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Preparation of ethynylsilane dendrimers

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Abstract

A dendritic macromolecule containing 144 phenylethynyl groups was created. 1,3,5-tris(dimethylvinylsilyl)benzene (G0) as the core and bis(phenylethynyl)methylsilyl groups as progressing units were used. The first generation (G1P-9Cl) was obtained by the reaction of G0 with trichlorosilane and was followed by the phenylethynyl-group-containing generation (G1-9PA) by the reaction of lithium phenylacethylide. Using the continuous iterative reactions of trichlorosilane and lithium phenylacethylide, the dendritic molecule progressed to the second generation (G2-27PA). For the formation of a less crowded model, the reaction of the first generation (G1-9PA) with dichloromethylsilane was allowed to progress to the 18 Si–Cl bonded second generation (G2P-18Cl). After that, by the use of the two iterative reaction mechanisms, the fifth generation with 144 phenylethynyl groups containing the carbosilane dendrimer was prepared. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Dendrimer; Carbosilane; Ethynylsilane; Hydrosilation; Platinum catalyst

1. Introduction

The characteristically unique functional groups on the periphery of dendritic macromolecules were obtained by the use of two or three iterative reaction mechanisms [1–3]. Following the appearance of organic dendritic works in the literature [4–7], studies on silicon-containing dendrimers appeared in the last decade [8,9]. The development in synthetic methods of carbosilane dendrimers used in hydrosilation and alkenylation as well as alkynylation cycles has been advanced by many scientists who used multifunctional molecules as the core and chlorosilanes as progressing units [10]. The unsaturated groups on carbosilane dendrimers were developed into the reactive Si–Cl-group-containing generations by the use of the hydrosilation method with chlorosilanes ($H–SiMe_nCl_{3-n}$; $n = 0–2$) using a platinum catalyst [8–10]. In general, the hydrosilation between unsaturated bonds and chlorosilanes occurred in very high yield. Moreover, side reactions such as α-addition as well as the dehydrogenate coupling reaction are not observed under experimental conditions [11]. A series of carbosilane dendrimers were synthesized by employing the Pt-catalyzed reaction [8]. In our previous results, the preparation of dendritic macromolecules by the use of hydrosilation resulted in very high yield [9,11,12]. However, in many cases, higher generations have not shown a unified structure [9,10]. This means that the dendritic molecule is built in the uniformly ordered structure under the limit generation. For the formation of a unified dendritic molecule, the sum of the size of additional groups must be smaller than the surface of reactive dendritic molecules. We then tried to show that a limit generation of the dendritic carbosilane macromolecule, on the 1,3,5-tris(dimethylvinylsilyl)benzene molecule, is composed of the core and the $Me_nSi(C{\equiv}CPh)_{3-n}$ groups ($n = 0$ and 1) as generating branches in the outer peripheral layer.

2. Results and discussion

The preparative method of carbosilane dendrimers by the use of 1,3,5-tris(dimethylvinylsilyl)benzene as the core (G0) and bis(phenylethynyl)methylsilyl groups as progressing units is suggested in Scheme 1. The core molecule possessing dimethylvinylsilyl groups on the benzene ring is prepared by the Grignard reaction of

