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Preparation and identification of dendritic carbosilanes containing allyloxy groups derived from 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane $(Me(CH_2{=}CH)SiO)_4$ and 1,2-bis(triallyloxysilyl)ethane $((CH_2{=}CHCH_2O)_3SiCH_2)_2$

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Abstract

Synthesis and characterization of dendritic macromolecules using 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane $(Me(CH_2{=}CH)SiO)_4$ and 1,2-bis(triallyloxysilyl)ethane $((CH_2{=}CHCH_2O)_3SiCH_2)_2$ as core molecules and allylalcohol/dichloromethylsilane as a building block have been described. The dendrimers containing dichloromethylsilyl-groups (**GS-1P** ~ **GS-4P** and **GH-1P** ~ **GH-3P**) were produced by the hydrosilation process of double bonds in vinyl and allyloxy-groups in the **GS-*n*** and **GH-n** type dendrimers with dichloromethylsilane in the presence of a platinum catalyst (Pt/C). The **GH-*n*** and **GS-*n*** type dendrimers containing allyloxysilyl-groups were prepared by the reaction of **GH-*n*P** and **GS-*nP*** type dendrimers containing Si–Cl bonds and allylalcohol in the presence of TMED at room temperature. The purification of the prepared **GH-*n*** and **GS-*n*** type dendrimers used simple column chromatography. The yields of the prepared dendrimers have been obtained almost quantitatively. The analyses of the ^{1}H- and ^{13}C-NMR, MALDI mass spectra, and elemental analysis made it possible to obtain the pure and unified dendrimers. In additive manner, the molar absorbities of each generation of **GH-*n*** and **GS-*n*** type dendrimers show increasing character by the increasing number of double bonds. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Allyoxy groups; Dendritic macromolecules; Hydrosilation

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1. Introduction

Dendritic macromolecules are prepared by using repetitive synthetic cycles, which are expected to be a particularly promising structural concept for new materials [1]. They exhibit interesting properties, such as a unified form, a spherical molecular shape, peripheral functional groups, etc. [2]. According to literature, dendrimers with organic skeleton were first studied, and later, transition metal-containing dendritic molecules and silicon-induced dendrimers such as carbosilane and siloxane have come to the fore [3]. The dendrimers with transition metal complex, such as ruthenium [4], osmium [5], platinum [6], palladium [7], iron [8], cobalt [9], gold [10], and copper [11] have been realized. The dendrimers including silicon metal may be classified into three main categories, such as

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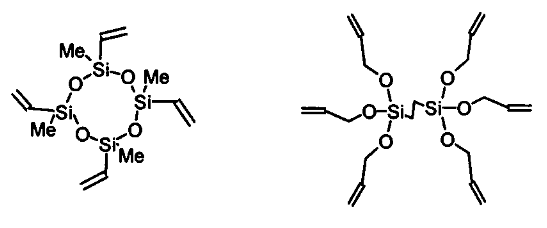
siloxane (Si–O) [12], carbosilane (Si–C) [13] and polysilane (Si–Si) [14] backbone. The synthetic procedure of carbosilane dendrimers derived from an alternating hydrosilation and alkenylation sequence has been first given by van der Made, who used chlorosilane as a core molecule and a Grignard reagent or lithiumorganyl as generating material [15].

Recently, we have reported a few methods for the preparation of silicon-containing dendrimers possessing allyl-, allyloxy- and alkynyl-groups on the periphery [16]. The preparation of these dendrimers using organometallic compounds and hydrosilation with a platinum catalyst allowed us to prepare a new class of multi-functionalized dendrimers. The synthesis and characterization of a dendritic carbosilane with allyloxy-groups, derived from 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (Me(CH$_2$=CH)SiO)$_4$ with trichlorosilane and allylalcohol, were performed only in the second generation with 36 allyloxy-groups ([16]g). This result is due to the surface saturation which is identified from other allyl- and alkynyl-group-containing carbosilane dendrimers [16]. As an extension of some of our previous studies ([16]a–f) we now report a detailed study on the reactions of chlorinated carbosilane dendrimers (**GH-*n*P** and **GS-*n*P** type) with allylalcohol in the presence of TMED and hydrosilation of double bonds on **GS-*n*** and **GH-*n*** type dendrimers using platinum in activated carbon (Pt/C, 10% platinum content in carbon) as a heterogeneous hydrosilation catalyst. The use of the Pt/C catalyst in hydrosilation procedure does possess a usable advantage that can control reaction rate and easily isolate the prepared **G-*n*P** type dendrimers from reaction mixture. The prepared dendrimers were characterized with NMR, Maldi mass, IR and UV spectroscopy. Considerably interesting results were found in the indirect identification method of the unified dendritic macromolecules by using UV spectroscopic attachments. We have obtained increasing molar absorbities of the given dendrimers by the increasing number of double bonds.

2. Results and discussion

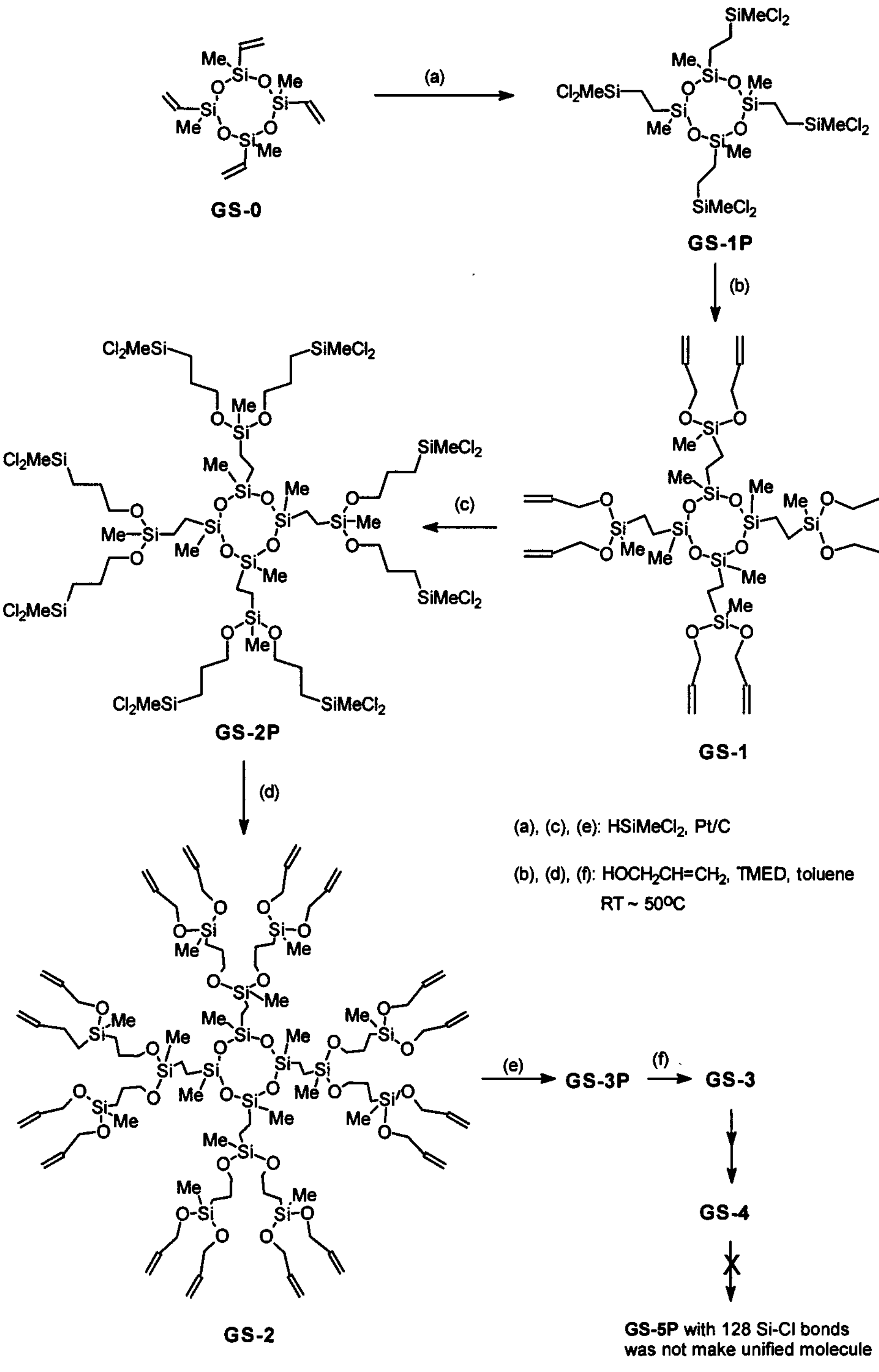
Our study for the preparation of dendritic carbosilane was established with two core molecules, which have 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (Me(CH$_2$=CH)SiO)$_4$ with a branching degree of 4 ($N_c = 4$) and 1,2-bis(triallyloxysilyl)ethane ((CH$_2$=CHCH$_2$O)$_3$SiCH$_2$)$_2$ with a branching degree of 6 ($N_c = 6$). The emanated steps of the given dendritic molecules used the same methods as those of hydrosilation with dichloromethylsilane and alcoholysis with allylalcohol ($N_b = 2$) (Scheme 1).

