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Synthesis of carbosilane dendrimers based on tetrakis(phenylethynyl)silane

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Abstract

Carbosilane dendrimers of first to third generation were synthesized, using alkynylation/hydrosilation cycles with lithium phenylacetylide and dichloromethylsilane as building blocks and tetrakis(phenylethynyl)silane as a core molecule. The analysis of the ^{1}H- and ^{13}C-NMR, MALDI mass spectra and elemental analysis made it possible to obtain pure and unified dendrimers. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

From the beginning, due to their intriguing supramolecular properties, dendritic macromolecules have received increasing attention [1,2]. Since the spearhead reports on dendritic macromolecules by Vögtle [3], Denkewalter [4], Newkome [5] and Tomalia et al. [6] have developed several synthetic pathways. The application of dendrimers includes nanoscale catalysts, micelle mimics, immunodiagnostics, agents for delivering drugs, chemical sensors, high performance polymers and liquid crystals [7–12].

The first preparation of the carbosilane dendrimers introduced by van der Made was performed by repetitive alkenylation–hydrosilation cycles using allylmagnesium bromide and trichlorosilane as building blocks and tetraallylsilane as a core molecule [13]. Seyferth and coworkers prepared the carbosilane dendrimers that contain ethynyl-groups on their periphery ([14]a and b). Meanwhile, numerous reports have also appeared on the syntheses and properties of dendritic carbosilane ([14]c and d). In the previous paper, we described a preparation of carbosilane dendrimers based on quantitative hydrosilation–alkenylation cycles with hexaallylethylenedisilane and siloxane tetramer [1,15]. The repeating of these cycles with hexaallylethylenedisilane as a core molecule and dichlomethylsilane and allylmagnesium bromide as building blocks resulted in **G3** with 48 allylic end groups in excellent yields ([15]b). The dendritic generations with alkynyl end groups with organic rest have been synthesized [16].

In this paper, we wish to report our results on the synthesis and identification of dendritic macromolecules based on tetrakis(phenylethynyl)silane as a core molecule and bis(phenylethynyl)methylsilyl groups as a repeat unit on its periphery. We reported the regioselective addition of hydrosilane to phenylalkynyl groups in the presence of Pt/C as a heterogeneous catalyst [1,15]. Identification of prepared silane dendrimers can be obtained by ^{1}H- and ^{13}C-NMR, MALDI mass, UV spectroscopic attachments as well as elemental analysis.

2. Results and discussion

The synthesis of carbosilane dendrimers (**G0**–**G3** and **G1P**–**G3P**) is based on the complete hydrosilation and alkynylation of alkynylsilane and chlorosilane as shown in Scheme 1. The hyperbranched dendrimers, based on tetrakis(phenylethynyl)silane ($(PhC{\equiv}C)_4Si$; $N_c = 4$) as a core molecule with bis(phenylethynyl)methylsilyl end

