCl_2 and 0.09 g of dried a platinum catalyst (Pt on activated carbon, 10% Pt content) in 25 mL THF was stirred for 24 h at room temperature. After completion of the reaction was monitored by ^1H NMR, excessive HSiMeCl_2 and THF were removed under vacuum. The catalyst was filtered off in pentane and the pentane was evaporated, leaving 3.27 g (1.40 mmol, 92%) of G4P ($\text{MeSiCH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}(\text{CH}_2\text{CH}=\text{CH}_2)_2)_2)_2)_2\text{O}_4$)

Table 4. UV Spectroscopic Data of **G_n** Type Dendrimers measured in Hexane

Compounds	Formula	Mw	No of end groups	Conc. (10 ⁻⁴ M)	λ _{max} (nm)	ε _{max}
G1	C ₄₈ H ₈₈ Si ₃ O ₄	953.91	12	6.28	214	3560
G2	C ₁₃₂ H ₂₅₆ Si ₂₀ O ₄	2469.16	24	4.30	214	5160
G3	C ₃₀₀ H ₅₉₂ Si ₄₄ O ₄	5499.76	48	1.45	214	16100
G4	C ₆₃₆ H ₁₂₆₄ Si ₉₂ O ₄	11560.90	96	0.64	212	35095

Table 5. IR Spectroscopic Data (ν_{C=C}) of **G_n** Type Dendrimers measured in KBr neat

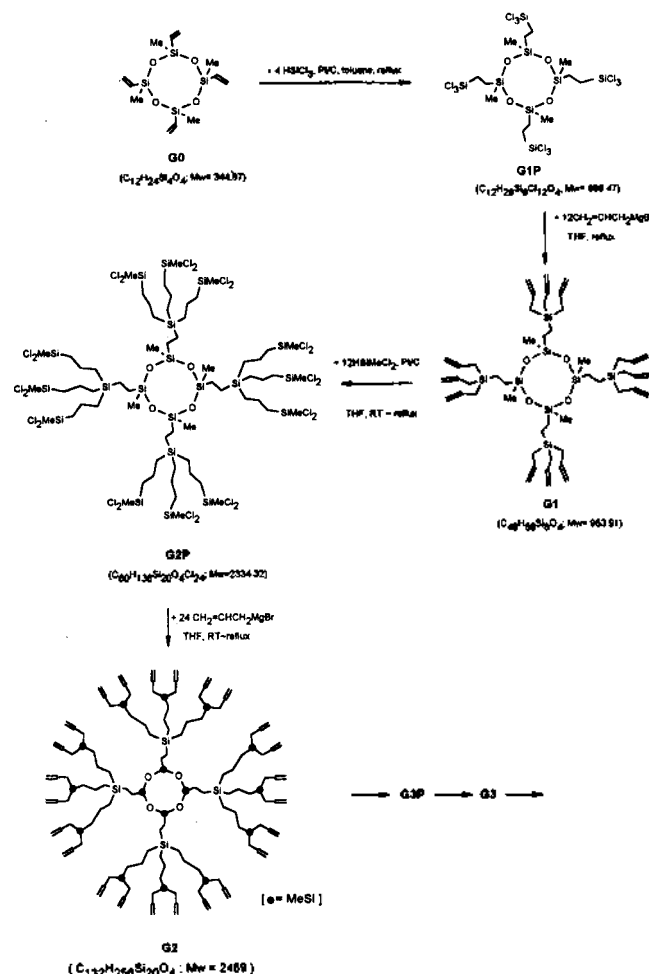
Compounds	ν _{C=C} (cm ⁻¹)
G0	1597.5
G1	1630.1
G2	1630.1
G3	1630.2
G4	1631.0

(CH₂CH₂CH₂SiMeCl₂)₂)₂)₃O)₄ as a clear, colorless oil, which proved very sensitive to moisture. ¹H and ¹³C NMR spectroscopic data are given in Table 2.

