Preparation and termination of carbosilane dendrimers based on a siloxane tetramer as a core molecule: silane arborols, part VIII [1]

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Abstract

Starting with 2,4,6,8-tetramethyl-2,4,6,8-tetravinyl-2,4,6,8-tetrasila-1,3,5,7-tetraoxacyclooctane (Me(CH₂=CH)SiO)₄ as a core molecule, a succession of alternate platinum-catalyzed hydrosilations of all vinyl groups with HSiMeCl₂, as well as alkenylation with allylmagnesium bromide, provided the third generation (G3) as divergent growth of siloxane-based dendrimers. The reaction path of the repetitive allylation/hydrosilation cycles is controlled with NMR spectroscopic analyses. Each of the two steps provided quantitative yields of pure dendrimers. We also changed the simple construction of the G3P molecule into materials with special functions, such as by adding phenylethynyl and p-bromophenoxy groups on its periphery. © 1997 Elsevier Science S.A.
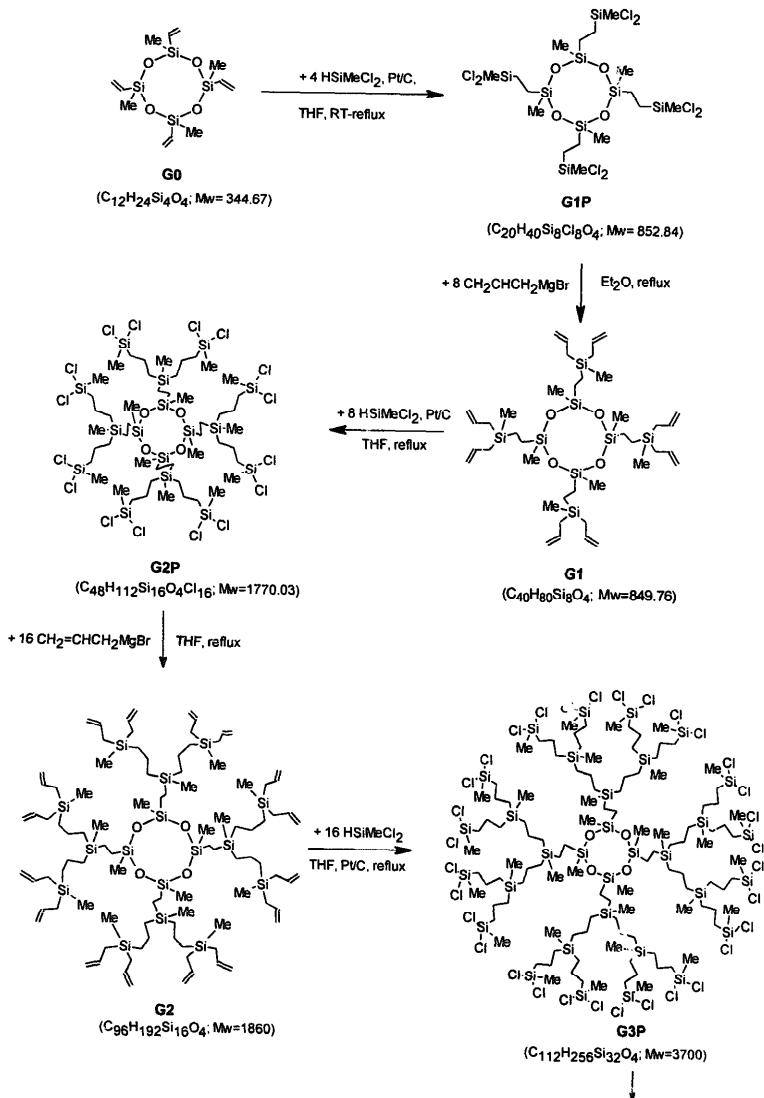
1. Introduction