The synthesis of **GS** and **GH** type dendrimers was based on the complete hydrosilation of the alkenyl-groups with dichloromethylsilane in the presence of a platinum catalyst, and the complete formation of allyl ether bonds (–MeSi(OCH$_2$CH=CH$_2$)$_2$) on silicon atoms by the reaction of the chlorosilyl-groups with allylalcohol as shown in Schemes 2 and 4. The **GS-1P** molecule containing eight growing branches of Si–Cl bonds was produced by the reaction of 4 equiv. of dichloromethylsilane and 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane at room temperature in the presence of a platinum catalyst. The solvent for hydrosilation must be dried. If a polar solvent such as THF is used in the system, it must not be put for a long time because it will be polymerized in this condition. By our experience, **GS-1P** generation can be prepared without a solvent and other **GS-*n*P** generations ($n = 2$–4) formed in THF or toluene at reflux temperature. **GS-1P** molecule is easily converted into **GS-1** via alcoholysis with allyl alcohol in the presence of TMED. The complete reaction of **GS-1P** to **GS-1** and so on was confirmed by NMR spectroscopy. The yields of the two products in the system were revealed quantitatively by NMR spectroscopy. The other chlorosilyl-containing **GS-*n*P** ($n = 2$–4) type dendrimers were produced by the same hydrosilation process of the allyloxy-groups in **GS-*n*-1** generation with dichloromethylsilane in the presence of a platinum catalyst (Pt/C, 10% platinum content). The prepared **GS-*n*P** generations were revealed without side products by the NMR spectroscopic view. The chlorosilylated generations contained Cl$_2$MeSi–groups (**GS-*n*P**) were converted into the corresponding dendritic carbosilanes by the treatment with allylalcohol in the mixed medium of toluene and TMED. The hyperbranched dendrimers based on 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (**GS-0**) as a core molecule with OCH$_2$CH=CH$_2$ end groups as a building block, progressed to **GS-4** generation (Scheme 3), have been synthesized by utilizing the two alternatives of hydrosilation-alcoholysis sequences. The formation of **GS-5P** by the reaction of **GS-4** and HSiMeCl$_2$ did not lead to result in a uniformed



GS-0 **GH-0**

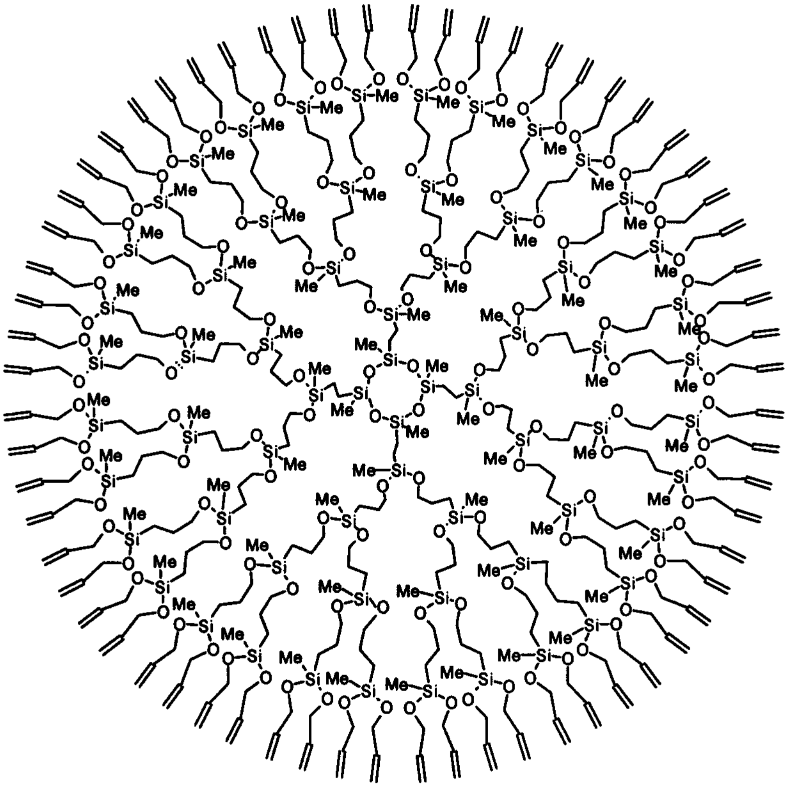
Scheme 1. Core molecules: (a) 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane represented by **GS-0** ($N_c = 4$) (b) 1,2-bis(triallyloxysilyl)ethane represented by **GH-0** ($N_c = 6$).



Scheme 2. Synthetic way of **GS-*n*** type dendrimers utilizing alcoholysis/hydrosilation process.

molecule according to the ^{1}H- and ^{13}C-NMR spectroscopic view. Eventually, the synthesis of **GS-5P** with 128 Si–Cl bonds will result in surface saturation, which will prevent further growth from all branching points so that the dendrimer will be difficult to be monodisphersed. But all the other synthetic pathways of lower generations produced uniformed dendrimers with quantitative yields (Fig. 1).