G4. 33 mmol of allylmagnesium bromide (25 mL of 1.36 M solution in ether) was slowly added to 3.27 g (1.40 mmol) of **G4P** in 25 mL THF. After the addition, the reaction mixture was refluxed for 2 h. After completion of the reaction was monitored by ¹H NMR, solvents were removed under reduced pressure. The magnesium salt was precipitated in pentane and filtered off. The volatile components were removed under reduced pressure, leaving 3.20 g of a colorless liquid. All portion of yielded compounds were chromatographed on silica gel with chloroform as an eluent. The product, **G4** (MeSiCH₂CH₂Si(CH₂CH₂CH₂SiMe(CH₂CH₂CH₂SiMe(CH₂CH=CH₂)₂)₂)₂)₃O)₄ was obtained as a clear, colorless oil (2.42 g; 0.98 mmol, 71%). ¹H and ¹³C NMR spectroscopic data are given in Table 1, UV spectroscopic data Table 4, analytical data Table 3 and IR spectroscopic data Table 5.

Results and Discussion

The basic procedure for the preparation of each generation of carbosilane dendrimers is outlined in Scheme 1. The synthesis of our silane dendrimers begins with the exhaustive hydrosilylation of vinyl groups in 2,4,6,8-tetramethyl-tetravinyltetrasiloxane with HSiCl₃ in the presence of a platinum catalyst (10% Pt content on activated carbon) to which **G1P** in quantitative yields is produced. The next step is preparation of **G1** generation in which allylmagnesium bromide is used as the alkylating agent. In this first alkylation step, a 12-fold initiator core (Si-Cl bonds) is reacted with 12 equiv. of allylmagnesium bromide in diethyl ether to produce **G1** in quantitative yields. Then the allyl groups are hydrosilylated with dichloromethylsilane (HSiMeCl₂) to give quantitative yields with 12 terminal SiMeCl₂ groups. Next, these SiMeCl₂ groups are reacted with allylmagnesium bromide to produce **G2** dendrimer with 24 allylic end groups. By repeating the hydrosilylation and alkylation steps, this **G2** dendrimer can be converted into **G3** with 48 allylic end groups and continued **G4** with 96 allylic end groups. In general, hydrosilylation of **G_n** molecules

**Scheme 1.** Synthetic way of dendrimeric silanes.

with HSiMeCl₂ in the presence of platinum catalyst in THF gave **G_nP** in quantitative yields as a colorless oil or glass. We found also that a platinum catalyst gives a 1,2-adduct with high regiospecificity. Thus the reaction of **G0** with 4 equiv. of HSiMeCl₂ in the presence of Pt/C at room temperature for 12 h produced the only hydrosilylation product **G1P**. No other structure was detected in the reaction mixture by NMR. A similar reaction of **G1** with MeSiHCl₂ afforded the corresponding hydrosilylation products. In contrast to this, the reaction of **G_n** dendrimers in the presence of a platinum catalyst by refluxing toluene produced a small amount of dehydrogenative coupling products but, at room temperature, were not found these products. On the basis of this result obtained from the hydrosilylation-rate of **G0** and **G1** in the presence of a platinum catalyst, it is probably faster than the dehydrogenative couplings process. We investigated the solvent effect on the rate of hydrosilylation of **G0** and **G1** with HSiMe_{3-n}Cl_n (n=1-3) in the presence of a platinum ca-

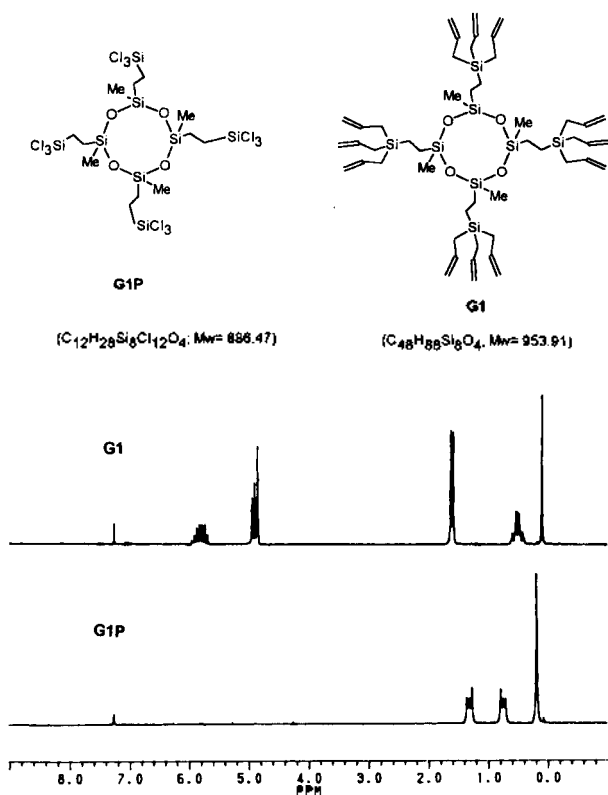


Figure 1. ^1H NMR spectra of **G1P** (under) and **G1** (up) measured in CDCl₃.