Since the pioneering reports on dendritic macromolecules by Denkenwalter et al. [2] and Tomalia and Dewald [3] in 1985, several synthetic pathways to dendrimers have been developed. A literature research shows that the number of publications in this field has increased exponentially over the last decade [4]. These dendritic macromolecules have a unique structure which is characterized by a high degree of branching originating from a core molecule. Recently, the emphasis has shifted from simple construction of macromolecules with dendritic topology to materials with specific functions and exhibiting intriguing supramolecular phenomena. These applications include nano-scale catalysts, agents for delivering drugs into cells, chemical sensors, high performance polymers, and molecular antennae for absorbing light energy [5–7].
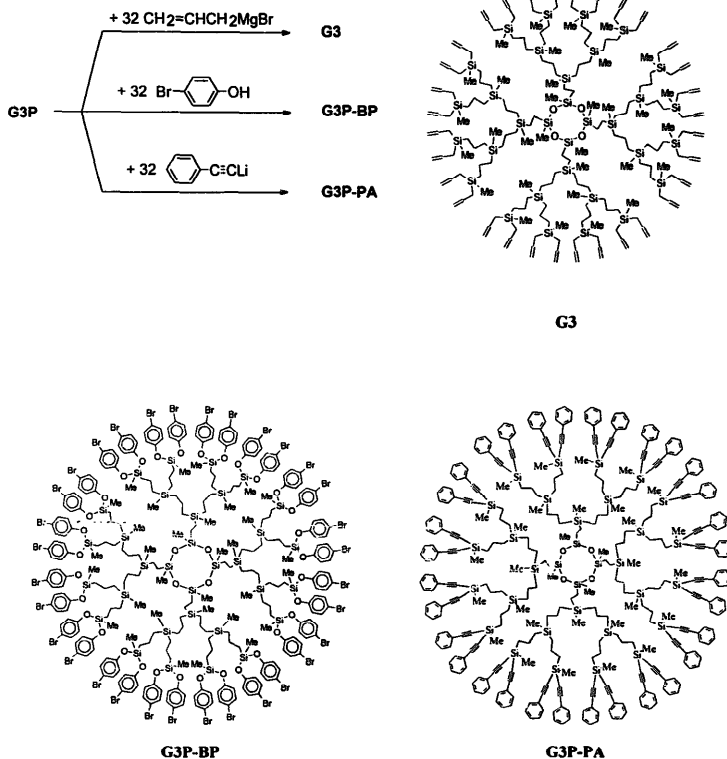
The first preparation of the carbosilane dendrimers reported by van der Made and co-workers was performed by repetitive alkenylation/hydrosilation cycles [8]. Seyferth and co-workers prepared the carbosilane dendrimers containing vinyl groups and ethynyl groups coordinated with Co₂(CO)₈ on its periphery [9]. Polysiloxane dendrimers were prepared by Kakimoto

and co-workers by the use of a convergent process [10]. To date, most of the synthetic methodologies for silicon-containing dendrimers have been demonstrated by repeating units possessing considerable flexibilities [11,10]. In the current paper, we also describe a convenient synthetic way to obtain carbosilane dendrimers, based on quantitative hydrosilation/alkenylation cycles [12,13]. These suggest that the dendrimeric growth has been limited. Eventually, this process will result in surface saturation, which will prevent further growth from all branch points so that the dendrimer will no longer be monodispersed. For example, the reaction of hexaallylethylenedisilane ((CH₂=CHCH₂)₃SiCH₂)₂ with HSiCl₃ in the presence of a platinum catalyst (Pt–activated carbon) did not completely form a molecule containing 18 Si–Cl bonds, but the reaction of it with HSiMeCl₂ in the same conditions completely formed dendrimeric carbosilane ((Cl₂SiCH₂CH₂CH₂)₃-SiCH₂)₂ containing 12 Si–Cl bonds. Moreover, the dendrimeric generation from hexaallylethylenedisilane with HSiMeCl₂ and allylmagnesium bromide was limited to G3 with 48 allylic end groups [13]. In this report, we wish to introduce a synthetic method and characterization of carbosilane dendrimers with 2,4,6,8-tetramethyl-2,4,6,8-tetravinyl-2,4,6,8-tetrasila-1,3,5,7-tetraoxacyclooctane (MeCH₂–CHSiO)₄ as a core molecule and using a hydrosilation/alkenylation cycle. We provide a simple construction of these molecules into materials with specific functions, such as intriguing supra-

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[1] For the previous publications in this series see Ref. [1].