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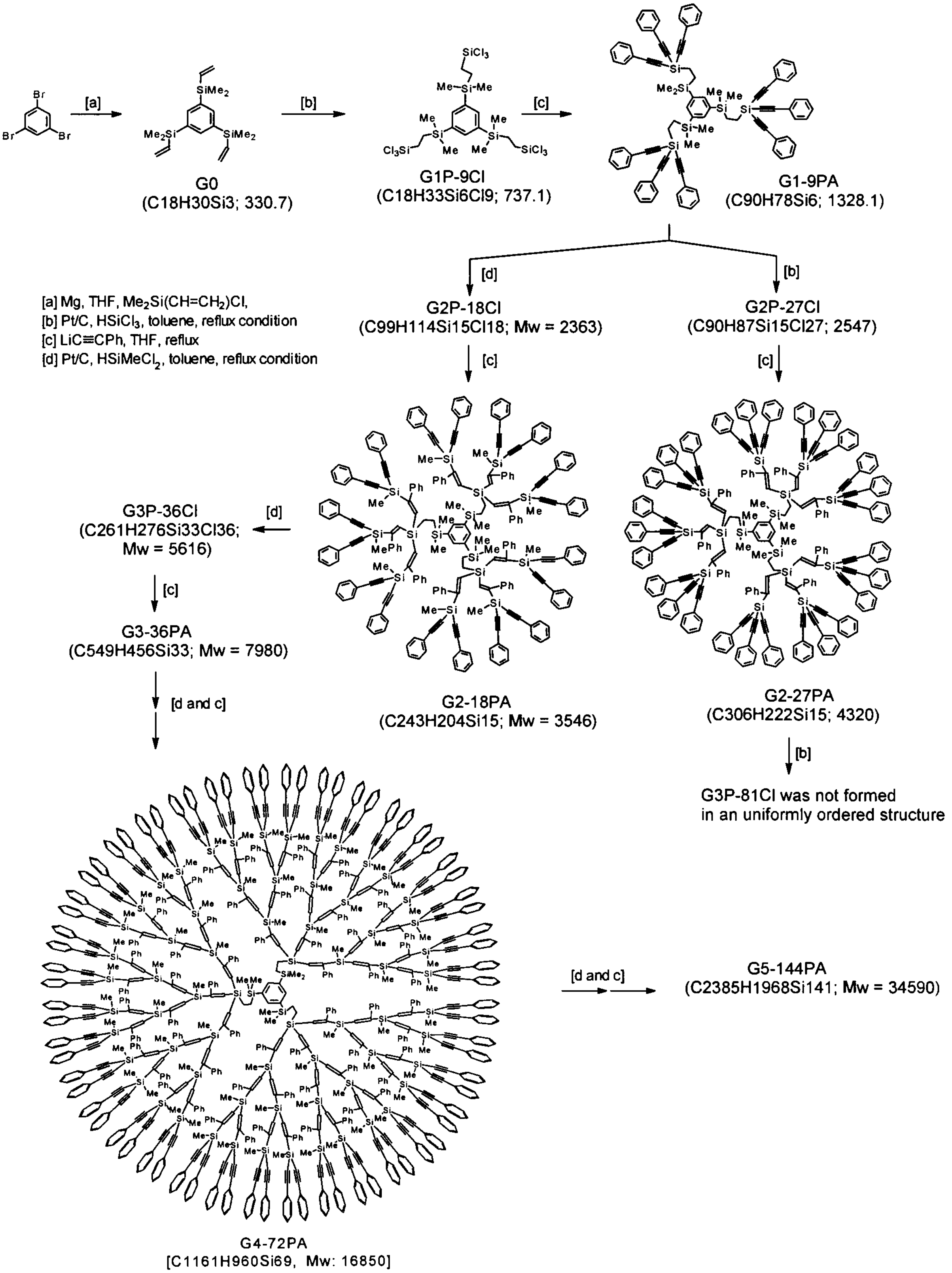


Scheme 1. Synthetic methods and schematic view of dendrimers.

1,3,5-tribromobenzene and dimethylvinylchlorosilanes in THF. By this method, the main product, 1,3,5-tris(dimethylvinylsilyl)benzene (G0) is obtained in up to 90% yield with 1,3-bis(dimethylvinylsilyl)benzene obtained as a minor product. The separation of the two components is carried out under vacuum distillation of

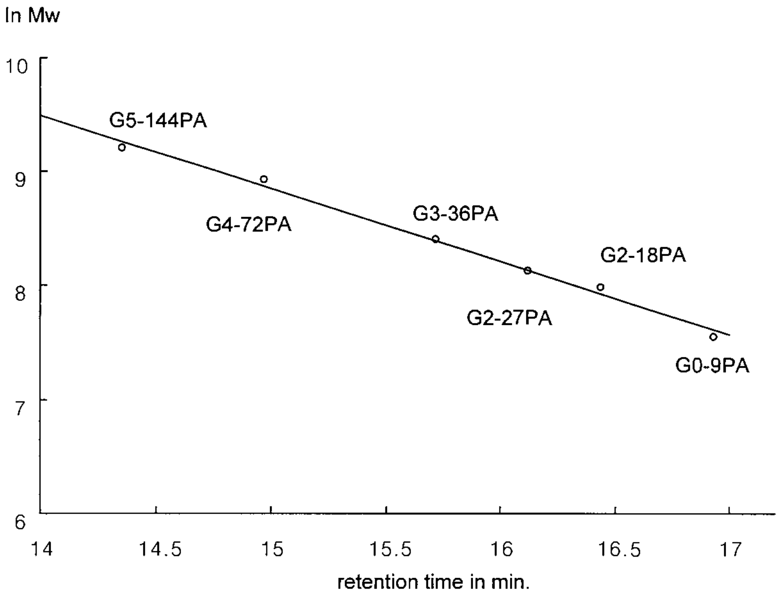


Fig. 1. Graphical view of SEC data.