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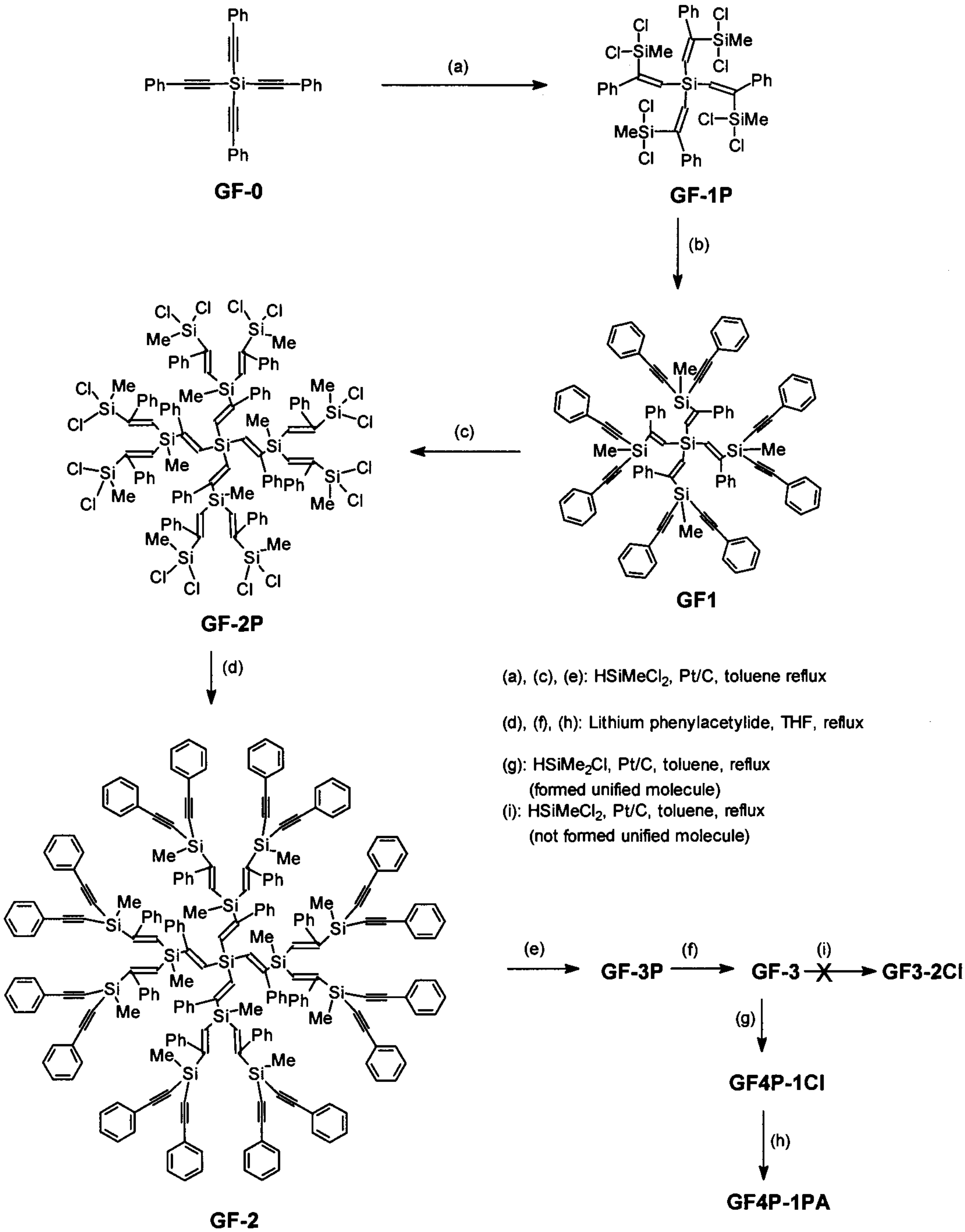


(a), (c), (e): $HSiMeCl_2$, Pt/C, toluene reflux

(d), (f), (h): Lithium phenylacetylide, THF, reflux

(g): $HSiMe_2Cl$, Pt/C, toluene, reflux
(formed unified molecule)
(i): $HSiMeCl_2$, Pt/C, toluene, reflux
(not formed unified molecule)

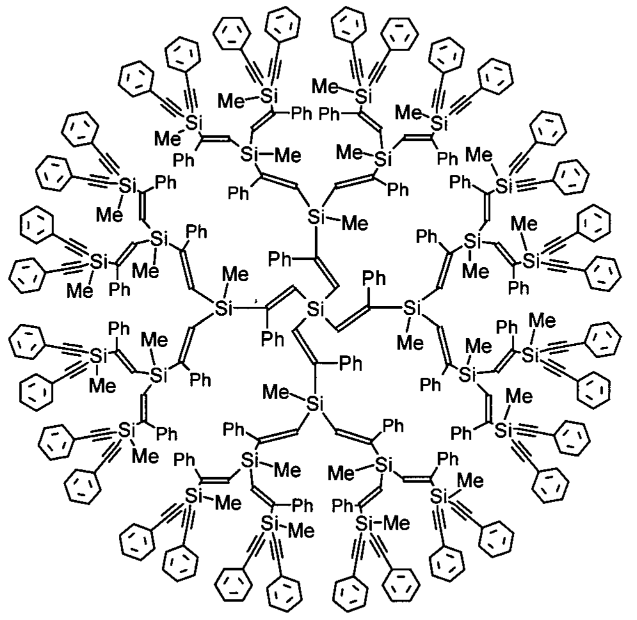
Scheme 1. Synthetic way of dendritic carbosilane.