G0

(C$_{12}$H$_{24}$Si$_4$O$_4$; Mw= 344.67)

+ 4 HSiMeCl$_2$, Pt/C,

THF, RT-reflux

G1P

(C$_{20}$H$_{40}$Si$_8$Cl$_8$O$_4$; Mw= 852.84)

+ 8 CH$_2$CHCH$_2$MgBr   Et$_2$O, reflux

+ 8 HSiMeCl$_2$, Pt/C
THF, reflux

G2P

(C$_{48}$H$_{112}$Si$_{16}$O$_4$Cl$_{16}$; Mw=1770.03)

G1

(C$_{40}$H$_{80}$Si$_8$O$_4$; Mw=849.76)

+ 16 CH$_2$=CHCH$_2$MgBr   THF, reflux

+ 16 HSiMeCl$_2$
THF, Pt/C, reflux

G2

(C$_{96}$H$_{192}$Si$_{16}$O$_4$; Mw=1860)

G3P

(C$_{112}$H$_{256}$Si$_{32}$O$_4$; Mw=3700)

Scheme 1.

molecular phenomena, with phenylethynyl and *p*-bromophenoxy groups on its periphery.

2. Results and discussion

The basic procedure for the preparation of each generation of carbosilane dendrimer is outlined in Scheme 1 and Fig. 1. The synthesis of our silane dendrimers begins with the exhaustive hydrosilation of vinyl groups in 2,4,6,8-tetramethyl-2,4,6,8-tetravinyl-2,4,6,8-tetrasila-1,3,5,7-tetraoxacyclooctane with HSiMeCl$_2$ in the presence of a platinum catalyst (10% Pt content on activated carbon). The reaction proceeds

to give G1P with four terminal SiMeCl$_2$ groups in quantitative yield. In the next step, the G1 generation is prepared by the use of 8 equiv. of allylmagnesium bromide in quantitative yield. Then the allyl groups in G1 are hydrosilylated with dichloromethylsilane in the presence of a platinum catalyst. Next, these groups are treated with allylmagnesium bromide to produce the G2 dendrimer with 16 allylic end groups. By hydrosilation, the G2 dendrimer can be converted into G3P with 32 Si~Cl end groups. In general, hydrosilation of the G*n* molecule with HSiMeCl$_2$ in the presence of a platinum catalyst (10^{-4}–10^{-5} mol per double bond) in THF gave G*n*P ($n = 1$–3) in quantitative yields as a colorless oil or glass, while reaction procedures of G*n*P to G*n*
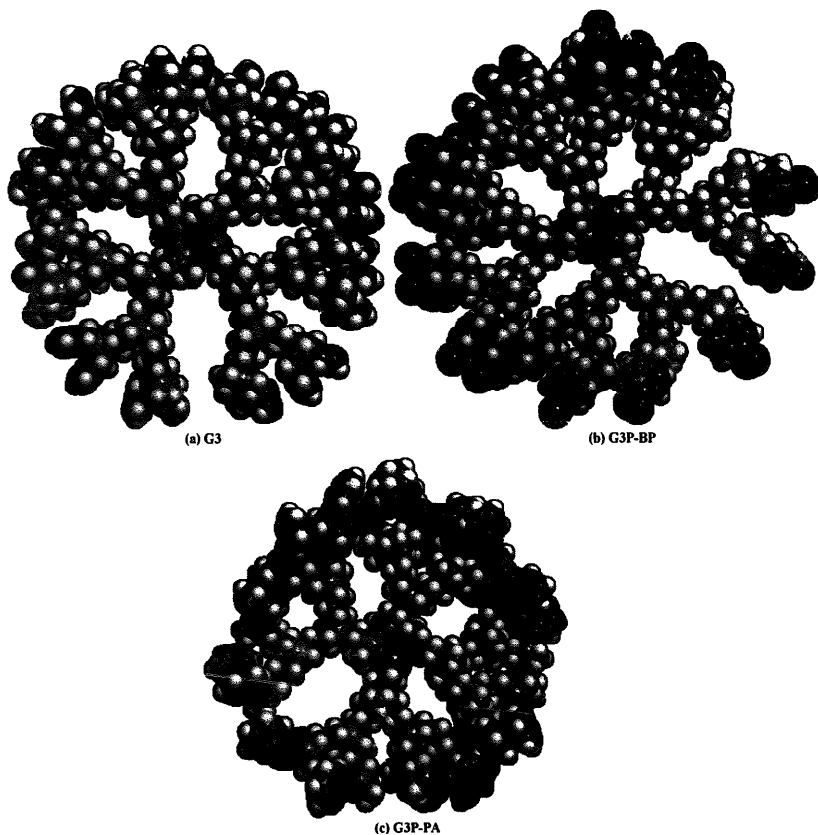
(a) G3

(b) G3P-BP

(c) G3P-PA

Fig. i.

