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Dendritic carbosilanes containing hydroxy groups on the periphery

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Abstract

Dendritic carbosilanes with hydroxy groups on the periphery have been prepared. The hydroxy-group-containing dendrimers were prepared by the use of the hydroboration of carbosilane dendrimers containing double bonds with 9-BBN and the subsequent oxidation of the prepared dendrimers. Oxidation of the hydroborated dendrimers in an alkali medium gave quantitative yields. The hydroboration and oxidation procedures were monitored by ^{1}H- and ^{13}C-NMR spectroscopy. Using MALDI mass spectroscopy, the carbosilane dendrimers with hydroxy groups have been characterized with respect to the unified form in all cases. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Dendrimer; Dendritic carbosilane; Dendritic polyol

1. Introduction

Dendrimers with refined inner and outer structural conformations have access to macromolecular materials having special properties such as nanoscale catalysts, drug delivery and chemical sensors and so on [1]. To date, a lot of papers concerning the synthesis and identification of the two-layered dendritic characters has been published [2]. A number of studies of carbosilane dendrimers with two different generating layers for inner and outer shells, which are well-defined highly branched macromolecules that emanate from the small core, have been focused on the modification of the important properties of such molecules by the functionalization of the dendritic surfaces [3]. Furthermore, the use of hydroxy groups on the periphery of the dendritic structure for the purpose of controlled drug release is discussed [4]. As part of our ongoing studies of carbosilane macromolecules, we recently reported several families of carbosilane dendrimers containing special functions, such as allyl, allyloxy, propagyloxy, and ethynyl groups [5]. The hydroxy-group-containing dendrimers are very attractive materials because of their possible applications as carriers of drugs and sensors [6]. This synthetic approach with hydroxy groups has been extended to carbosilane dendrimers [7]. We report here the preparation of hydroxy-group-containing dendrimers with two models such as 2,4,6,8-tetramethyl-2,4,6,8-tetravinyl-2,4,6,8-tetrasila-1,3,5,7-tetraoxacyclooctane $(Me(CH_2{=}CH)SiO)_4$ (GS type dendrimers) and 1,2-bis(triallylsilyl)ethane $((CH_2{=}CHCH_2)_3SiCH_2)_2$ (GH type dendrimers) as core molecule which have allyl and methylsiyl groups as generating groups ($N_l = 3$, $N_b = 2$). The synthesis of the new dendritic hydroxy-group-containing dendrimer was clearly achieved by the hydroboration of allyl-group-containing dendrimers and the subsequent oxidation of the prepared compounds [7,10]. All hydroxy-group-containing dendrimers were characterized by the use of MALDI mass spectroscopic attachments.

2. Results and discussion

The preparation of dendritic carbosilanes was established with two core molecules, which have $(Me(CH_2{=}CH)SiO)_4$ (GS type dendrimer with a branching degree of 4; $N_c = 4$) and $((CH_2{=}CHCH_2)_3SiCH_2)_2$ (GH type dendrimer with branching point 6; $N_c = 6$) [8,9]. The dendrimers which have 6, 12, 24, 48 allylic end groups for GH*n* type and 8, 16, 32 and 64 allylic end groups for GS*n* type dendrimers were prepared by