groups as a building block, to **G3** ($l = 2$, $N_b = 2$) have been synthesized by the use of hydrosilation-alkynylation sequences Scheme 2. The dichloromethylsilyl-capped dendrimers (**G1P**–**G3P**) were produced by the hydrosilation of alkynyl groups in **Gn-1** generation with dichloromethylsilane in the presence of a platinum catalyst [17] (Pt/C; 10% platinum content on activated carbon) with quantitative yields. The silylated generations (Cl_2MeSi-: **GnP**) were converted to the corresponding dendritic carbosilanes containing phenylethynyl groups by the treatment with lithium phenylacetylide in THF. Carbosilane dendrimers with 8 (**G1**), 16 (**G2**), and 32 (**G3** and **G4P**–**1PA**) alkynyl end groups were obtained by using this synthetic approach.

Table 1
NMR spectroscopic data of **Gn** type dendrimers

Compounds		MeSi	C=CH	C≡C	Ph (ppm)
G0	^{1}H	—	—	—	6.97–7.05, 7.26–7.30
	^{13}C	—	—	86.03 106.57	128.22 (m), 129.45 (o) 132.49 (p), 122.01 (q)
G1	^{1}H	0.31 (s, 12H)	6.10 (s, 4H)		7.19–7.25, 7.39–7.40
	^{13}C	−0.93	147.14 156.18	89.47 107.21	127.82 (o, G0), 128.14 (o, G1) 128.30 (m, G0), 132.01 (m, G1) 126.61 (p, G0), 128.69 (p, G1) 143.25 (q, G0), 122.81 (q, G1)
G2	^{1}H	−0.91 (s, 12H, G1) 0.32 (s, 24H, G2)	5.53 (s, 4H, G1) 6.42 (s, 8H, G2)		7.30–7.40 (m, 20H, G0) 7.11–7.25 (m, 80H, G2) 6.86–7.07(m, 80H, G2)
	^{13}C	−3.08 (G1) −0.91 (G2)	157.47 (G1) 160.82 (G1) 107.43 (G2) 126.37 (G2)	89.42 107.35	145.69 (m, G0),142.92 (o, G0), 144.97 (p, G0), 144.57 (q, G0), 128.05 (o, G1), 128.16 (o, G2), 126.37 (p, G1), 127.87 (p, G2), 127.59 (q, G1), 122.72 (q, G2)
G3	^{1}H	−0.92 (s, 12H, G1) 0.35 (s, 24H, G2) 0.29 (48H, G3)	5.78 (s, 4H, G1) 6.40 (s, 8H, G2) 6.52 (s, 16H, G3)		6.68–7.50 (m, 300H, G1–G3)
	^{13}C	−1.96 (G1) −3.28 (G2) −0.91 (G3)	107.39 (G3) 89.18 (G3)	89.32 107.48	132.01 (m, G3), 128.17 (o, G3), 127.56 (p, G3) 122.62 (q, G3), 89.32, 129.00, 145.56, 107.39, 142.64, 157.71, 126.35, 142.77, 157.99, 128.01, 144.51, 161.07, 128.80, 145.25, 162.96
G4P–1PA	^{1}H	−0.97 (s, 12H, G1) −0.75 (s, 72H, G2–G3) 0.12 (s, 192H, G4)	5.36 (s, 4H, G1) 5.63 (s, 8H, G2) 6.06 (s, 16H, G3) 6.14 (s, 32H, G4)		6.61–7.36 (m, G0–G4)
	^{13}C	−1.57 (G4) −2.63 (G1–G3)		92.51 (G4) 106.69 (G4)	131.83 (m, G4), 128.20 (o, G4), 127.63 (p, G4), 123.13 (q, G4), 77.20, 132.11, 144.62, 125.99, 142.80, 145.06, 128.47, 143.71, 161.29, 128.85, 143.93

The subsequent generation **G4P** with 64 Si–Cl groups did not make a unified form by the hydrosilation step. But, the formation of **G4P–1Cl** by the reaction of **G3** and $HSiMe_2Cl$ was unified as announced by NMR spectroscopic views. This result means that dendritic growth has been limited [1,15]. Eventually, synthesis of **G4P** with 64 Si–Cl bonds will result in surface saturation, which will prevent further growth from all branch



Scheme 2. Planar view of third generation (**G3**) with 32phenylethynyl groups ($N_c = 4$, $N_b = 2$ and $M_w = 7331$).

points so that the dendrimer will no longer be unified. But the other synthetic pathways of lower generations (**G0**–**G3** and **G1P**–**G3P** and **G4P**–**1Cl**) produced quantitative and unified dendrimers.