($n = 1$–3) by the use of a Grignard reaction also gave quantitative yields. The hydrosilation/alkenylation procedures are followed by NMR spectroscopic analyses of the reaction mixture. We also found that a platinum catalyst gives a 1.2-adduct with high regiospecificity. Thus, the reaction of **G0** with 4 equiv. of $HSiMeCl_2$ in the presence of Pt–C at room temperature for 12 h produced only the hydrosilation product **G1P**. No other structure was detected in the reaction mixture by ^{1}H and ^{13}C NMR. A similar reaction of other **Gn**-type ($n = 1$–3) dendrimers with $MeSiHCl_2$ afforded the corresponding hydrosilation products. In contrast to this, the reaction of **G0** and **G1** in the presence of a platinum catalyst in refluxing toluene for 12 h produced a small amount of dehydrogenative coupling products [14]. However, at room temperature these products were not found. We also investigated the solvent effect on the rate of the hydrosilation of **Gn** ($n = 0$–3) dendrimers with $HSiMe_{3-n}Cl_n$ ($n = 1$–3) in the presence of a platinum catalyst in various solvents, such as pentane, toluene, Et_2O, and THF, and found that the polarity of the solvent influences markedly the rate of the hydrosilation

in this system. When **G1** was treated with HSiMeCl$_2$ in THF at room temperature, **G2P** was completely formed in 12 h. In toluene, however, under the same conditions we found unreacted **G1**. By increasing the amount of the catalyst and raising the reaction temperature the rates of reaction were accelerated considerably.

We found that the termination reaction of **G3P** with lithium phenylacetylide and *p*-bromophenol provided intriguing end groups on its periphery. There is continuing research from dendrimeric topology on materials with specific functions. The reaction of **G3P**, containing 32 Si–Cl end groups, with lithium phenylacetylide in refluxing THF proceeds readily and completely to **G3P-PA**, which contains 32 alkynyl groups. After simple chromatography on silica gel with chloroform as an eluent, the pure product was observed by NMR spectroscopy (^{1}H and ^{13}C). Similarly, the reaction of **G3P** with *p*-bromophenol in the presence of TMED gave **G3P-BP** as a pure substance. Both compounds possessed similar spectral patterns to one of the previously obtained analogs [15].

UV–vis, IR and ^{1}H and ^{13}C NMR spectroscopic determinations of **G**n generations ($n = 1$–3), as well as **G3P-PA** and **G3P-BP**, clearly indicate the presence of ethenyl, phenylethynyl, and bromophenoxyl groups respectively on the periphery of the given dendrimers. The ^{1}H NMR spectra reflect the transition from **G**n**P** to **G**n generations: there are three main signals in the region of 0 ppm for MeSi groups, 0.45–1.55 ppm for CH$_2$ groups, and multiplets at 4.81 and 5.76 ppm for

protons of characteristic allylic double bonds for **G**n molecules (while the formation of **G**n**P** makes the resonance attributed to **G**n disappear); for **G**n**P** generations, signals in the region of 0 ppm for MeSi groups and 0.77 ppm for MeSiCl$_2$ groups are found (Tables 1 and 2). In the ^{13}C NMR spectra, three kinds of methyl carbon atom, attached to **G1**, **G2** and **G3** silicon atoms, could be distinguished in the region of -6.3 to -1.2 ppm. These ^{13}C spectra were clearly separated in **G**n and **G**n**P** molecules. The peaks of the methylenyl groups were observed at 4.21–21.5 ppm for **G**n molecules and at 4.37–25.91 ppm for **G**n**P** molecules with sharp single signals, which implied high purity of these dendrimers (Tables 1 and 2). NMR spectroscopy is a valuable tool for monitoring the growth and subsequent surface modification reactions of the dendrimers, whereas the sensitivity of the integration is an assessment of the structural perfection and purity of the dendrimers at each stage of the generations. Information concerning the perfect building-block of **G**n ($n = 1$–3) dendrimers can be obtained, for example, by directly comparing its UV absorption spectra at λ_{max} (between 214 and 220 nm). The increasing number of double bonds for each generation is in direct proportion to the molar absorption coefficient (ε_{max}, see Table 3). We expect a good possibility of determining molecular mass of these types of dendrimer by the use of these phenomena. The characterization of large molecules like dendrimers is a difficult task. For general organic and inorganic compounds, the technique based on mass