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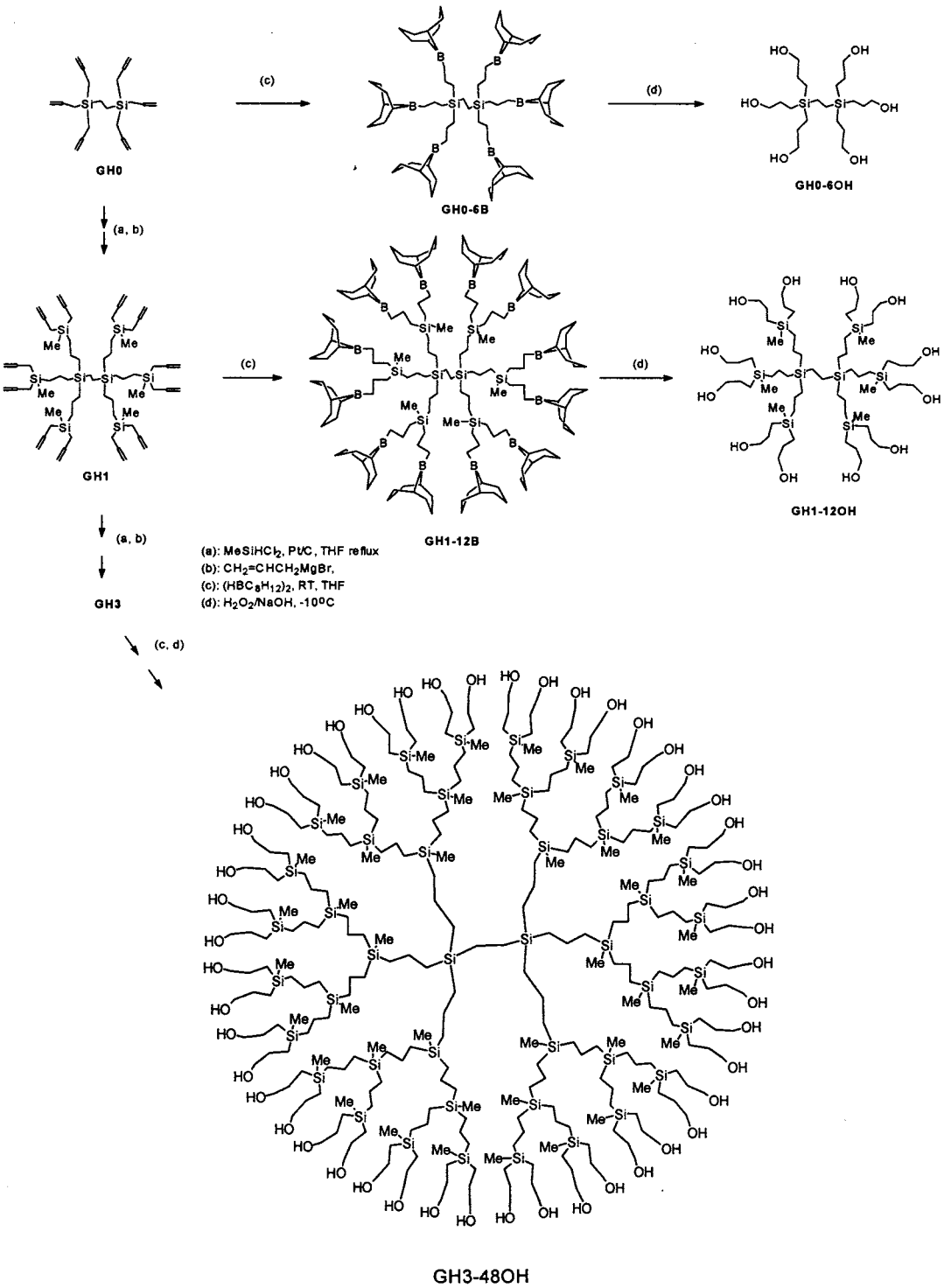
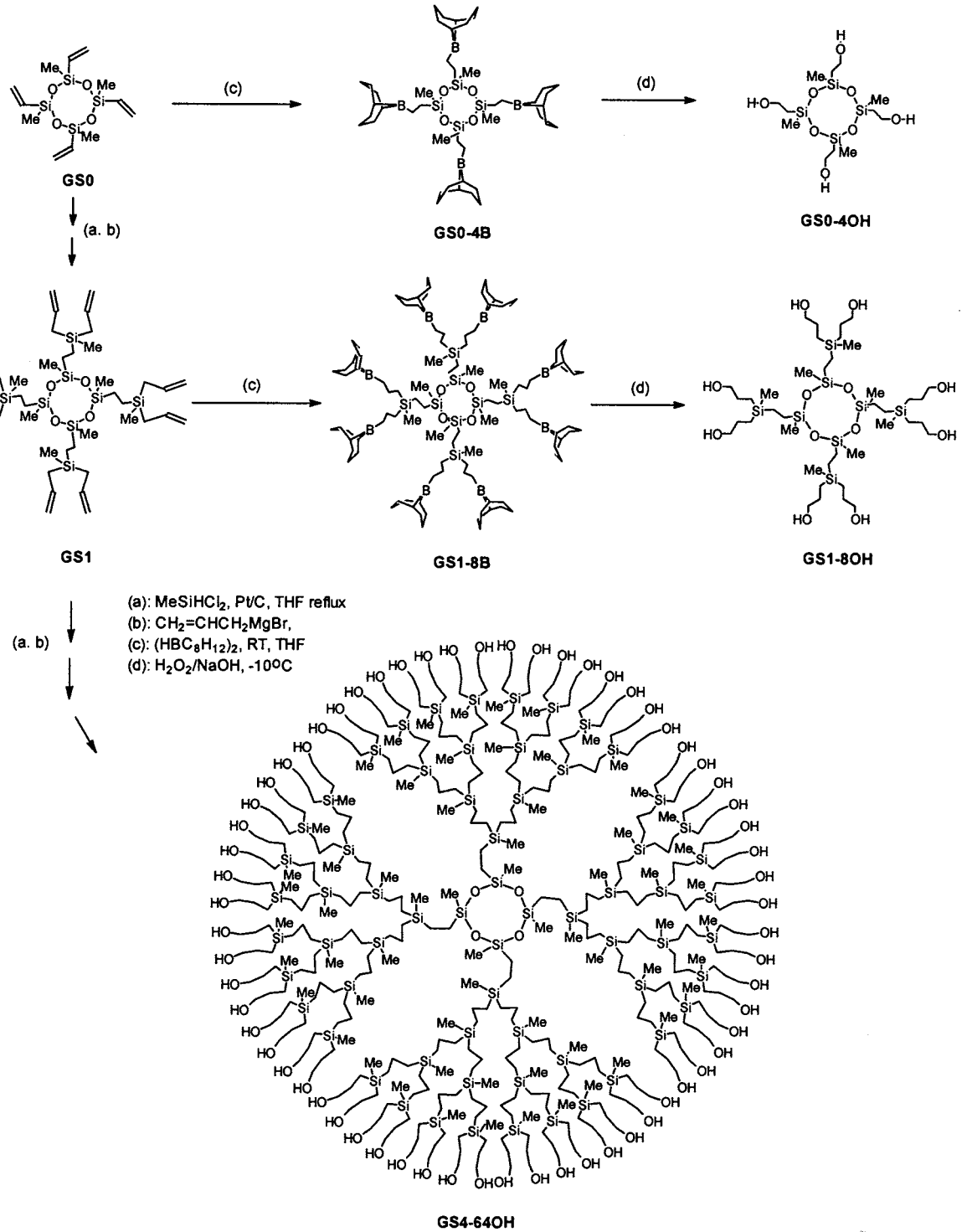
the use of alternative procedures such as hydrosilylation with methyldichlorosilane and subsequent alkenylation with allylmagnesium bromide [5,9]. Carbosilane dendrimers with allylic end groups using this synthetic method were produced in a very high yield [9].