Purification of the dendrimers was performed by chromatography with a freshly prepared column after each alkynylation step. Carbosilane dendrimers with 8 (**G1**), 16 (**G2**), 32 (**G3**), and 32 (**G4P**–**1PA**) phenylethynyl end groups were obtained using this synthetic approach.

The prepared dendrimers were structurally characterized by ^{1}H- and ^{13}C-NMR spectroscopy (Tables 1 and 2, and Fig. 1), elemental analyses (Table 3), MALDI mass (Fig. 3), IR (Table 4), and UV–VIS spectroscopy (Table 5 and Fig. 2). Firstly, both reactions to **G4P**–**1PA** generations seem to be free of side reaction by the NMR spectroscopic observations (^{1}H and ^{13}C). The ^{1}H- and ^{13}C-NMR spectroscopic analyses of **G0**–**G3** as well as **G0P**–**G3P** in $CDCl_3$ show perfect building of dendrimers. The NMR spectra reflect the transformation from **Gn**-type dendrimers with phenylethynyl end groups to **GnP**-type dendrimers with $SiMeCl_2$ end groups and the transition from **GnP** to **Gn**. By ^{1}H-NMR spectroscopic attachment, the formation of alkenyl bonds (=C–H) showed 6.10 ppm (for **G1**), 5.53 and 6.42 ppm (**G2**), 5.78, 6.40 and 6.52 ppm (**G3**) with single signals consistent with 1:2 for **G2** and 1:2:4 (**G3**) of area ratio. The formation of methylsilyl groups (MeSi) showed 0.31 ppm (for **G1**), −0.91 and 0.32 ppm (**G2**), −0.92, −0.35 and 0.29 ppm (**G3**) with single signals consistent with 1:2 for **G2** and 1:2:4 (**G3**) of area ratio. The ^{13}C-NMR spectra of **Gn**-type dendrimers show resonance at −0.93 ppm (**G1**), −3.08 and −0.91 ppm (**G2**), and −1.96, −3.28 and −0.91

Table 2
NMR spectroscopic data of **GnP**-type dendrimers

Compounds		MeSi	C=CH	Ph
G1P	^{1}H	0.62	5.89	6.94–6.99, 7.29–7.32
	^{13}C	4.53	146.48	128.49 (o), 127.97 (p), 128.14 (m)
			156.56	140.26 (q)
G2P	^{1}H	−0.39 (G1)	6.16 (G1)	7.22–7.27 (G1)
		1.13 (G2P)	6.87 (G2)	7.67–7.77 (G2P)
	^{13}C	−3.32 (G1)	126.65 (G1)	128.03 (o, G1), 146.33 (o, G2P),
		4.44 (G2P)	129.00 (G1)	127.80 (p, G1), 144.07 (p, G2P)
			156.84 (G2P)	127.3 (m, G1), 139.92 (m, G2P),
			157.80 (G2P)	125.25 (q, G1), 144.26 (q, G2P)
G3P	^{1}H	−0.82 (G1)	158.38 (G1)	6.57–6.77, 7.03–7.30 (G1–G3P)
		−0.32 (G2)	5.89 (G2)	
		0.62 (G3P)	6.38 (G3P)	
	^{13}C	−2.03 (G1)	139.92, 143.69	128.05 (o, G3P), 127.85 (p, G3P)
		−3.49 (G2)	145.34, 146.15	129.41 (m, G3P), 129.04 (q, G3P)
		4.49 (G3)	157.28, 161.63	127.66, 126.35, 125.29
G4P–**1Cl**	^{1}H	−0.90 (G1)	5.30 (G1)	6.16–7.25 (G1–G4P)
		−0.72 (G2–G3)	5.44 (G2)	
		0.29 (G4P)	6.07 (G3)	
			6.16(G4P)	
	^{13}C	−2.77	137.86, 142.28	125.29, 126.04, 126.55, 127.71,
		(G1–G3)	142.45, 143.65,	128.21, 128.34, 129.04
		1.45(G4P)	161.05	