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

Compound		MeSi	CH$_2$	CH$_2$ =[a]	CH=[a]
G0	^{1}H	0.24 (q, 3H)	—	6.01 (m, 12H)	
	^{13}C	−0.80	—	133.50	136.12
G1	^{1}H	−0.01 (s, 12H, G1)	0.42 (m, 16H)	4.86 (m, 16H)	5.76 (m, 8H)
		0.07 (s, 12H, 00)	1.58 (dd, 16H, G1, $J = 8.0$ Hz)		
	^{13}C	−6.34 (G1)	4.21, 8.96 (G0)	113.09	134.69
		−1.39 (G0)	21.10 (G1)		
G2	^{1}H	−0.06 (s, 12H, G1)	0.40 (m, 16H, G0)	4.81 (m, 32H)	5.75 (m, 16H)
		−0.01 (s, 24H, G2)	0.58 (m, 32H, G1)		
		0.08 (s, 12H, G0)	1.32 (m, 16H, G1)		
			1.56 (d, 32H, G2 $J = 8.0$ Hz)		
	^{13}C	−5.71 (G2)	5.16, 9.21 (G0)	113.05	134.77
		−5.51 (G1)	17.99, 18.19, 18.24 (G1)		
		−1.53 (G0)	21.49 (G2)		
G3	^{1}H	−0.07 (s, 36H, G1, G2)	0.40 (m, 16H, G0)	4.81 (m, 64H)	5.86 (m, 32H)
		−0.01 (s, 48H, G3)	0.59 (m, 80H, G1–G2)		
		0.07 (s, 12H, G0)	1.31 (m, 64H, G2)		
			1.52 (d, 64H, G3 $J = 8.0$ Hz)		
	^{13}C	−5.67 (G3)	5.28 (G0)	113.07	134.78
		−4.96 (G1, G2)	9.09 (G0)		
		−1.21 (G0)	17.99, 18.28 (G2)		
			18.54 (G1, G2)		
			18.81 (G1)		
			21.50 (G3)		

[a] Multiplet for CH$_2$ =CH– viewed characteristic allylic signals.

Table 2
^{1}H and ^{13}C NMR spectroscopic data of **Gn**P-type dendrimers measured in CDCl$_3$

Compound		MeSi	MeSiCl$_2$	CH$_2$
G1P	^{1}H	0.15	0.78	0.69 (m, 8H)
		(s, 12H)	(s, 12H)	
				1.00 (m, 8H)
	^{13}C	−1.40	8.04	4.37
				13.68
G2P	^{1}H	−0.02	0.77	0.43 (m, 16H)
		(s, 12H, G1)	(s, 24H)	
		0.08		0.67 (m, 16H)
		(s, 12H, G0)		
				1.22 (m, 16H)
				1.54 (m, 16H)
	^{13}C	−5.61 (G1)	5.50	4.87 (G0)
		−1.36 (G0)		9.11 (G0)
				16.88 (G1)
				17.31 (G1)
				25.91 (G1)
G3P	^{1}H	−0.06	0.77	0.41 (m, 16H, G0)
		(s, 12H, G1)	(s, 48H)	
		−0.01		0.62
		(s, 24H, G2)		(m, 80H, G1, G2)
		0.07		1.21 (m, 32H, G2)
		(s, 12H, G0)		
				1.54 (m, 32H, G2)
	^{13}C	−5.56 (G1)	5.48	5.22, 9.22 (G0)
		−5.49 (G2)		17.31, 17.48 (G2)
		−1.31 (G0)		18.27, 18.45
				18.64 (G1)
				25.89 (G2)

spectrometric techniques and colligative properties can be used to determine molecular mass. For our dendrimeric molecules, the use of the above technique is not advisable because of the high number of the molecular mass. In spite of the above difficulties, a reliable characterization of our dendrimers has been achieved by using a variety of techniques.

(1) Each of the generation steps was accurately monitored by ^{1}H NMR spectroscopic techniques. For the products of the **Gn**-family obtained in each growth step, the ratio of alkenyl end groups to MeSi-groups in the NMR spectra was consistent with the expected formulation. Also, the **Gn**P-family obtained in each generation step with the perfect disappearance of alkenyl groups of **Gn** generations and the ratio of MeSi resonance signals to the multiplets of methylenyl chains proved the expected formula.