In the next model, the hyperbranched dendrimers to **GH-3** based on 1,2-bis(triallyloxysilyl)ethane as a core molecule have been synthesized by utilizing the two alternative hydrosilation-alcoholysis sequences. The

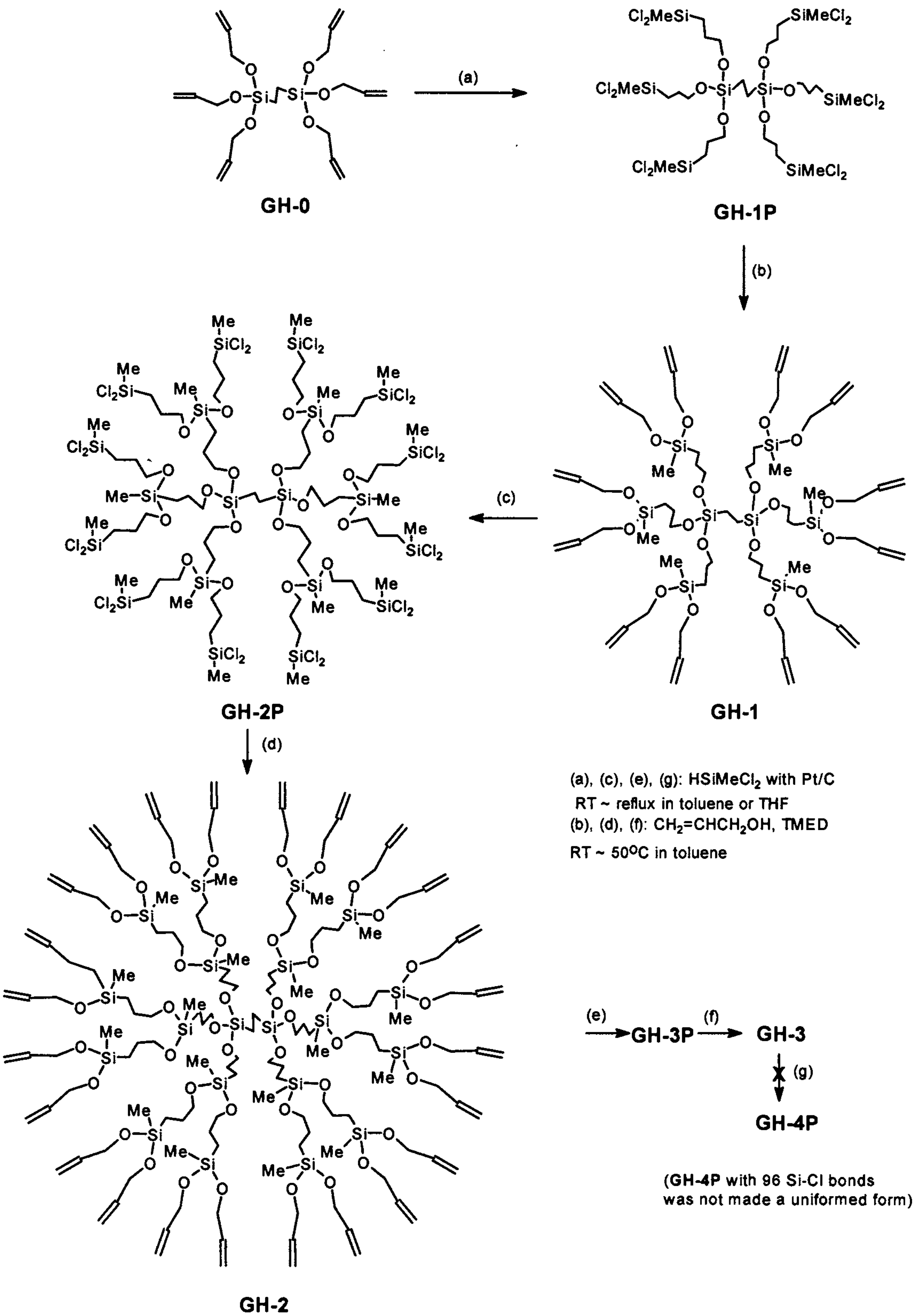


Scheme 3. Planar view of **GS-4** generation: $N_c = 4$, $N_b = 2$, Mw = 8457 and 64 allyloxy end groups.

chlorosilyl-containing dendrimers (**GH-1P** to **GH-3P**) (Scheme 5) were produced by the same method of hydrosilation process as shown in 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane-based dendrimers. This process also produced quantitative yields. The silylated generations (Cl_2MeSi–: **GH-*n*P**) were converted into the corresponding dendritic carbosilanes with allylether groups by the treatment with allylalcohol and TMED in toluene or THF. The formation of **GH-4P** by the reaction of **GH-3** and $HSiMeCl_2$ did not result in a uniformed molecule according to the ^1H- and ^{13}C-NMR spectroscopic view. The synthesis of **GH-4P** with 96 Si–Cl bonds will result in surface saturation, which will be the same result of **GS-*n*** type dendrimers, preventing further growth from all branching points so that the dendrimer will be difficult to be monodisphersed. But all the other synthetic pathways of lower generations produced uniformed dendrimers with quantitative yields as in Fig. 1.

In the case of carbosilane dendrimers with allyl groups derived from 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane as a core molecule ($N_c = 4$) and dichloromethylsilane as a building block ($N_b = 2$), produced the fifth generation with 64 allylic end groups. The allyl-group containing carbosilane dendrimers with $((CH_2{=}CHCH_2)_3SiCH_2)_2$ as a core molecule and dichloromethylsilane as a building block ($N_c = 6$, $N_b = 2$), produced the third generation with 48 allylic end groups by the same manner ([16]a, b, d). Therefore, the **GH-0** ($N_b = 3$) with trichlorosilane did not produce a unified form with 18 Si–Cl bond-containing generation, but with dichloromethylsilane produced unified **GH-1P** ($N_b = 2$) with 12 Si–Cl bonds. By the same evidence, the **GH-3** with dichloromethylsilane did not have a unified form (**GH-4P**, $N_b = 2$), but with dimethylchlorosilane produced a unified form (**GH-4P**, $N_b = 1$; Scheme 6). They are cause the same result and are termed 'surface congestion'.

By the reaction of the **GS-*n*** and **GH-*n*** type dendrimers with dichloromethylsilane in the presence of a platinum catalyst, we observed two different branches in one molecule. One of them is dehydrogenative coupling products as a minor product (Scheme 6, Figs. 1 and 2). There is no doubt that the major compounds were hydrosilation products. This result indicated that the hydrosilation process and dehydrogenative coupling process occurred simultaneously in the reaction medium. But, the former is faster than the latter in this condition. Accordingly, the yield of the former is major (above 95%). If the reaction temperature is low, the major product is more. Therefore, **GH-1** to **GH-3** and **GS-2** to **GS-4** dendrimers have been ethenyl branches



Scheme 4. Synthetic way of **GH-*n*** type dendrimers utilizing alcoholization/hydrosilation process.

as minor products. But the dehydrogenative branches in the prepared dendrimers were small influenced by molecular mass because the ethenyl-branches kept on living.