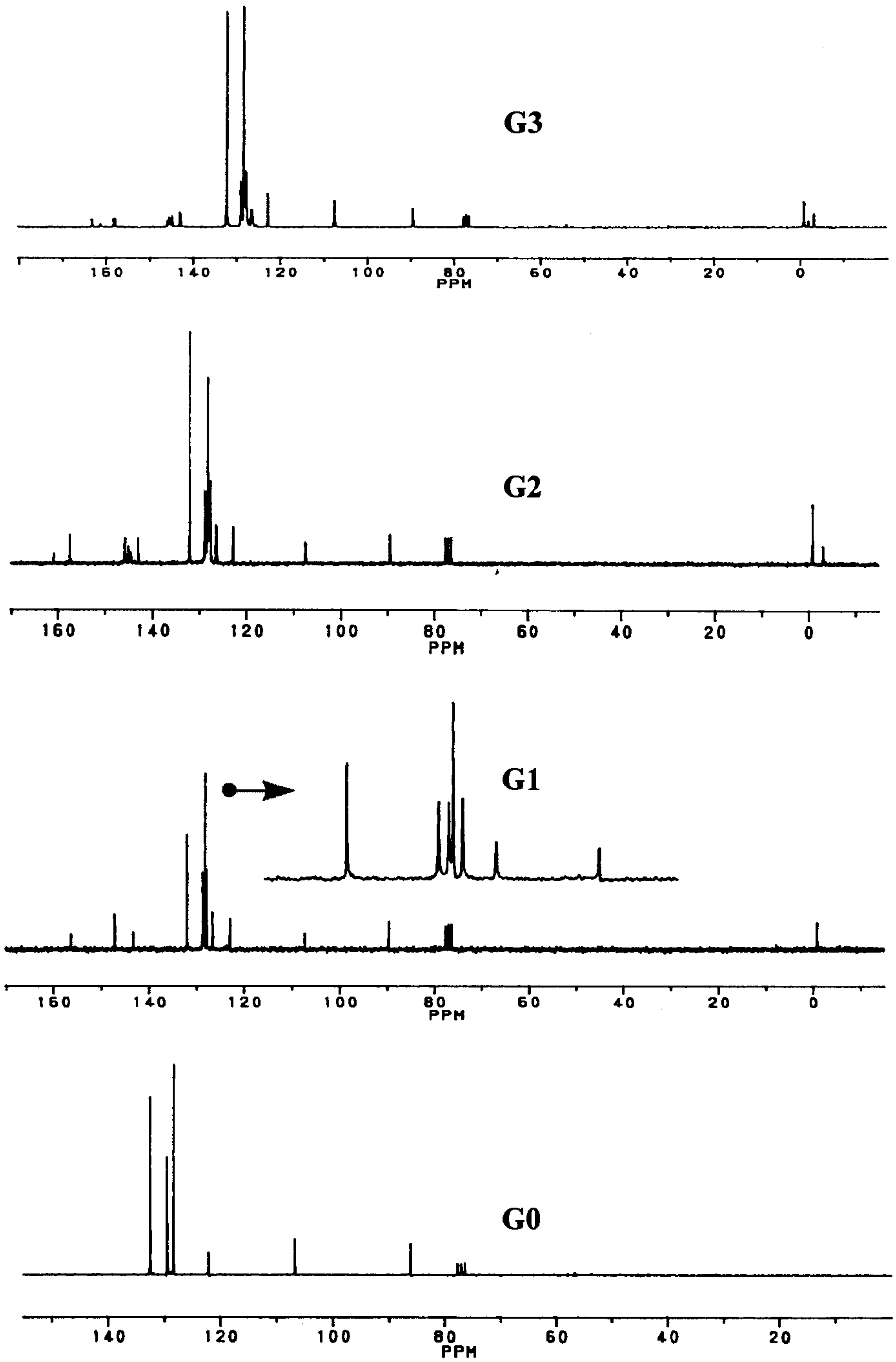


Fig. 1. ^{13}C-NMR spectroscopic view of **G0**–**G3** measured in $CDCl_3$.