The hydroboration using 9-BBN with GH*n* and GS*n* type dendrimers with allylic end groups leads to anti-Markovnikov addition of borane at double bonds [11]. This functionalization route is illustrated in Schemes 1 and 2, showing the synthesis of borane groups on the dendritic carbosilane periphery (GH*n*–*m*B; $n = 0$–3, $m = 6$, 12, 24, 48, and GS*n*–*m*B; $n = 1$–4, $m = 8$, 16, 32, 64). Further isolation of the dendrimers was not available because they were unstable against moisture.



Scheme 1. Synthetic routes for GH*n*–*m*B and GH*n*–*m*OH ($n = 0$–3; $m = 6$, 12, 24 and 48).



Scheme 2. Synthetic routes for GSn–mB and GSn–mOH ($n = 0$–4; $m = 4$, 8, 16, 32 and 64).

However, the NMR spectra of the prepared GHn–mB and GSn–mB showed only hydroboration products (see Figs. 1 and 3). The oxidation of the prepared dendritic boranes produced in an alkali medium. The separation of hydroxy-group-containing dendrimers from their mixture with 1,5-cyclooctanediol is an important step in the synthesis of GHn–mOH and GSn–mOH. The mixture of hydroxy-group-containing dendrimers and 1,5-cyclooctanediol has been separated easily from the gelatin-type boric acid by the use of a decantation process. The 1,5-cyclooctanediol as side product could be removed by vacuum distillation.

Figs. 1 and 3 show the ^{13}C-NMR spectra which reflect the transition from a Gn type to Gn–mB and Gn–mOH with slightly different chemical environments from all different models. The NMR spectral evidence

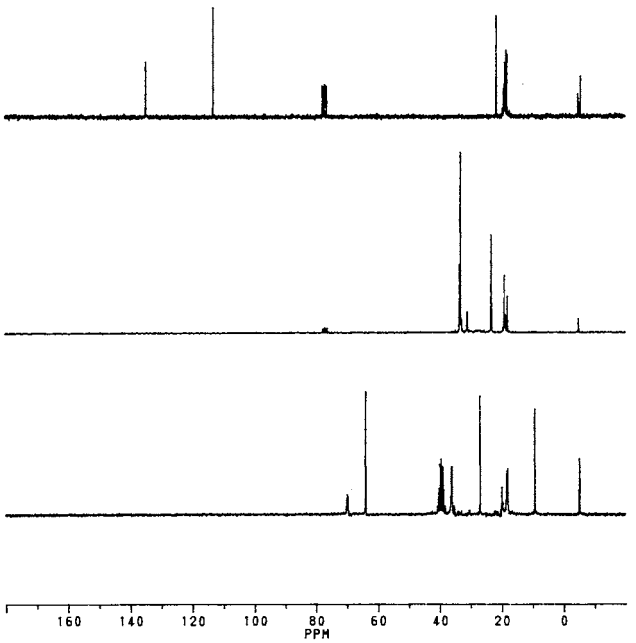


Fig. 1. ^{13}C-NMR spectra of GH3 (top) with 48 allylic end groups in $CDCl_3$, GH3–48B with 48 9-BBN in $CDCl_3$ (middle) and GH3–48OH with 48 hydroxy groups in DMSO-d_6 on the outmost periphery (bottom), which have a trace of 1,5-cyclooctanediol as a byproduct.