The purification of **GS-*n*** and **GH-*n*** type dendrimers was carried out by chromatography after each alcoholysis step. The purification of **GS-*n*P** and **GH-*n*P** type dendrimers was not produced because of their sensiti-

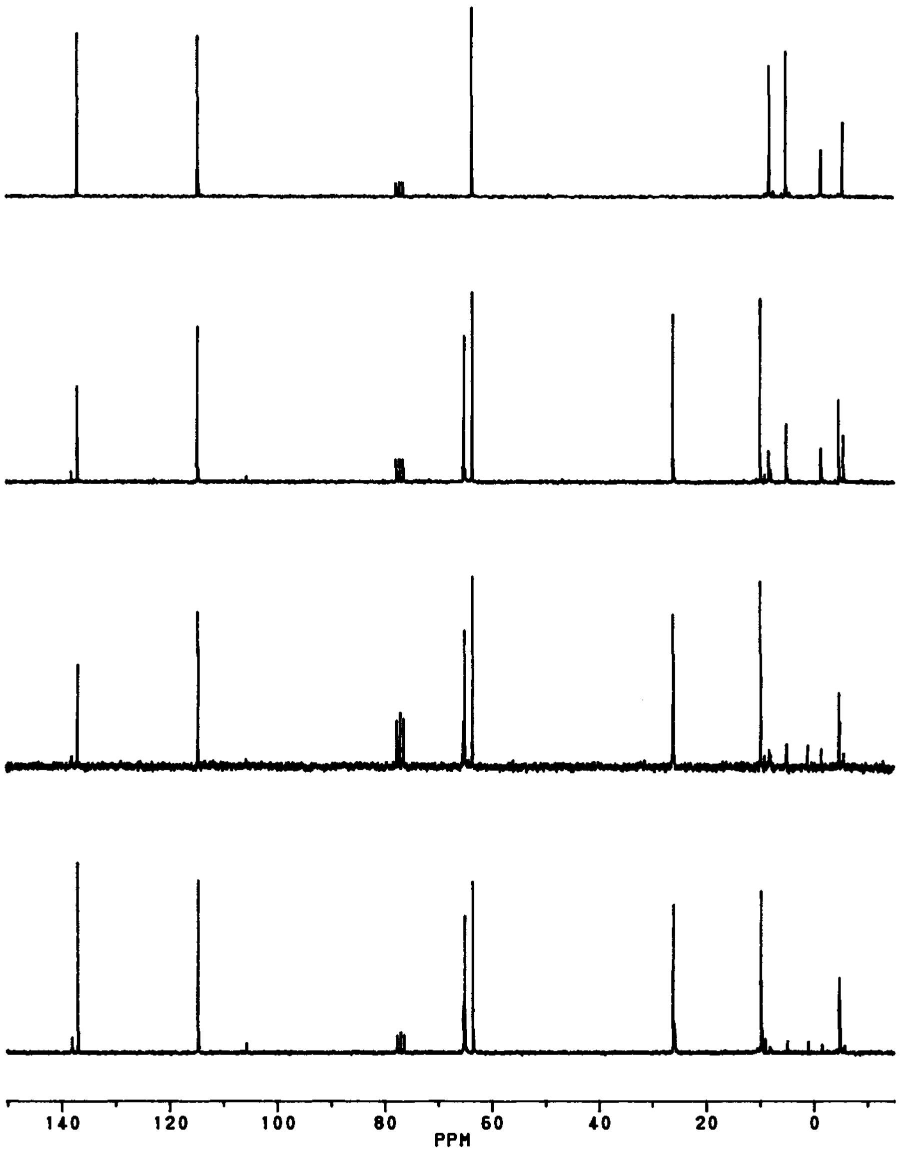
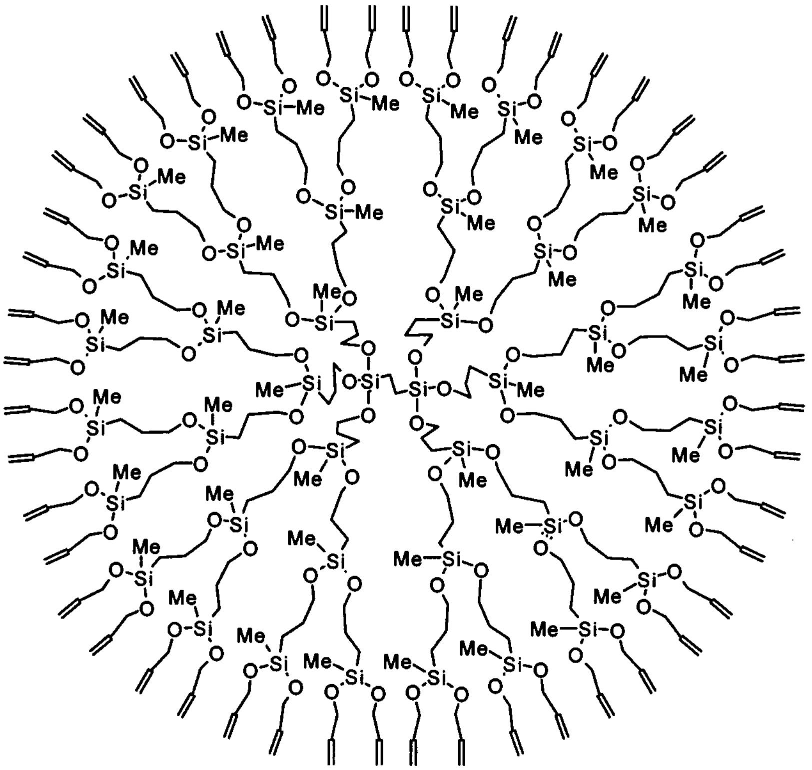


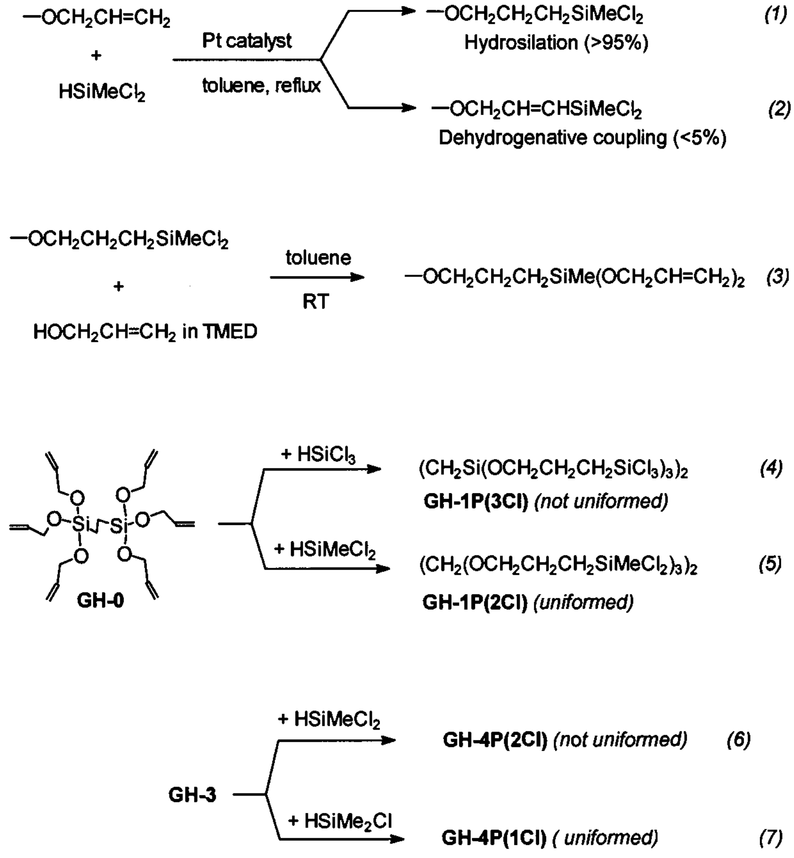
Fig. 1. ^{13}C-NMR spectroscopic view of **GS-*n*** type dendrimers ($n = 1$ (up) to 4 (down)).

vity against moisture. But, the NMR spectroscopic view of them showed a perfect formation of all generations. The prepared dendrimers were structurally characterized by ^{1}H- and ^{13}C-NMR spectroscopy, elemental analyses, MALDI mass, IR, and UV-VIS spectroscopy. Both reactions with **GS-4** and **GH-3** generations seemed to be free of a side reaction except the small amount of dehydrogenative coupling branches which were observed by NMR spectroscopy (Figs. 1 and 2). The ^{1}H- and ^{13}C-NMR spectroscopic analyses of **GS-*n*** ($n = 1$–3) and **GH-*n*** ($n = 2$–4) type dendrimers as well as **GS-*n*P** and **GH-*n*P** in $CDCl_3$ showed buildings of dendrimers without defects. The small signals at 105.46 and 137.66 ppm mean dehydrogenative branches of **GH-*n*** and **GS-*n*** by hydrosilation procedure (Figs. 1 and 2).