(2) Each **Gn** generation was purified by chromatographic techniques.

In conclusion, dendrimers with various branching points resulted in totally different physical properties. Perfect building on the periphery of given dendrimers can be observed by NMR and UV spectroscopic techniques. Such synthetic routes will greatly enhance studies on these new materials.

3. Experimental

3.1. General procedures

All reactions and manipulations were carried out under a dried N$_2$ atmosphere that had been passed through three columns (4.0 × 100 cm^2) of molecular sieves (3 Å), CaCl$_2$ and KOH. Ether and THF were dried by distillation from the blue solution of sodium-benzophenone ketyl, and solvents such as pentane and toluene were dried and distilled from Na–K$_{2.8}$ amalgam. Glassware was dried under vacuum with ca. 100 °C/10^{-2} Torr. 2,4,6,8-Tetramethyl-2,4,6,8-tetravinyl-2,4,6,8-tetrasila-1,3,5,7-tetraoxacyclooctane purchased from Aldrich Chemical Co. was dried by molecular sieves (4 Å). Hydrosilanes (HSiMeCl$_2$ and HSiCl$_3$) were used after reduced distillation before each experiment. Platinum catalysts (Pt on activated carbon, 10% Pt content) were used after vacuum drying at room temperature. NMR spectra were measured using samples in CDCl$_3$ solution: ^{1}H NMR spectra were recorded at 200.13 MHz and ^{13}C NMR spectra at 50.32 MHz using a Bruker AC-200 spectrophotometer. FT-IR spectra were measured by IFS 55 (Bruker). UV spectra were measured using an HP 8452A diode array UV–vis spectrophotometer. Elemental analyses were performed by the Seoul Branch of the Korean Basic Science Institute.

3.2. G1P

A mixture of 3.70 g (10.37 mmol) of G0, 7.41 g (64.38 mmol, 1.5 equiv.) of HSiMeCl$_2$ and 0.10 g of dried platinum catalyst (Pt on activated carbon, 10% Pt content) in 25 ml THF was stirred for 12 h at room temperature. When the reaction was complete according

Table 3
UV spectroscopic data of **Gn**-type dendrimers measured in hexane

Compound	No. of double bonds χ	Conc. × 10^{-4} (mol l^{-1})	λ_{max} (nm)	ε_{max} (l mol^{-1} cm^{-1})	ε_{max}/χ
G0	4	49.20	212	430	107
G1	8	18.10	214	1370	171
G2	16	6.56	220	2890	181
G3	32	3.30	218	6069	190
G3P-BP	—	1.69	230	15312	—
G3P-PA	—	1.93	266	14253	—

to ^{1}H NMR, excess HSiMeCl₂ and THF were removed under vacuum. The catalyst was filtered off in pentane and the pentane was evaporated, leaving 8.49 g (9.95 mmol; 93%) of **G1P** (MeSiCH₂CH₂SiMeCl₂O)₄ as a clear, colorless oil, which was very sensitive to moisture. ^{1}H and ^{13}C NMR spectroscopic data are given in Table 2.

3.3. G1

103 mmol of allylmagnesium bromide (76 ml of 1.36 M solution in ether, 1.3 equiv.) was slowly added to 8.49 g (9.95 mmol) of **G1P** in 25 ml THF. After the addition was finished, the reaction mixture was refluxed for 2 h. When the reaction was complete according to ^{1}H NMR, solvents were removed under reduced pressure. The magnesium salt was precipitated in 150 ml pentane and filtered off. The volatile components were removed under reduced pressure, leaving 8.10 g of a colorless liquid. All portions of the resulting compounds were chromatographed on silica gel with chloroform as an eluent. The product, **G 1** (MeSiCH₂CH₂SiMe(CH₂CH=CH₂)₂O)₄, was obtained as a clear, colorless oil (5.10 g, 6.00 mmol, 60%). ^{1}H and ^{13}C NMR spectroscopic data are given in Table 1, analytical data in Table 4, IR spectroscopic data in Table 5, and UV spectroscopic data in Table 3.