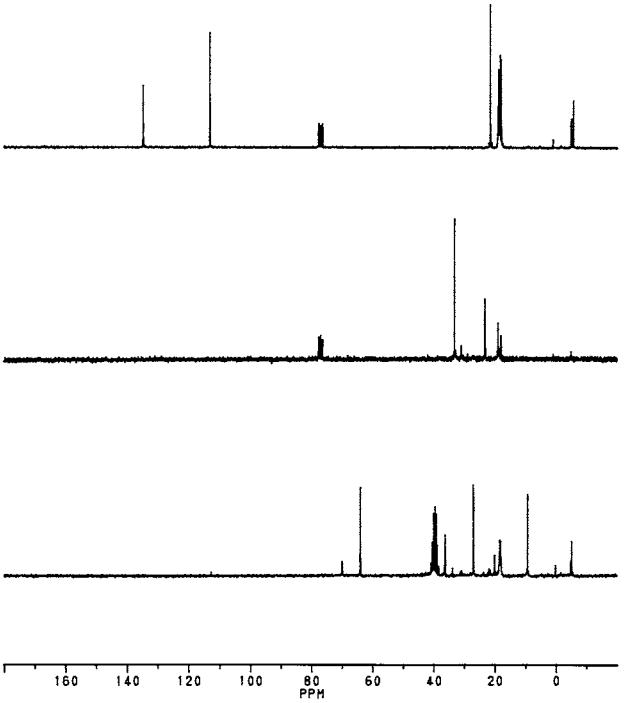


Fig. 3. ^{13}C-NMR spectra of GS4 (top) with 64 allylic end groups in $CDCl_3$, GS4–64B with 64 9-BBN in $CDCl_3$ (middle) and GS4–64OH with 64 hydroxy groups on the outmost periphery (bottom), which have trace of 1,5-cyclooctanediol as a side product.

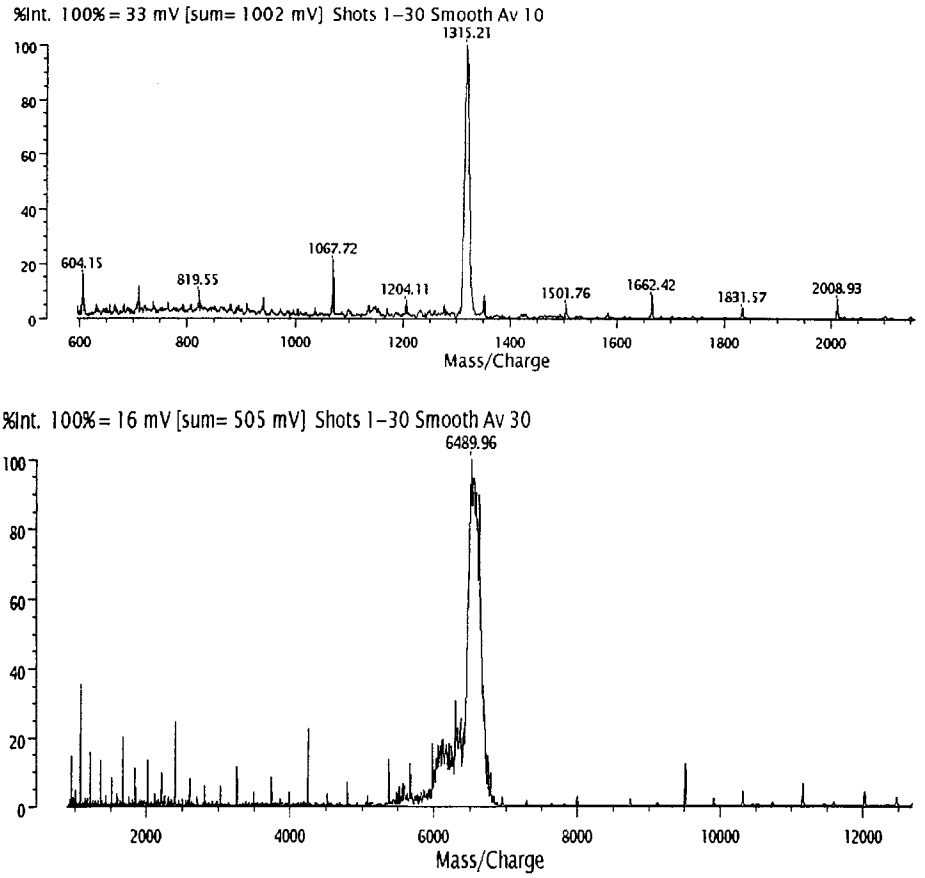


Fig. 2. MALDI mass spectra of GH1–12OH (top) and GH3–48OH (bottom).