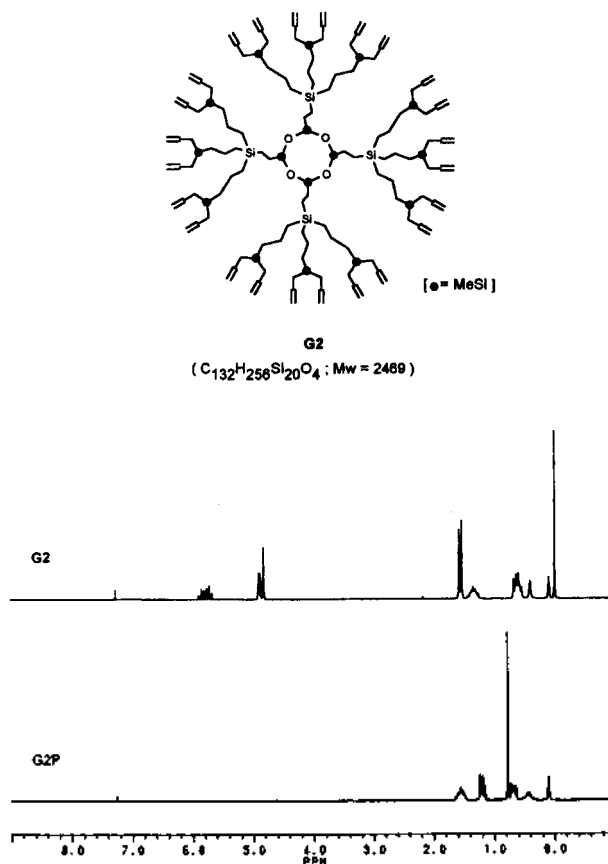


Figure 2. ^1H NMR spectra of **G2P** (under) and **G2** (up) measured in CDCl₃.

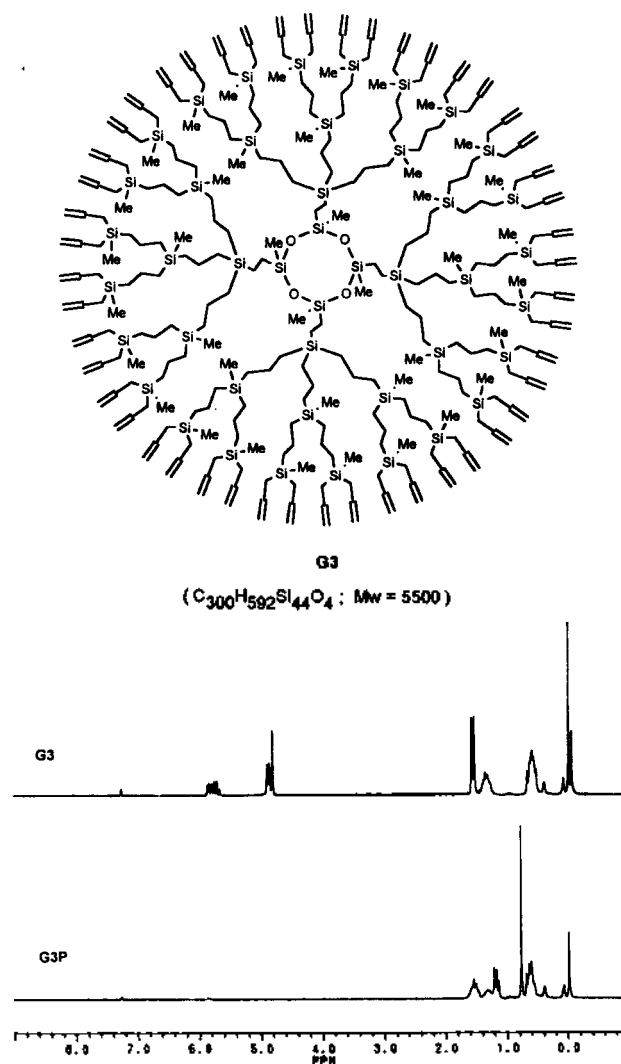


Figure 3. ^1H NMR spectra of **G3P** (under) and **G3** (up) measured in CDCl₃.