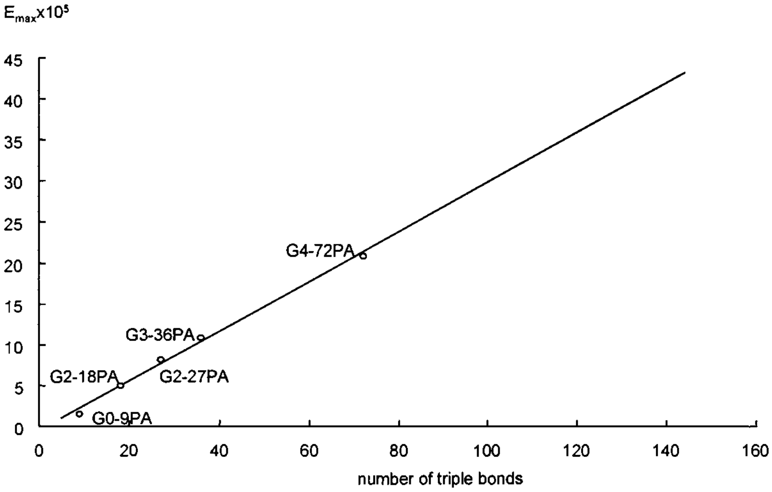


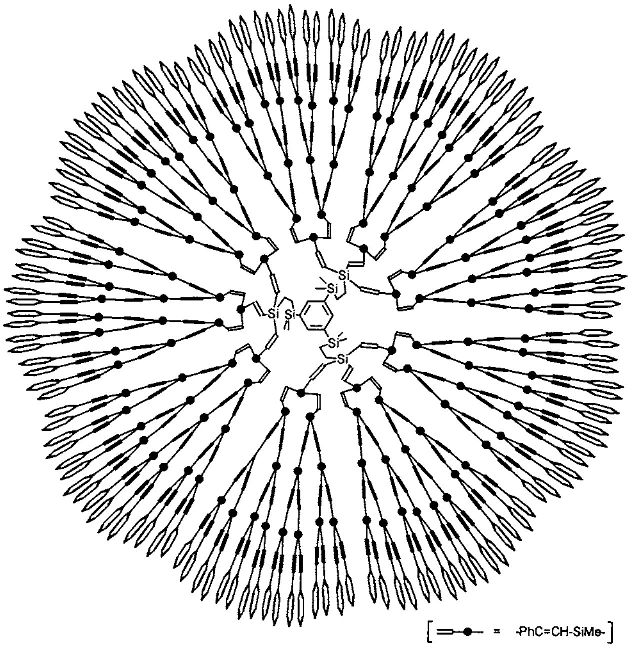
Fig. 2. Graphical view of UV data.

the minor product at 58°C. The first generation (G1P-9Cl) was prepared by the use of hydrosilation of G0 with trichlorosilane. The reaction was followed by the preparation of G1-9PA by alkynylation with lithium phenylacetylides. The NMR spectra of the reaction medium quantitatively revealed the yields of G1P-9Cl and G1-9PA. The formation of double-bonded inner shells is easily accomplished under reflux (toluene) with the addition of platinum-catalyzed chlorosilane to the alkynyl groups (G1P-9Cl). Under these conditions, we did not observe any other side reaction such as double- or α-hydrosilylation. Platinum in activated carbon as a heterogeneous catalyst is very useful for the reaction and separation of chlorinated dendrimers from the reaction medium, because the pure reaction product may be obtained by simple filtration. For example, G2P-27Cl was prepared by the reaction of G1-9PA and trichlorosilane under reflux (toluene) using Pt–C catalytic conditions. G2P-27Cl was quantitatively obtained and was separated along with Pt–C from the platinum catalyst by filtration.

The alkynylation with lithium phenylethynyl groups at Si–Cl moieties in GnP-mCl dendrimers clearly gave Gn-mPA in high yield. For example, the alkynylation of Si–Cl moieties in G2P-27Cl gave G2-27PA in high yield (see Table 3). The following hydrosilation reaction of G2-27PA and trichlorosilane could not form G3P-81Cl as a uniformly ordered structure. This result means that, the surface of G2-27PA does not have enough place for 81 Si–Cl functional groups. Therefore, the second generation for this model has limited groups for the formation of the unified form on the periphery.