Table 1
^{1}H- and ^{13}C-NMR spectroscopic data of GHn–mB type dendrimers measured in $CDCl_3$

Compounds		MeSi	CH_2Si	CH_2	CH_2B	9-BBN
GH0–6B	^{1}H		0.44 (s, 4H, G0)	0.57 (m, 4H, G0)	1.19 (m, 12H, G0)	1.86–1.20
	^{13}C		4.59 (G0)	16.23, 19.05 (G0)	30.91 (G0)	23.26, 23.19, 33.14, 33.43
GH1–12B	^{1}H	−0.50 (s, 18H, G1)	0.34 (s, 4H, G0)	0.53 (m, 48H, G1), 0.53 (m, 36H, G0)	1.19 (s, 24H, G1)	1.84–1.19
	^{13}C	−4.87 (G1)	4.77 (G0)	18.04, 18.99 (G1), 17.11, 18.68, 19.14 (G0)	30.93 (G1)	23.21, 23.28, 33.15, 33.43
GH2–24B	^{1}H	−0.04 (s, 36H, G2), −0.07 (s, 18H, G1)	0.33 (s, 4H, G0)	0.55 (m, 96H, G2), 0.55 (m, 108H, G0–G1)	1.20 (m, 48H, G2)	1.85–1.20
	^{13}C	−4.84 (G2), −4.98 (G1)	4.85 (G0)	18.06, 19.01 (G2), 17.23, 18.64, 19.31 (G0–G1)	30.99 (G2)	23.20, 23.30, 33.17, 33.45
G3–48B	^{1}H	−0.04 (s, 72H, G3), −0.07 (s, 54H, G2–G1)	0.30 (s, 4H, G0)	0.56 (m, 192H, G3), 0.56 (m, 252H, G0–G2)	1.25 (m, 96H, G3)	1.87–1.25
	^{13}C	−4.84 (G3), −4.97 (G2–G1)	4.79 (G0)	18.04, 19.00 (G3), 17.58, 18.65, 19.35 (G0–G2)	30.80 (G3)	23.19, 23.30, 33.16, 33.43

Table 2
^{1}H- and ^{13}C-NMR spectroscopic data of GHn–mOH type dendrimer measured in DMSO-d_6

Compounds		MeSi	CH_2Si	CH_2	CH_2O	OH
GH0–6OH	^{1}H		0.37 (s, 4H, G0)	0.48 (m, 12H, G0), 1.40 (m, 12H, G0)	3.33 (m, 12H, G0)	4.41 (m, 6H, G0)
	^{13}C		3.86 (G0)	7.41, 27.04 (G0)	64.09 (G0)	
GH1–12OH	^{1}H	−0.87 (s, 18H, G1)	0.37 (s, 4H, G0)	0.53 (m, 24H, G1), 1.40 (m, 24H, G1), 0.46 (m, 36H, G0)	3.35 (m, 24H, G1)	4.38 (m, 12H, G1)
	^{13}C	−5.12 (G1)	4.44 (G0)	9.34, 26.98 (G1), 16.59, 18.15 (G0)	63.94 (G1)	
GH2–24OH	^{1}H	−0.09 (s, 36H, G2), −0.10 (s, 18H, G1)	0.37 (s, 4H, G0)	0.52 (m, 48H, G2), 1.40 (m, 48H, G2), 0.45 (m, 108H, G0–G1)	3.32 (m, 48H, G2)	4.40 (m, 24H, G2)
	^{13}C	−5.10 (G2), −4.82 (G1)	4.43 (G0)	9.32, 27.00 (G2), 18.09, 18.25, 18.40 (G0–G1)	63.96 (G2)	
GH3–48OH	^{1}H	−0.09 (s, 72H, G3), −0.08 (s, 54H, G1–G2)	0.38 (s, 4H, G0)	0.52 (m, 96H, G3), 1.40 (m, 96H, G3), 0.46 (m, 252H, G0–G2)	3.35 (m, 96H, G3)	4.41 (m, 48H, G3)
	^{13}C	−5.15 (G3), −4.90 (G1–G2)	4.30 (G0)	9.28, 26.96 (G3), 18.12, 18.36, 18.45 (G1–G2)	63.95 (G3)	

shows the disappearance of the resonance of the olefin protons at 4.81 and 5.75 ppm for Gn type dendrimers, forming at 0.55 and 1.20 ppm for Gn–B type dendrimers and transforming to 0.52 and 3.35 ppm for Gn–OH type dendrimers. This special region could be generally shown in all spectra of the formation of Gn–OH type dendrimers with the same pattern.