talyst under various conditions, and found that the polarity of the solvent markedly influences the rate of hydrosilation in this system. When **G1** was treated with HSiMeCl₂ in THF at room temperature, **G2P** was completely formed in 12 h. In toluene, however, at the same condition, we found that of unreacted **G1**. By increasing the amount of the catalyst and raising reaction temperature, the rate of reaction was considerably accelerated.

UV, IR, ^1H and ^{13}C NMR spectroscopic determination of **Gn** generations ($n=1-4$) clearly indicates the presence of ethenyl groups, in the periphery of given dendrimers. Figure 1-4 shows the NMR spectra of the dendrimers from **G1P** to **G4**. The spectra reflect the transition from **GnP** to **Gn** generations, which show three main regions at the environs of zero ppm for MeSi groups, 0.45-1.55 ppm for CH₂ groups and multiplet at 4.81 and 5.76 for protons of allylic double bonds for **Gn** molecules, (while the formation of **GnP** disappears the resonance of double bonds) and for the **GnP** generations at the environs of zero ppm for MeSi groups, 0.77 ppm for MeSiCl₂ groups (Figure 1-4 and Table 1 and 2). In ^{13}C NMR spectra, four kinds of methyl carbons, attached to

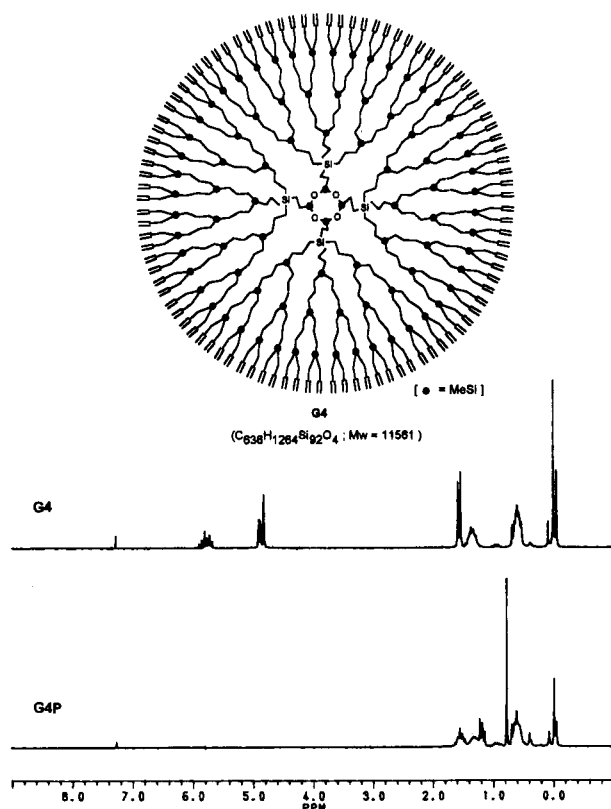


Figure 4. ^1H NMR spectra of G4P (under) and G4 (up) measured in CDCl_3 .

G1-G4, could be distinguished by the region between -6.3 – -1.2 ppm. These carbon spectra were clearly separated in G n and G n P molecules. The peak of methylenyl groups observed at 4.21-21.5 for G n molecules and at 4.37-25.91 for G n P molecules with sharp single signals, and that implied high purity of these dendrimers by ^1H and ^{13}C NMR (Table 1-2). These NMR spectroscopy is a valuable tool for monitoring growth and subsequent surface modification reaction of the dendrimers, while the sensitivity of the integration was an assessment of structural perfection and purities of the dendrimers at the stage of all generations.