ppm (**G3**) attributed to terminal MeSi groups, resonance with 107–160 ppm, due to alkenyl carbon (C=CH), and resonance with 86.03–89.40 ppm and 106.5–107.0 ppm, introducing alkynyl triple bonds on the periphery of each **Gn** dendrimer. The ^{1}H-NMR spectra of **GnP** type dendrimers reflect the same evidence of **Gn** generations, which show three main signals at the environs of zero ppm for MeSi groups, 5.50–6.50 ppm for C=C–H groups, and at multiple environ 7.25 ppm for protons of characteristic phenyl group for **Gn** and **GnP** molecules (while the formation of **GnP** makes the resonance attributed to **Gn** disappear: Tables 1 and 2).

UV-VIS spectroscopy is used to examine the solution of **Gn**-type dendrimers (**G0**–**G3** and **G4P**–**1PA**) in toluene. The spectra of given compounds are similar and consist of a broad band with a maximum at a wave length (λ_{max}) of about 288 nm. The molar

Table 3
Elemental analyses

Compounds	Formula	C (found/calcd.)	H (found/calcd.)
G0	$C_{32}H_{20}Si$	88.00/88.85	4.64/4.66
G1	$C_{100}H_{76}Si_5$	83.85/84.70	5.58/5.40
G2	$C_{236}H_{188}Si_{13}$	83.29/83.64	5.78/5.57
G3	$C_{508}H_{412}Si_{29}$	83.16/83.23	5.81/5.66
G4P–1PA	$C_{828}H_{796}Si_{61}$	78.75/79.84	6.43/6.46

absorbities (ϵ_{max}) of all phenylethynylsilyl-capped dendrimers [**G0** (4 alkynyl groups), **G1** (8 alkynyl groups), **G2** (16 alkynyl groups), **G3** (32 alkynyl groups), and **G4P–1PA** (32 alkynyl groups)] are approximately in proportion to the number of alkynyl groups. We expect the possibility of determining molecular mass of these types of dendrimers by the use of increasing phenomena of molar absorbities of given compounds (Table 5 and Fig. 2).

Table 4
FT–IR spectroscopic data

Compounds	IR $\nu_{C\equiv C}$	νC=C cm^{-1}
G0	2163.5	
G1	2158.8	1594.4
G2	2157.9	1594.7
G3	2157.8	1595.0
G4P–1PA	2157.4	1596.3

MALDI mass spectroscopy has recently found application in this area [18]. A method on laser desorption of molecules dissolved in a suitable matrix. The potential of MALDI mass spectroscopy for direct analysis of dendritic macromolecules is intensely explored at present [2]j, [12]a. Thus, the MALDI mass spectroscopy is a highly valuable method for the analysis of the structural perfection of dendrimers. This is demonstrated by the recent investigation of polyethynyl dendrimers, polyesters and carbosilane based dendritic polyols with excellent results [12]a. The MALDI mass spectrum of **G3** ($M_w = 7331$) mainly shows two signals that are clearly due to the 32 phenylethynyl end groups

Table 5
UV spectroscopic data

Compounds	M_w	χ	λ_{max} (mm)	$\epsilon_{max} \times 10$ (mole^{-1} cm^{-1})	$\epsilon_{max} \times 10^3$
G0 ($C_{32}H_{20}Si$)	432.60	4	287	136	34
G1 ($C_{100}H_{76}Si_5$)	1418.1	8	289	593	74
G2 ($C_{236}H_{188}Si_{13}$)	3389.2	16	288	1498	94
G3 ($C_{508}H_{412}Si_{29}$)	7331	32	287	3173	99
G4P–1PA ($C_{828}H_{796}Si_{61}$)	12 460	32	288	3572	112

χ number of triple bonds.