Among the most useful techniques for the characterization of **GH-*n*** and **GS-*n*** type dendrimers is matrix assisted laser desorption ionization (MALDI) mass spectroscopy. MALDI mass spectroscopy is demonstrated by the recent investigation of polyesters and carbosilane-based dendritic polyols, with excellent results ([13]h). The MALDI mass spectrum of **GH-*n*** and **GS-*n*** type dendrimers mainly shows the fragmentation of the given compounds. Both spectra show a regular fragmentation with ion mass 157 and m/z within 1% of the expected molecular weight. The m/z value of the dominant signal for **GH-*n*** type dendrimers corresponds to the fragmentation of the calculated value of m/z for **GH-1** (Mw: 1376) and **GH-2** (Mw: 3275) dendrimers. Signals are observed between these peaks, which clearly confirms that the fragmentation of



Scheme 5. Planar view of **GH-3** generation: $N_c = 6$, $N_b = 2$, Mw = 7074 and 48 allyloxy end groups.



Scheme 6. Mechanistic aspects for synthetic procedure of various dendritic generations.

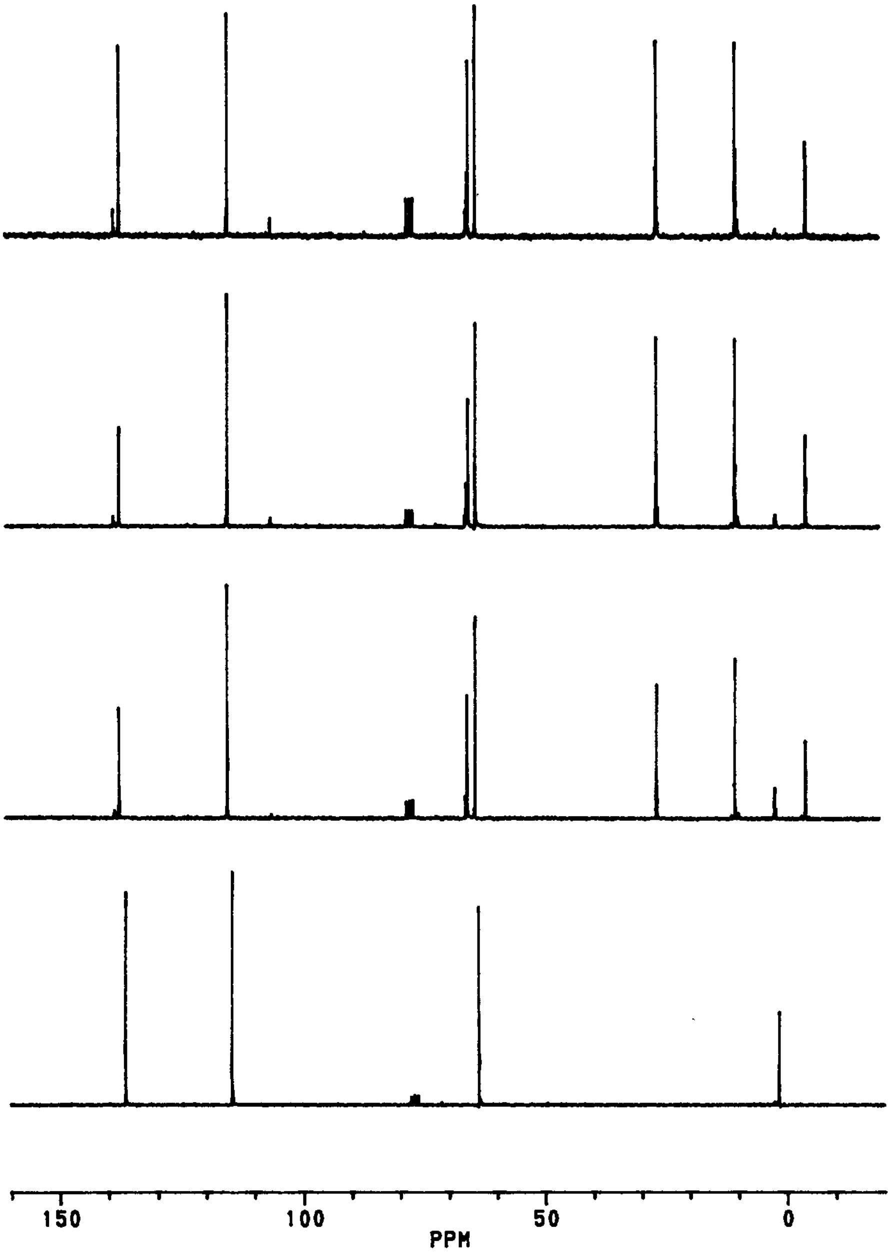


Fig. 2. ^{13}C-NMR spectroscopic view of **GH-*n*** type dendrimers ($n = 3$ (up) to 0 (down)).

$MeSi(OCH_2CH{=}CH_2)_2$ groups (m/z, 157) on the molecular surface does not affect the analysis. **GH-3** dendrimer was not observed at the molecular peak. However, this may be a consequence of aggregation as we have observed a similar behavior with **GH-2**. The m/z value of the dominant signals for **GS-*n*** type dendrimers shows the same evidence in **GH-*n*** type dendrimers. MALDI mass spectrometry was not useful for **GH-3** and **GS-4** due to their unusual formation of matrix (Fig. 3).

The identification of molecular weight and the unified character of the prepared dendrimers is very difficult. GPC and MALDI mass spectroscopic attachments were used for this purpose [17]. In order to define dendritic carbosilanes, MALDI mass spectrometry was employed. So far, the high generation of carbosilane dendrimers without mass spectroscopic assessment has been carried out. But, it is very difficult to measure compounds with high molecular weight. We observed the phenomena that the molar absorbities of **GS-*n*** and **GH-*n*** type dendrimers were proportional to the increasing number of double bonds in UV spectroscopy. The spectra of the given compounds are similar and consist of a broad band with a maximum wave length (λ_{max}) at

Table 1
NMR spectroscopic data of **GH-*n*** type dendrimers measured in $CDCl_3$