3.4. G2P

A mixture of 4.28 g (5.03 mmol) of **G1**, 6.94 g (60.36 mmol, 1.5 equiv.) of HSiMeCl₂ and 0.08 g of a dried platinum catalyst (Pt on activated carbon, 10% Pt content) in 25 ml THF was stirred for 12 h at room temperature. The reaction mixture was refluxed for 1 h. When the reaction was complete according to ^{1}H NMR, excess HSiMeCl₂ and THF were removed under vacuum. The catalyst was filtered off in pentane and the pentane was evaporated, leaving 8.55 g (4.83 mmol, 96%) of **G2P** (MeSiCH₂CH₂SiMe(CH₂CH₂CH₂-SiMeCl₂)₂O)₄ as a clear, colorless oil, which was very

Table 4
Elemental analysis data of **G*n*-type dendrimers

Compound	Mw	Analysis (found/calcd.) (%)	
		C	H
G1 (C₄₀H₈₀Si₈O₄)	849.76	56.74/56.54	9.42/9.49
G2 (C₉₆H₁₉₂Si₁₆O₄)	1859.95	61.94/61.98	10.41/10.42
G3 (C₂₀₈H₄₁₆Si₃₂O₄)	3881.12	63.95/64.36	10.77/10.82
G3P-BP	8070.04	45.06/45.24	5.37/4.81
(C₃₀₄H₃₈₄Si₃₂Br₁₂O₃₆)			
G3P-PA	5802.08	76.04/76.17	7.17/7.24
(C₃₆₈H₄₁₆Si₃₂O₄)			

Table 5
IR spectroscopic data of **G*n*-type dendrimers ($\nu_{C=C}$) measured in KBr neat

Compound	$\nu_{C=C}$ (cm⁻¹)
G0	1597.5
G1	1630.5
G2	1630.2
G3	1630.5
G3P-BP	1876.4 (aromatic)
G3P-PA,[a]	1595.7 (aromatic)

[a] **G3P-PA**: $\nu_{C=C} = 2161.6 \text{cm}^{-1}$.

sensitive to moisture. ^{1}H and ^{13}C NMR spectroscopic data are given in Table 2.

3.5. G2

100 mmol of allylmagnesium bromide (61 ml of 1.65 M solution in ether, 1.3 equiv.) was added slowly to 8.55 g (4.83 mmol) of **G2P** in 25 ml THF. After the addition was completed, the reaction mixture was refluxed for 2 h. When the reaction was complete according to ^{1}H NMR, the 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 8.2 g of a colorless liquid. All of the resulting compounds were chromatographed on silica gel with chloroform as an eluent. The product, **G2** MeSiCH₂CH₂SiMe-(CH₂CH₂CH₂SiMe(CH₂CH=CH₂)₂)₂O)₄, was obtained as a clear, colorless oil (6.85 g, 3.68 mmol, 76%). ^{1}H and ^{13}C NMR spectroscopic data are given in Table 1, analytical data are in Table 4, IR spectroscopic data in Table 5, and UV spectroscopic data in Table 3.

3.6. G3P

A mixture of 6.02 g (3.23 mmol) of **G2**, 8.92 g (77.52 mmol) of HSiMeCl₂ and 0.20 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. The reaction mixture was refluxed for 2 h. When the reaction was complete according to ^{1}H NMR, excess HSiMeCl₂ and THF were removed under vacuum. The catalyst was filtered off in pentane and the pentane was evaporated, leaving 11.76 g (3.18 mmol, 96%) of **G3P** MeSiCH₂CH₂SiMe(CH₂CH₂CH₂SiMe(CH₂CH₂-CH₂SiMeCl₂)₂)₂O)₄ as a clear, colorless oil, which was very sensitive to moisture. ^{1}H and ^{13}C NMR spectroscopic data are given in Table 2.

3.7. G3

21 mmol of allylmagnesium bromide (13 ml of 1.65 M solution in ether) was slowly added to 1.84 g

(0.50 mmol) of **G3P** in 25 ml THF. Then, the reaction mixture was refluxed for 2 h. When the reaction was complete according to ^{1}H NMR, the solvents were removed under reduced pressure. The magnesium salt was precipitated in pentane and filtered off. The volatile components were removed under reduced pressure. All of the resulting compounds were chromatographed on silica gel with chloroform as an eluent. The product, **G3**, was obtained as a clear, colorless oil (1.36 g, 0.35 mmol, 70%) (MeSiCH$_2$CH$_2$SiMe(CH$_2$CH$_2$CH$_2$-SiMe(CH$_2$CH$_2$CH$_2$SiMe(CH$_2$CH=CH$_2$)$_2$)$_2$)$_2$O)$_4$. ^{1}H, and ^{13}C NMR spectroscopic data are given in Table 1, analytical data in Table 4, IR spectroscopic data in Table 5, and UV spectroscopic data in Table 3.