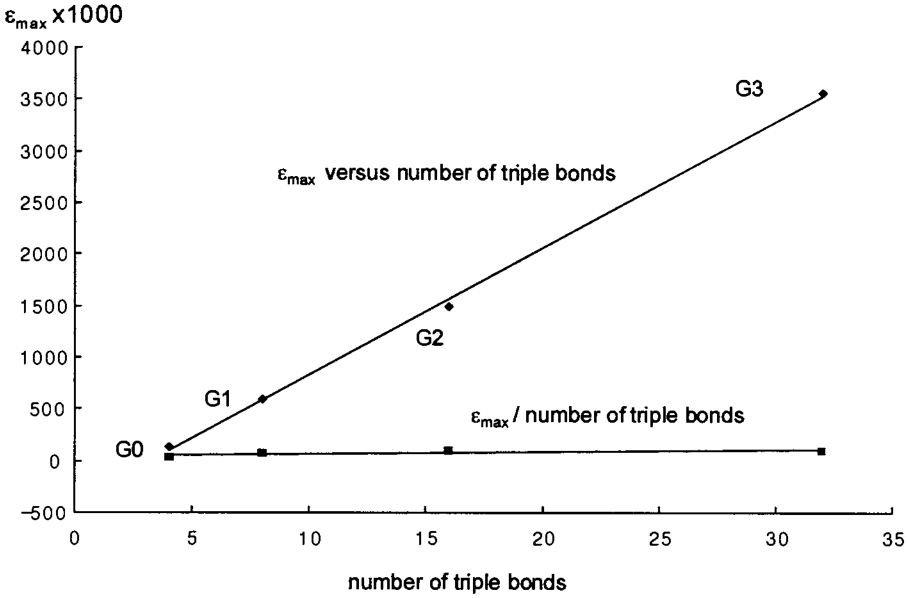


Fig. 2. Plot of ϵ_{max} versus number of triple bonds in **Gn** ($n = 1$–3) type dendrimers.