Compounds		MeSi	CH_2	–OCH_2–	CH_2=	–CH=
GH–0	^{1}H		0.74 (s, 4H, G0)	4.24∼4.36 (m, 12H, G0)	5.04∼5.40 (m, 12H, G0)	5.76∼6.07 (m, 6H, G0)
	^{13}C		1.58 (G0)	63.69 (G0)	114.63 (G0)	136.50 (G0)
GH-1	^{1}H	0.14 (s, 18H, G1)	0.59∼0.78 (m, 16H, G0) 1.52–1.80 (m, 12H, G0) 3.61∼3.80 (m, 12H, G0)	4.18∼4.31 (m, 24H, G1)	5.02∼5.36 (m, 24H, G1)	5.80∼6.03 (m, 12H, G1)
	^{13}C	−4.86 (G1)	1.43 (G0) 9.61, 25.81, 65.11 (G0)	63.41 (G1)	114.55 (G1)	136.78 (G1)
GH-2	^{1}H	0.08 (s, 18H, G1) 0.13 (s, 36H, G2)	0.52∼0.77 (m, 40H, G0–G1) 1.50∼1.78 (m, 36H, G0∼G1) 3.54∼3.77 (m, 36H, G0∼G1)	4.18∼4.32 (m, 48H, G2)	5.03∼5.36 (m, 48H, G2)	5.80∼6.07 (m, 24H, G2)
	^{13}C	−5.61 (G1) −5.48 (G2)	0.74 (G0) 8.91, 25.18, 64.66 (G0) 9.00, 25.27, 64.27 (G1)	62.78 (G2)	113.95 (G2)	136.12 (G2)
GH-3	^{1}H	0.08 (s, 54H, G1∼G2) 0.13 (s, 72H, G3)	0.55∼0.76 (m, 88H, G0∼G2) 1.45∼1.79 (m, 84H, G0∼G2) 3.50∼3.78 (m, 84H, G0∼G2)	4.18∼4.35 (m, 96H, G3)	5.03∼5.38 (m, 96H, G3)	5.76∼6.03 (m, 48H, G3)
	^{13}C	−5.02 (G1∼G2) −4.87 (G3)	1.29 (G0) 9.38, 25.69, 65.14 (G0) 9.50, 26.00, 65.05 (G1) 9.61, 25.88, 64.89 (G2)	63.40 (G3)	114.58 (G3)	136.74 (G3)

240 and 242 nm. The molar absorbities (ε_{max}) of all allylether-capped dendrimers are approximately increasing according to the number of double bonds (see Table 5). This shows that there are no unusual effects and that the allyloxy end groups contribute to the UV-absorption in an additive manner. We expect the possibility of determining the molecular mass of these types of dendrimers by using the increasing phenomena of molar absorbities of the given compounds.

In conclusion, by the use of hydrosilation and alcoholysis reaction sequences, carbosilane dendrimers have been employed to prepare a series of noble dendritic carbosilanes. Using MALDI mass has been directly characterized with respect to molecular weight distribution. By the formation of allyloxy-group containing dendrimers, we expect the possibility of a determining method for the molecular mass of these type dendrimers by using UV spectroscopic attachments. Carbosilane dendrimers with allyloxy-group have been critical generations caused by surface congestion. All dendrimers were soluble in organic solvents, such as THF, Et_2O, and toluene (Tables 1–4, 6 and 7).

3. Experimental

All reactions were carried out under dried N_2 atmosphere. Ether and THF were dried by sodium-benzophenone ketyl, while solvents, such as pentane, toluene and benzene, were dried and distilled from Na metal. All glassware was thoroughly dried with vacuum before use. Allylalcohol and 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane were purchased from Aldrich. A platinum catalyst (Pt on activated carbon, 10% Pt) was used after vacuum dry at room temperature. Chlorosilane was distilled before use. NMR spec-

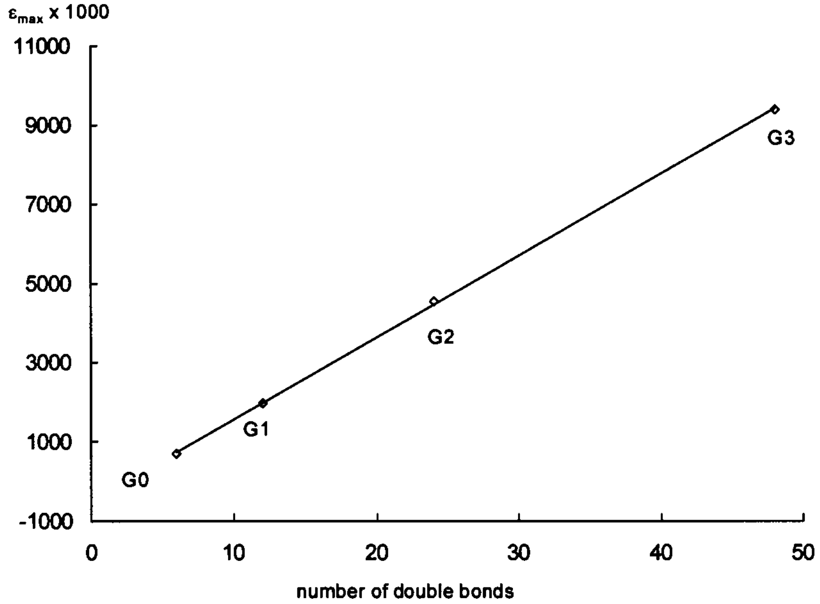


Fig. 3. MALDI mass spectroscopic view of **GS-*n*** type dendrimers.

Table 2
NMR spectroscopic data of **GH-*n*P** dendrimers measured in $CDCl_3$

Compounds		MeSi	$MeSiCl_2$	CH_2
GH-1P	^1H		0.79	0.65 (s, 4H, G0)
			(s, 18H, G1P)	1.08 ~ 1.29 (m, 12H, G0)
				1.65 ~ 1.91 (m, 12H, G0)
				3.66 ~ 3.90 (m, 12H, G0)
	^{13}C		5.17 (G1P)	1.54 (G0)
				17.69, 25.46, 64.09 (G0)
GH-2P	^1H	0.16	0.83	0.52(s, 4H, G0)
	(s, 18H, G1)	(s, 36H, G2P)	0.60–0.79 (m, 12H, G0)	
				1.10 ~ 1.32 (m, 24H, G1)
				1.71 ~ 1.92 (m, 36H, G0 ~ G1)
				3.65 ~ 3.87 (m, 36H, G0 ~ G1)
	^{13}C	−4.88 (G1)	5.20 (G2P)	1.57(G0)
				9.49, 25.91, 65.20 (G0)
				17.79, 25.57, 64.22 (G1)
GH-3P	^1H	0.10	0.78	0.49(s, 4H, G0)
		(s, 18H, G1)	(s, 72H, G3P)	0.52 ~ 0.73 (m, 36H, G0 ~ G1)
		0.12		1.10 ~ 1.25 (m, 48H, G2)
		(s, 36H, G2)		1.69–1.89 (m, 84H, G0 ~ G2)
				3.55 ~ 3.82 (m, 84H, G0 ~ G2)
	^{13}C	−5.01 (G1)	5.15 (G3P)	0.38 (G0)
		−4.95 (G2)		9.51, 25.95, 64.91 (G0 ~ G1)
				17.77, 25.42, 63.73 (G2)

tra were recorded on a Bruker AC-200 Spectrometer in $CDCl_3$. NMR chemical shifts refer to the signals of the solvents used. FT-IR spectra were measured by an IFS 55 (Bruker). UV spectra were measured by a HP 8452A Diode Array UV/VIS. Spectrophotometer (HP). Elemental analysis and MALDI mass spectroscopy (KRATOS KOMPACKT MALDI 2) attachments were performed by the Pusan and Daejon Branches of the Korean Basic Science Institute.