3.8. G3P-PA

12.48 mmol (1 M in THF) of lithium phenylacetylide solution was added slowly to 2.17 g (1.04 mmol) of **G3P** in 25 ml toluene. After the addition was completed, the reaction mixture was refluxed for 4 h. When the reaction was complete according to ^{1}H NMR, the solvents were removed under reduced pressure. All of the resulting compounds were chromatographed on silica gel with chloroform as an eluent. The product **G3-PA** was obtained as a clear, yellow-brown glass (2.10 g, 0.73 mmol, 70%). ^{1}H NMR (ppm): −0.15 (s, 12H, MeSi, G1), −0.03 (s, 24H, MeSi, G2), 0.05 (s, 12H, MeSi, G0), 0.35 (m, 16H, CH$_2$, G0), 0.39 (s, 48H, MeSi, G3), 0.69 (m, 48H, CH$_2$, G1), 0.90 (m, 32H, CH$_2$, G2), 0.94 (m, 32H, CH$_2$, G2), 1.55 (m, 32H, CH$_2$, G2), 7.23–7.48 (m, 160H, Ph). ^{13}C NMR (ppm): −5.40 (MeSi, G0–G2), −1.03 (MeSi, G3), 18.05 (CH$_2$, G1–G2), 18.38 (CH$_2$, G1–G2), 18.71 (CH$_2$, G0), 20.67 (CH$_2$, G1–G2), 90.12 (≡CSi), 106.38 (≡CPh), 122.76 (C$_{quan}$), 128.19 (C-o), 128.76 (C-p), and 132.10 (C-m). IR (cm^{-1}, KBr): 1595.7 ($\nu_{aromatic}$), 2161.6 ($\nu_{C≡C}$), and 3079 (ν_{C-H}). UV (in cyclohexane): λ_{max} 266 nm, ε_{max}, 142501 mol^{-1} cm^{-1}. Anal. Calcd. for C$_{368}$H$_{416}$O$_4$Si$_{32}$: C, 76.17; H, 7.24. Found: C, 76.04; H, 7.17.

3.9. G3P-BP

12.48 mmol of bromophenol solution (1 M in THF) was added slowly to 2.17 g (1.04 mmol) of **G3P** in 25 ml toluene (in the presence of 5 ml of TMED). After the addition was completed, the reaction mixture was stirred for 5 h. When the reaction was complete according to ^{1}H NMR, the solvents and unreacted TMED were removed under reduced pressure. The TMED · HCl salt was precipitated in pentane and filtered off. All the resulting compounds were chromatographed on silica gel with chloroform as an eluent. The product **G3-BP**

was obtained as a clear, colorless glass (1.38 g, 0.37 mmol, 71%). ^{1}H NMR (ppm): −0.16 (s, 24H, MeSi, G0–G1), 0.05 (s, 24H, MeSi, G2), 0.18 (m, 16H, CH$_2$, G0), 0.27 (s, 48H, MeSi, G3), 0.52 (m, 80H, CH$_2$, G1–G2), 0.92 (m, 32H, CH$_2$, G2), 1.37 (m, 32H, CH$_2$, G2), 6.67 (m, 64H, Ph-o), 7.30 (m, 64H, Ph-m). ^{13}C NMR (ppm): −5.25 (MeSi, G0–G1), −3.79 (MeSi, G3), 17.08 (CH$_2$, G0), 16.44 (CH$_2$, G1), 17.93 (CH$_2$, G0–G2), 18.52 (CH$_2$, G1–G2), 114.61 (C$_{quan}$), 121.44 (C-o), 132.54 (C-m), and 154.12 (C-Br). IR (cm^{-1}, KBr): 1876 ($\nu_{aromatic}$). UV (in cyclohexane): λ_{max} 230 nm, ε_{max}, 153101 mol^{-1} cm^{-1}. Anal. Calcd. for C$_{304}$H$_{384}$Br$_{32}$O$_{36}$Si$_{32}$: C, 45.24; H, 4.81. Found: C, 45.06; H, 5.37.

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