The MALDI mass spectra of GHn–mOH ($n = 1$ and 3) and GSn–mOH ($n = 1$–3) type dendrimers (Figs. 2 and 4) show mainly one signal that is clearly due to the hydroxy-group-containing dendrimers. The m/z value of the dominant signals in Figs. 2 and 4 corresponds to the calculated value within 1%. Therefore, the MALDI mass spectra of GHn–mOH ($n = 1$–3; $m = 12$, 24 and 48) and GSn–mOH ($n = 1$–4; $m = 8$, 16, 32 and 64) are characterized by a single signal with molecular weight for each dendrimer. The observation of the M^+ peak within the limit of the calculated value in all spectra means that the production of Gn–mOH type dendrimers through hydroboration and oxidation proceeded quantitatively. In addition, the Gn–mOH type dendrimers were obtained as highly viscous liquids after purification. All dendrimers were very soluble in alcohol and polar solvents.

3. Experimental

All reactions were carried out under a dried N_2 atmosphere. The $(Me(CH_2{=}CH)SiO)_4$ and platinum cat-

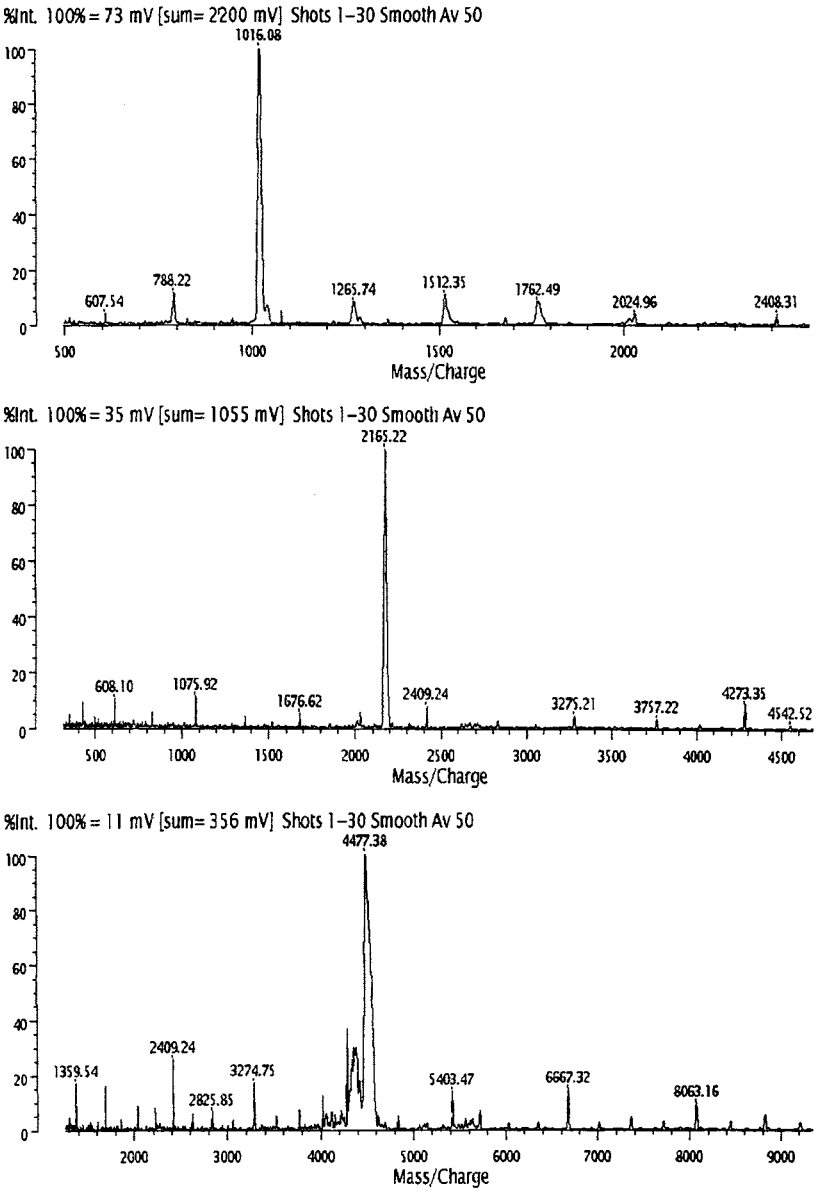


Fig. 4. MALDI mass spectroscopic views of GS1–8OH (top), GS2–16OH (middle) and GS3–32OH (bottom).

alyst (Pt on activated carbon, 10% Pt) were purchased from Aldrich. All chlorosilanes were used after fresh distillation from vacuum set. The NMR spectra were recorded on a Bruker AC-200 spectrometer in $CDCl_3$. 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.