Table 3
^{1}H- and ^{13}C-NMR spectroscopic data of **GS-*n*** type dendrimers measured in CDCl$_3$

Dendrimers		MeSi	CH$_2$CH$_2$	OCH$_2$CH$_2$CH$_2$	CH$_2$	=CH$_2$	CH=
GS-1	^{1}H	0.07 (s, 12H, G0) 0.13 (s, 12H, G1)	0.43∼0.69 (m, 16H, G0)		4.20∼4.29 (m, 16H, G1)	5.06∼5.37 (m, 16H, G1)	5.83∼6.01 (m, 8H, G1)
	^{13}C	−5.59 (G1) −1.54 (G0)	4.98 (G0) 8.04 (G0)		63.47 (G1)	114.54 (G1)	136.89 (G1)
GS-2	^{1}H	0.07 (s, 12H, G0) 0.08 (s, 12H, G1) 0.13 (s, 24H, G2)	0.43∼0.54 (m, 16H, G0)	0.56–0.70 (m, 16H, G1) 1.51–1.71 (m, 16H, G1) 3.58–3.72 (m, 16H, G1)	4.20∼4.24 (m, 32H, G2)	5.05∼5.37 (m, 32H, G2)	5.78∼6.03 (m, 16H, G2)
	^{13}C	−1.57 (G0) −5.71 (G1) −4.84 (G2)	4.88 (G0) 8.13 (G0) 64.94 (G1)	9.72 (G1) 25.94 (G1)	63.44 (G2)	114.55 (G2)	136.82 (G2)
GS-3	^{1}H	0.06 (s, 24H, G0∼G1) 0.09 (s, 24H, G2) 1.14 (s, 48H, G3)	0.45∼0.54 (m, 16H, G0)	0.54–0.70 (m, 48H, G1–G2) 1.53–1.70 (m, 48H, G1–G2) 3.58–3.70 (m, 48H, G1–G2)	4.20∼4.31 (m, 64H, G3)	5.06∼5.37 (m, 64H, G3)	5.70∼6.02 (m, 32H, G3)
	^{13}C	−1.52 (G0) −5.64 (G1) −4.92 (G2) −4.79 (G3)	4.89 (G0) 8.15 (G0)	9.76, 26.11 65.14 (G1) 9.67, 25.97 64.94 (G2)	63.48 (G3)	114.59 (G3)	136.86 (G3)
GS-4	^{1}H	0.06 (s, 24H, G0∼G1) 0.08 (s, 72H, G2∼G3) 0.13 (s, 96H, G4)	0.42∼0.59 (m, 16H, G0)	0.60–0.72 (m, 112H, G1–G3) 1.50–1.71 (m, 112H, G1–G3) 3.52–3.71 (m, 112H, G1–G3)	4.20∼4.29 (m, 128H, G4)	5.05∼5.35 (m, 128H, G4)	5.68∼6.03 (m, 64H, G4)
	^{13}C	−1.59 (G0) −5.75 (G1) −4.94 (G2∼G3) −4.81 (G4)	4.87 (G0) 8.13 (G0)	65.17, 8.98 25.84 (G1) 65.07, 9.64 26.07 (G2) 9.74, 25.94 64.92 (G3)	63.45 (G4)	114.56 (G4)	136.83 (G4)

The combination of hydrosilation and alcoholysis reactions has been recently described in other articles[16]. Therefore, we only show a representative example of the slightly modified procedure for the preparation of all dendrimers.

The following abbreviations are used in the experiments: **GS-*n*** refers to each generation of dendritic silane with 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane in the core molecule. **GS-*n*P** refers to the generation of dendritic silane with dichloromethylsilyl groups in **GS-*n*** type dendrimers. **GH-*n*** refers to each generation of dendritic silane with 1,2-bis(triallyloxysilyl)ethane groups in the core molecule. **GH-*n*P** refers to the generation of dendritic silane with dichloromethylsilyl groups in **GH-*n*** type dendrimers. N_c refers to the number of the initiator core (in the case of **GS-*n***, $N_c = 4$; **GH-*n***, $N_c = 6$). N_b refers to the number of branching for each new layer (in our experiment, all N_b is 2). **G-*n*** refers to each generation of dendritic silane with all **GH-*n*** and **GS-*n*** types. Full experimental details will appear elsewhere but the following may serve as an example:

3.1. General procedure of *GS-nP* type dendrimers

GS-1P. A mixture of 5.20 g (14.94 mmol) of 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane, 8.90 g (77.39 mmol) of HSiMeCl$_2$ and 0.10 g of a hydrosilation catalyst (10% Pt content on activated carbon) was stirred for 12 h at room temperature. When the reac-

Table 4
^{1}H- and ^{13}C-NMR spectroscopic data of **GS-*n*P** type dendrimers measured in CDCl$_3$

Compounds		MeSi	MeSiCl$_2$	CH$_2$CH$_2$	OCH$_2$CH$_2$CH$_2$
GS-1P	^{1}H	0.13 (s, 12H, G0)	0.43 (s, 12H, G1P)	0.49 ~ 0.62 (m, 8H, G0) 0.69 ~ 0.85 (m, 8H, G0)	
	^{13}C	−1.47 (G0)	0.95 (G1P)	8.41, 10.58 (G0)	
GS-2P	^{1}H	0.09 (s, 12H, G0) 0.11 (s, 12H, G1)	0.78 (s, 24H, G2P)	0.43 ~ 0.60 (m, 16H, G0)	1.11 ~ 1.22 (m, 16H, G1) 1.70 ~ 1.82 (m, 16H, G1) 3.65 ~ 3.75 (m, 16H, G1)
	^{13}C	−1.48 (G0) −5.72 (G1)	5.19 (G2P)	4.88, 8.11 (G0)	17.86, 25.63, 63.81 (G1)
GS-3P	^{1}H	0.06 (s, 12H, G0) 0.09 (s, 12H, G1) 0.12 (s, 24H, G2)	0.78 (s, 48H, G3P)	0.41 ~ 0.54 (m, 16H, G0)	0.54 ~ 0.69 (m, 16H, G1) 1.10 ~ 1.20 (m, 32H, G2) 1.47 ~ 1.82 (m, 48H, G1–G2) 3.57 ~ 3.80 (m, 48H, G1–G2)
	^{13}C	−1.51 (G0) −5.70 (G1) −4.99 (G2)	5.19 (G3P)	4.80, 8.06 (G0)	9.52, 25.99, 65.00 (G1) 17.79, 25.56, 63.78 (G2)
GS-4P	^{1}H	0.06 (s,24H,G0 ~ G1) 0.10 (s, 24H, G2) 0.12 (s, 48H, G3)	0.78 (s, 96H, G4P)	0.40 ~ 0.51 (m, 16H, G0)	0.51 ~ 0.68 (m, 48H, G1–G2) 1.09 ~ 1.21 (m, 64H, G3) 1.48 ~ 1.81 (m, 112H, G1–G3) 3.52 ~ 3.79 (m, 112H, G1–G3)
	^{13}C	−1.19 (G0) −5.37 (G1) −4.55 (G2) 1.01 (G3)	5.22 (G4P)	5.01, 8.54 (G0)	13.60, 30.89, 67.97 (G1) 9.60, 26.02, 64.97 (G2) 17.85, 25.61, 63.80 (G3)

tion was completed (by ^{1}H-NMR), excess HSiMeCl$_2$ was removed under vacuum. The platinum catalyst was filtered off with pentane. The volatile components were removed under reduced pressure, leaving 11.67 g (97%) of **GS-1P** as a colorless liquid. Further purification was not available because of their sensitivity against moisture. But, the ^{13}C-NMR spectrum of **GS-1P** showed only one dendrimer. For the characterization of **GS-*n*P** type dendrimers, (Table 4) (^{1}H- and ^{13}C-NMR). Reaction conditions and yields of all **GS-*n*P** type dendrimers were recorded in Table 8.