The information concerning a perfect building of G n ($n=1-4$) dendrimers can be obtained, such as a direct comparison of its maximal molar absorption coefficients (ϵ_{max}) at λ_{max} (214-220 nm) and the number of double bonds. The absorption spectra of compounds G1-G4 in cyclohexane solution show extremely intense bands in the UV region. The highest intense bands in the UV region can be assigned to $\pi \rightarrow \pi^*$ transition. An increasing number of double bonds for each generation are in direct proportion to molar absorption coefficients in the UV spectrum (Table 4).

The characterization of large molecules such as dendrimers is a difficult task. For general organic and inorganic compounds, technique based on mass spectrometric attachments as well as colligative properties can be used to determine the perfect molecular mass. For our dendrimeric molecules, the use of the above technique is not an advisable tool because of the high number of molecular mass. In spite of the above difficulties, a reliable characterization of our dendrimers has been achieved by using a variety of

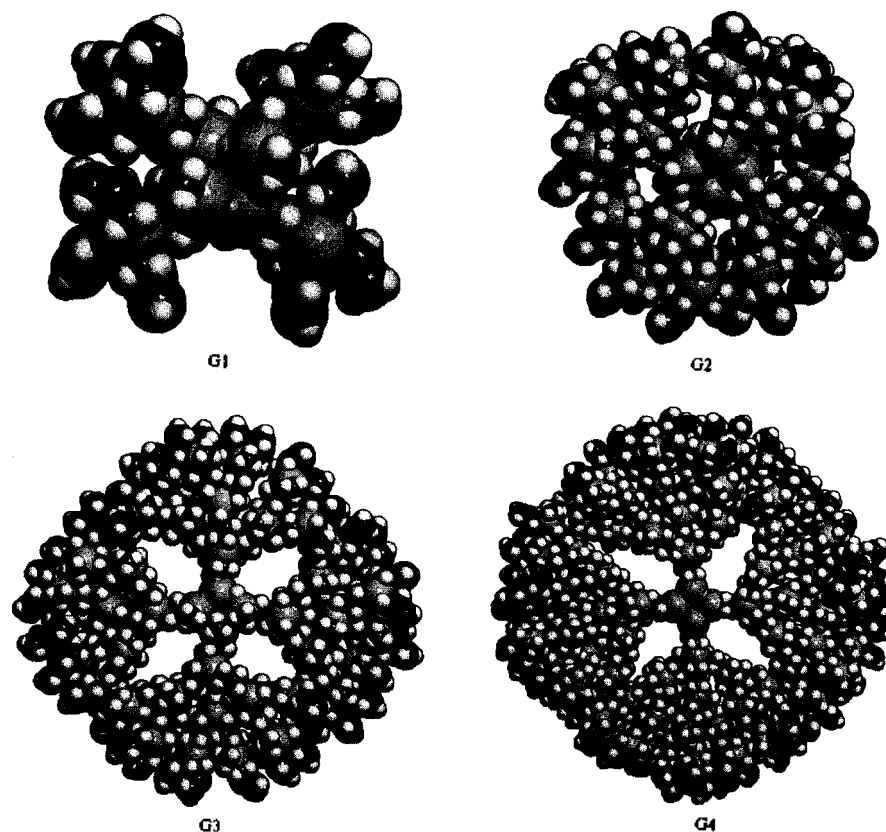


Figure 5. Computer simulation model of G1-G4 dendrimer: Calculated surface area are for G1; 590 \AA^2 , G2; 1550 \AA^2 , G3; 3350 \AA^2 , and G4; 6880 \AA^2 and average radius of the G1 is 18 \AA , G2 26 \AA , G3 43 \AA and G4 54 \AA .

technics: (1) Every steps was accurately monitored by ^1H and ^{13}C NMR spectroscopic measurements. For the products of **Gn**-family obtained in each growth step, the ratio of alkenyl end groups (new generations) to MeSi-groups (old generations) in the NMR spectrum was consistent with the expected formulations (Figure 1-4). Also **GnP**-family obtained in each step with perfect disappearance of alkenyl groups of **Gn** generations and the ratio of MeSi resonance signals to the multiplet of methylenyl chains proved the expected formula (Figure 1-4). (2) Each **Gn** generations was purified by chromatographic attachments.

Figure 5 shows their geometrical beauty and intriguing supramolecular properties (surface area and average radius) in **G1-G4** dendrimers which are obtained from the computer simulation program.²¹

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