The following abbreviations are used in the experiments: GS*n* refers to each generation of dendritic silanes with 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane in the core molecule. GS*n*–*m*B refers to the generation of dendritic silanes with 9-BBN groups on the periphery of GS*n*. GS*n*–*m*OH refers to the generation of dendritic silanes with hydroxy groups in the periphery. GH*n* refers to each generation of dendritic silanes with bis(triallylsilyl)ethane in the core molecule. GH*n*–*m*B refers to the generation of dendritic silanes with 9-BBN groups on the periphery of GH*n*. GH*n*–*m*OH refers to the generation of dendritic silanes with hydroxy groups on the periphery. G–*n* refers to each generation of dendritic silanes with all GH*n* and GS*n* types. 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 branches for each new layer. Full experimental details for the syntheses of GH*n* and GS*n* type dendrimers will appear in Ref. [9].

3.1. General procedure for Gn–B type dendrimers (GH1–6B)

Bis(triallylsilyl)ethane GH0 2.40 g (7.25 mmol) and 150 ml THF were added to a 500 ml flask. The solution

Table 3
^{1}H- and ^{13}C-NMR spectroscopic data of GS*n*–*m*B type dendrimer measured in $CDCl_3$

Compounds		MeSi	$SiCH_2$–	–CH_2–	–CH_2B	9-BBN
GS0–4B	^{1}H	0.12 (s, 12H, G0)	0.59 (t, 8H, G0),		1.39 (m, 8H, G0)	1.86–1.18
	^{13}C	−1.14 (G0)	9.39 (G0)		30.93 (G0)	33.44, 33.21, 23.27, 23.19
GS1–8B	^{1}H	0.05 (s, 12H, G0), −0.05 (s, 24H, G1)	0.55 (t, 16H, G1),	0.55 (m, 16H, G1), 0.42 (m, 16H, G0),	1.21 (m, 16H, G1)	1.86–1.21
	^{13}C	−1.52 (G0), −5.49 (G1)	17.37 (G1)	18.92 (G1), 9.24, 5.05 (G0)	30.97 (G1)	33.23, 33.13, 23.25, 23.09
GS2–16B	^{1}H	0.06 (s, 12H, G0), −0.07 (s, 24H, G1), −0.05 (s, 48H, G2)	0.53 (m, 32H, G2),	0.53 (m, 32H, G2), 0.40 (m, 64H, G0–G1)	1.20 (m, 32H, G2)	1.86–1.18
	^{13}C	−1.46 (G0), −5.60 (G1), −4.90 (G2)	18.03 (G2)	18.97 (G2), 9.19, 5.25 (G0), 18.32, 18.58, 18.97 (G1),	30.93 (G2)	33.42, 33.15, 23.28, 23.15
GS3–32B	^{1}H	0.05 (s, 12H, G0), −0.06 (s, 24H, G1), −0.08 (s, 48H, G2), −0.05 (s, 96H, G3)	0.55 (m, 64H, G3)	0.55 (m, 64H, G3), 0.37 (m, 160H, G0–G2)	1.24 (m, 64H, G3)	1.86–1.19
	^{13}C	−1.15 (G0), −5.36 (G1), −5.01 (G2), −4.86 (G3)	18.04 (G3)	18.99 (G3), 9.24, 5.27 (G0), 18.99, 18.63, 18.40, 18.04 (G1–G2),	30.95 (G3)	33.43, 33.16, 23.29, 23.18
GS4–64B	^{1}H	−0.03 (s, 24H, G1), −0.05 (s, 48H, G2), −0.08 (s, 96H, G3), −0.05 (s, 192H, G4)	0.55 (m, 128H, G4)	0.55 (m, 128H, G4), 0.37 (m, 352H, G0–G3)	1.26 (m, 128H, G4)	1.87–1.20
	^{13}C	−5.08 (G1), −4.99 (G2), −4.92 (G3), −4.84 (G4)	18.04 (G4)	19.00 (G4), 18.04, 18.39, 18.64, 19.00 (G1–G3)	30.96 (G4)	33.24, 33.16, 23.30, 23.08

Table 4
^{1}H- and ^{13}C-NMR spectroscopic data of GS*n*–*m*OH type dendrimer measured in DMSO-d_6 (^{1}H: 200MHz, ^{13}C: 50.32MHz)