Table 5
UV spectroscopic data of **GH-*n*** and **GS-*n*** type dendrimers measured in toluene

Compounds (Mw)[a]	χ	λ_{max} (nm)	ε_{max} (l mol^{-1} cm^{-1})	ε_{max}/χ
GH-0 (426.70)	6	240	678	113
GH-1 (1376)	12	240	1953	162
GH-2 (3275)	24	240	4547	189
GH-3 (7074)	48	240	9414	196
GS-1 (977.75)	8	242	902	112
GS-2 (2243)	16	242	2307	144
GS-3 (4776)	32	242	6913	216

χ, Number of double bond.
[a] All compounds were colorless oil.

Table 6
Elemental analysis data of **GH-*n*** and **GS-*n*** type dendrimers

Compounds	Formular	C (found/calculated)	H (%) (found/calculated)
GH-0	$C_{20}H_{34}Si_2O_6$	56.03/56.30	8.05/8.03
GH-1	$C_{62}H_{118}Si_8O_{18}$	54.16/54.11	8.63/8.64
GH-2	$C_{146}H_{286}Si_{20}O_{42}$	53.40/53.54	8.34/8.80
GH-3	$C_{314}H_{622}Si_{44}O_{90}$	53.05/53.31	8.69/8.86
GS-1	$C_{40}H_{80}Si_8O_{12}$	48.95/49.14	8.53/8.25
GS-2	$C_{96}H_{192}Si_{16}O_{28}$	50.88/51.39	8.85/8.62
GS-3	$C_{208}H_{416}Si_{32}O_{60}$	52.15/52.31	8.92/8.78
GS-4	$C_{432}H_{864}Si_{64}O_{124}$	52.63/52.73	8.76/8.85

Table 7
IR spectroscopic data of **GH-*n*** and **GS-*n*** type dendrimer measured in KBr neat

Compounds	$\nu_{C=C,}$ (cm^{-1})
GH-0	1640.1 (s)
GH-1	1648.0 (w), 1667.0 (s)
GH-2	1647.8 (w), 1668.7 (s)
GH-3	1642.0 (s), 1660.0 (w)
GS-1	1646.7 (s)
GS-2	1663.3 (s), 1646.8 (w)
GS-3	1663.5 (s), 1646.8 (w)
GS-4	1663.5 (w), 1646.9 (w)

3.2. General procedure of ***GS-n*** type dendrimers

GS-1. Allylalcohol (5.40 g, 92.9 mmol) in 50 ml toluene was slowly added to a mixture of 9.34 g (11.6 mmol) of **G1P** and 10.80 g of TMED in 150ml toluene for about 2 h. After the addition was finished, the reaction mixture was warmed to about 50°C for 30 min. When the reaction was completed by ^{1}H-NMR, the salt was filtered off and washed with pentane. The volatile components were removed under reduced pressure, leaving a colorless liquid. All yielded compounds were chromatographed on silica gel with toluene as an eluent. The product, **GS-1,** was obtained as a clear and colorless oil. Yields: 8.41 g (8.6 mmol, 74%). For the characterization of all dendrimers, see Table 3 (^{1}H- and ^{13}C-NMR), 5 (UV), 7 (IR), and 6 (EA).

3.3. ***GH-0P***

A mixture of 6.38 g (39.5 mmol) of trichlorovinylsilane, 7.58 g (55.96 mmol) of trichlorosilane, and 0.07 g of platinum based on a hydrosilation catalyst was stirred for 12 h at room temperature. When the completed reaction was checked by ^{1}H-NMR spectroscopy, excessive trichlorosilane was removed under vacuum. The catalyst was filtered off with pentane. The product was crystallized with pentane. Yields: 10.80g (36.34 mmol, 92%) of **GH-0P** $Cl_3SiCH_2CH_2SiCl_3$ as white crystals (mp, 41°C). The preparation of **GH-*n*** and **GH-*n*P** type dendrimers used the same methods in **GS-*n*** and **GS-*n*P** dendrimers under the following conditions (as in Table 8).

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Table 8
Reaction condition and yields of **GH** and **GS** type dendrimers

Compounds No (Mw)	Reactants[a] g (mmol)	Reaction conditions solvent (ml)/ T (°C) h^{-1}	Yields[b] g (mmol, %)
GS-1P (804.80)	S, 5.2 (14.94); D, 6.9 (59.8); C, 0.10	THF (50)/RT–reflux/3	11.67 (14.5, 97)
GS-1 (977.75)	GS-1P, 9.34 (11.6); A, 5.40 (92.9); T, 10.8	Toluene (150)/RT–60/2	8.4 1 (8.6, 74)
GS-2P (1898)	GS-1/ 8.40 (8.6); D, 7.9 (69.0); C: 0.15	THF (50)/RT–60/2	14.9 (7.9, 91)
GS-2 (2244)	GS-2P, 14.7 (7.8); A, 7.2 (124.0); T, 14.4	Toluene (150)/RT–50/1	13.27 (5.9, 76)
GS-3P (4084)	GS-2, 1.93 (0.86); D, 1.6 (13.8); C, 0.1	THF (50)/RT ∼ 60/3	3.20 (0.78, 90)
GS-3 (4776)	GS-3P, 3.50 (0.86); A, 1.6 (27.5); T, 3.2	Toluene (150)/RT–50/1	2.45 (0.51, 60)
GS-4P (8457)	GS-3, 1.20 (0.14); D, 0.87 (7.5); C, 0.1	THF (50)/RT/3	1.82 (0.22, 92)
GS-4 (9841)	GS-4P, 1.20 (0.14); A, 0.88 (15.1); T, 1.8	Toluene (100)/RT–60/3	0.85 (0.09, 64)
GH-0 (426.70)	H, 11.0 (37.04); A, 13 (222); T, 25	Toluene (50)/0–50/1	7.8 (18.35, 50)
GH-1P (1116)	GH-0, 2.7 (6.40); D, 4.4 (38.4); C, 0.10	THF (50)/RT/2	6.3 (5.6, 90)
GH-1 (1376)	GH-1P, 6.3 (5.60); A, 3.9 (67.6); T, 7.5	Toluene (150)/RT–50/1	11.7 (4.2, 86)
GH-2P (2756)	GH-1, 6.6 (4.80); D, 6.7 (57.8); C, 0.12	THF (50)/RT/3	11.7 (4.24, 88)
GH-2 (3275)	GH-2P, 11.7 (4.24); A, 5.9 (101.8); T, 11.8	Toluene (150)/RT/12	11.7 (3.57, 84)
GH-3P (6036)	GH-2, 11.7 (3.57); D, 4.4 (38.4); C, 0.10	THF (50)/RT/2	18.32 (3.03, 85)
GH-3 (7074)	GH-3P, 5.29 (0.9), A:2.4 (42.06); T, 4.9	Toluene (150)/RT/12	5.1 (0.72, 82)

[a] A, Allylalcohol; D, Dichloromethylsilane; C, Catalyst; H, Hexachloroethylenedisilane; S, 2,4,6,8-Tetramethyl-2,4,6,8-tetravinyl-2,4,6,8-tetesila-1,3,5,7-teteraoxacyclooctane; T, TMED.

[b] The **GH-0** type dendrimer was obtained as colorless crystals; **GH-*n*** ($n = 1$–3) and **GS-*n*** dendrimers were obtained as colorless oil; **GH-*n*P** and **GS-*n*P** were obtained as colorless glass.

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