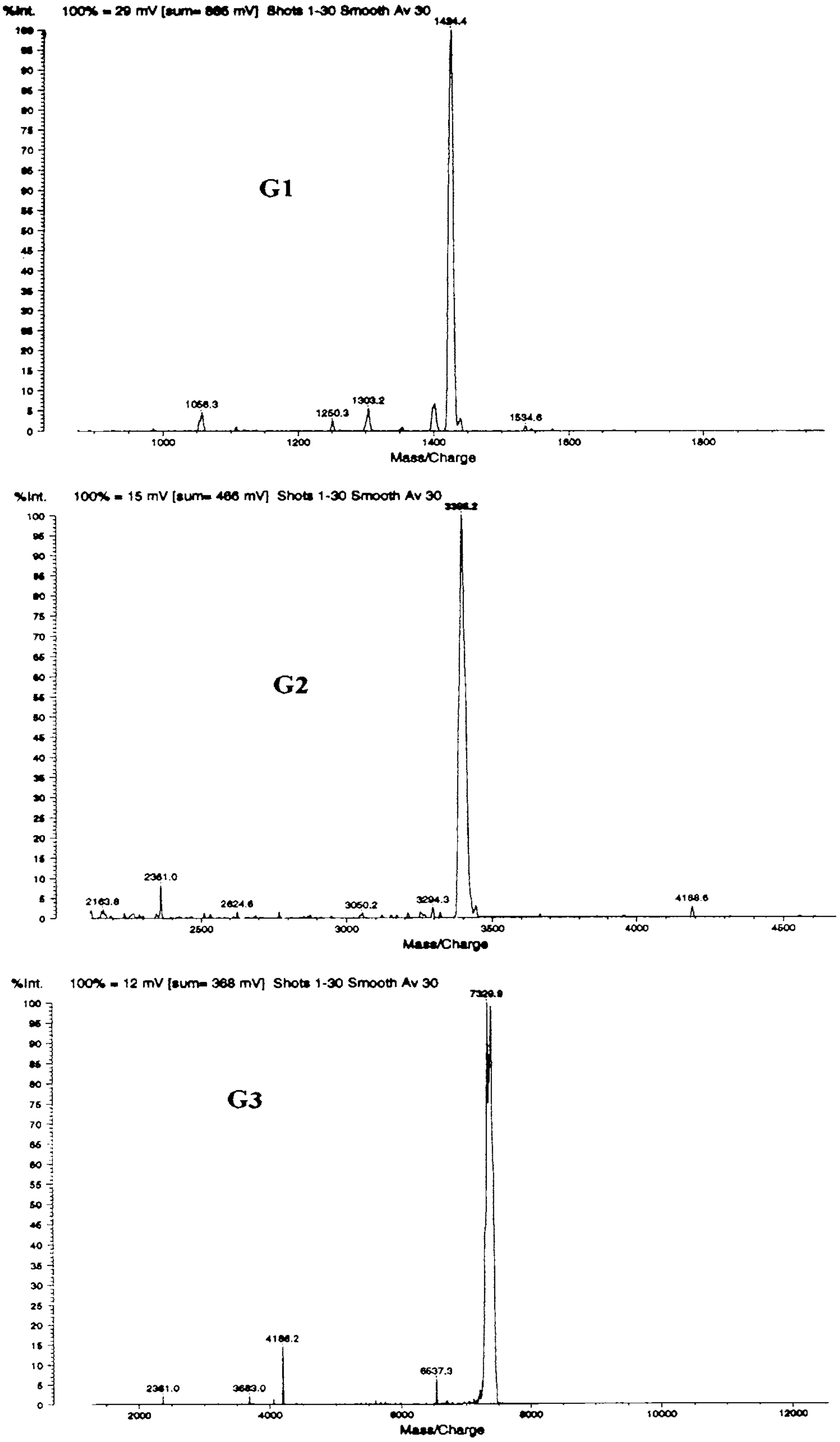


Fig. 3. MALDI mass spectroscopic view of dendritic silanes **G1**, **G2** and **G3**.

containing dendrimers. The m/z value of the dominant signal corresponds to the calculated value of m/z for **G3** dendrimer (Fig. 3). No signals are observed between these peaks, which clearly confirms that fragmentation of phenylethynyl groups on the molecular surface does not affect the analysis.

The glass transition (T_g) temperature has been measured for a number of dendritic molecules. Whereas, no crystallization was observed for terminated dendrimers. All dendrimers were soluble in THF, Et_2O, and toluene but practically insoluble in hydrocarbons and alcohols.

3. Experimental

3.1. General procedures

All reactions were carried out under a static pressure of dried N_2 atmosphere. 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 Na metal. A platinum catalyst (Pt on activated carbon, 10% Pt content) was used after vacuum dry at room temperature. NMR spectra were recorded on Bruker AC-200 Spectrometer in $CDCl_3$. NMR chemical shifts refer to the signals of the solvents used. FT–IR spectra were measured by IFS 55 (Bruker). UV spectra were measured by HP 8452A Diode Array UV/Vis. Spectrophotometer (HP). Elemental analysis and MALDI mass spectroscopic attachments were performed by the Pusan and Daejon Branch of the Korean Basic Science Institute.

3.2. Alkynylation (**G0**)

5.90 g (34.73 mmol) of $SiCl_4$ in 50 ml THF was slowly added over a period of 2 h to 150 ml of 1 mol ml^{-3} LiC≡CPh (150 mmol) in THF. After the addition was finished, the reaction mixture was refluxed for 4 h. When the reaction was completed by ^{1}H-NMR, solvents were removed under reduced pressure. The salt was precipitated in 150 ml toluene and filtered off. The volatile components were removed under reduced pressure, leaving 15.0 g of a yellow precipitate. All yielded compounds were chromatographed on silica gel with toluene as an eluent. The product, **G0** ($Si(C{\equiv}CPh)_4$), was obtained as a clear, yellow solid. Yield: 12.10 g (27.97 mmol, 80%) of tetraphenylethynylsilane. **G0** to **G3** and **G4P–PA** were synthesized by this method. For characterization of **Gn**-type dendrimers **G0** to **G4P–PA**, see Tables 1 and 3–5.

3.3. Hydrosilation (**G1P**)

A mixture of 10 g (23.12 mmol) of **G0**, 18 g (157.47 mmol) of $HSiMeCl_2$ and 0.10 g of a common hydrosilation catalyst (e.g. 10% Pt content on activated carbon) in 50 ml toluene was refluxed for 48 h. When the reaction was complete (^{1}H-NMR), excess $HSiMeCl_2$ was removed under vacuum. The platinum catalyst was filtered off and the volatile components were removed under reduced pressure, leaving 20.64 g of **G1P** as a yellow solid. Further purification was not available because sensitivities against moisture. But, ^{13}C-NMR spectrum showed only one dendrimer. Yields: 20.00 g (97%) of **G1P** as a yellow solid. **G1P–G3P** and **G4P–1Cl** were synthesized by this method. For characterization of **GnP**-type dendrimers **G1P** to **G4P–1Cl** see Tables 2–5.

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