Compounds		MeSi	Si–CH_2	–CH_2–	CH_2O	OH
GS0–4OH	^{1}H	0.08 (s, 12H, G0)	0.86 (m, 8H, G0)		3.54 (m, 8H, G0)	4.38 (t, 4H, G0)
	^{13}C	−0.12 (G0)	22.38 (G0)		56.57 (G0)	
GS1–8OH	^{1}H	0.05 (s, 12H, G0), −0.07 (s, 24H, G1)	0.40 (m, 16H, G1)	1.36 (m, 16H, G1), 0.46 (m, 16H, G0)	3.32 (m, 16H, G1)	4.36 (t, 8H, G1)
	^{13}C	−1.52 (G0), −5.72 (G1)	8.73 (G1)	27.12 (G1), 4.46, 4.70 (G0)	63.88 (G1)	
GS2–16OH	^{1}H	0.03 (s, 12H, G0), −0.05 (s, 24H, G1), −0.07 (s, 48H, G2),	0.42 (m, 32H, G2)	1.36 (m, 32H, G2), 0.51 (m, 64H, G0–G1)	3.34 (m, 32H, G2)	4.36 (t, 16H, G2)
	^{13}C	−1.62 (G0), −5.49 (G1), −5.17 (G2)	9.29 (G2)	26.95 (G2), 4.68 (G0) 17.72, 17.99, 18.16 (G1)	63.90 (G2)	
GS3–32OH	^{1}H	0.01 (s, 12H, G0), −0.09 (s, 24H, G1), −1.10 (s, 48H, G2), −0.09 (s, 96H, G3)	0.40 (m, 64H, G3)	1.34 (m, 64H, G3), 0.49 (m, 160H, G0–G2)	3.34 (m, 64H, G3)	4.38 (t, 32H, G3)
	^{13}C	0.17 (G0), −4.89 (G1), −5.52 (G2), −5.12 (G3)	9.32 (G3)	27.00 (G3), 4.65 (G0), 18.09, 18.28, 18.40 (G1–G2)	63.97 (G3)	
GS4–64OH	^{1}H	−0.05 (s, 24H, G1), −0.05 (s, 48H, G2), −0.08 (s, 96H, G3), −0.08 (s, 192H, G4)	0.43 (m, 128H, G4)	1.36 (m, 128H, G4), 0.50 (m, 352H, G0–G3)	3.32 (m, 128H, G4)	4.38 (t, 64H, G4)
	^{13}C	−5.48 (G1), −5.42 (G2), −5.15 (G3), −4.93 (G4)	9.30 (G4)	26.96 (G4), 18.05, 18.21, 18.38 (G1–G3)	63.95 (G4)	

was cooled to −10°C and then 62.5 mmol (125 ml of 0.5 M solution in THF) of a 9-BBN solution was added slowly to the cooled solution at this temperature. The solution was stirred for 3 h at −10°C and at room temperature (r.t.) overnight. The NMR observation of the reaction mixture showed the perfect building of G*n*–B type dendrimers (see Figs. 1 and 3). Further purification was not available because of their sensitivity to moisture.

3.2. General procedure for Gn–mOH type dendrimers

Subsequently, the reaction mixture of GH1–6B in THF solution was cooled to −10°C again and 15 ml of a 6 N solution of NaOH was added. Immediately, 20

Table 5
MALDI mass spectroscopic data of GH*n*–*m*OH and GS*n*–*m*OH type dendrimers

Dendrimers	Calculated mass	Observed M^+	Remarks
GH0–6OH	438.75	439	[a]
GH1–12OH	1304	1315	
GH2–24OH	3035	3037	
GH3–48OH	6498	6490	
GS0–4OH	416.84	417	[a]
GS1–8OH	994	1016	observed (M^+ + Na ion)
GS2–16OH	2148	2165	
GS3–32OH	4457	4477	
GS4–64OH	9073	[b]	

[a] Observed by GC mass.
[b] Not observed M^+ peak.

ml (194 mmol) of a 30% aqueous solution of H_2O_2 was added slowly. The reaction mixture was stirred for an additional 1 h at -10°C, and warmed to r.t., and for 1 h at 50°C. After being cooled to r.t., the THF solution was decanted from the precipitated boric acid and the aqueous medium and washed three times with a saturated solution of NaCl. The product solution was dried with $MgSO_4$. The solvent and 1,5-cyclooctanediol were removed by vacuum (10^{-3} torr). The product, GH0–6OH, was obtained as a clear and colorless oil to solid. Yields: 8.41 g (8.6 mmol, 74%). For the characterization of all dendrimers, see Tables 1–4 (^{1}H and ^{13}C-NMR) and Table 5 for MALDI mass spectroscopic data.

Acknowledgements

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