Thus, the limit generation of this model has 27 phenylethynyl groups on the outer-most periphery. For the preparation of a less crowded model, the reaction of the first generation (G1-9PA) and dichloromethylsilane moieties has been quantitatively produced to the second generation with 18 Si–Cl bonds (G2P-18Cl). Repeating the two procedures, namely, hydrosilation with dichloromethylsilanes and alkynylation with lithium phenylacetylides, produced the second generation containing 18 phenyl ethynl groups, third generation with 36, fourth generation with 72 and fifth generation with 144 phenylethynyl groups. The G*n*-*m*PA and G*n*P-*m*Cl ($n = 1-5$: $m = 9$, 18, 36, 72 and 144) dendrimers were soluble in many organic solvents such as toluene, THF and chloroform.

The monitoring of the reaction process by NMR spectroscopy is a very useful method. For example, the transition of G1P-9Cl to G1P-9PA clearly revealed triple bond character in the ^{13}C-NMR, due to decay of the previous generation. The transition of the NMR signals by the hydrosilation process of G1-9PA to G2P-27Cl also revealed the same pattern. The reaction procedure of G*n*P-*m*Cl ($n = 1-5$: $m = 9$, 27, 18, 36, 72 and 144) type dendrimers and terminal triple bonds containing carbosilane dendrimers was monitored by this method. The triple bonded carbon signals in each generation were clearly observed in the ^{13}C-NMR spectrum at δ 87 and 107 ppm. During the reaction process, the transition of Si–C≡CPh to Si–C=CPhSiCl$_3$ or Si–C=CPhSiMeCl$_2$ clearly revealed double bond character in the range 140 and 160 ppm. The methyl groups in G*n*P generations were observed in the range 0.5–0.7 ppm but G*n* generations were observed at a lower region in the ^{1}H-NMR.



G5-144PA
(C2385H1968Si141; Mw = 34590)

Scheme 2. Schematic view of G5-144PA.

MALDI-TOF mass spectroscopy is a useful direct method for the determination of molecular weights for macromolecular compounds. But one of the key problems encountered with molecules of high mass is that they are very difficult to observe in the spectrum. The MALDI-TOF mass spectrum of G1-9PA (m.w. 1328) with nine phenylethynyl groups on the periphery mainly shows two signals at 1350 and 1226 amu, which are clearly due to the nine-arm dendrimer molecule. The *m*/*z* value of the main signal at 1350 amu is as a result of $[M^+ + 23]$ (Na^+) and at 1226 amu is as a result of the $[M^+ - C{\equiv}CPh + Na^+]$ ion. G2-18PA with the 18 phenylethynyl-group containing second generation showed one main signal at 3609 amu. The *m*/*z* value $[M^+ + 64]$ could be explained by the M^+ peak containing K^+ and Na^+ ions. The MALDI-TOF mass spectrum of G2-27PA showed the same pattern as G1-9PA. The spectrum demonstrates the presence of Na^+ and K^+ as substrates of the *m*/*z* value of the many signals with ca. 1% error of the calculated value. The G3-36PA spectrum has a peak at $[M^+ + 64]$ amu, which also means that Na^+ and K^+ are substrates of the dendrimers. Thus, from the MALDI-TOF spectrum, the prepared G1–G3 dendrimers do not contain any other structure defects. However, the higher generations (G4 and G5) were not observed in any of the MALDI-TOF mass spectra. For the higher dendritic generations, we tried measurement by UV spectroscopy and GPC.

The UV spectroscopic measurement of G*n*-*m*PA type dendrimers results in some interesting results. We proposed this method as an indirect identification method for the unified character of dendritic macromolecules. The applications of UV absorption methods are also touching upon every field in which quantitative chemical information is required. We observed the following trend: the molar absorbtivities (E_{max}) of phenylethynyl-group-containing dendrimers were proposed to be proportional to the number of triple bonds (see Table 2 and Fig. 2). This method can assist in the determination of molecular weight instead of the MALDI mass spectroscopic determination of high molecular weight dendrimers, which are in most cases unavailable. Fig. 2 shows the increasing trend in molar absorbities of ethynyl group containing dendrimers. However the fifth generation with 144 phenylethynyl group containing dendrimers does not follow the general trend, because it could contain a lot of toluene moieties in the inner shell lattice and as a result the purity of the G5 dendrimer is low. In practice, the ^{1}H-NMR spectrum has about 5% of toluene as observed in G5-144PA (Scheme 2).

Size-exclusion chromatography (SEC) provided additional information on the perfect building of each gen-

Table 1
NMR spectroscopic data of G0, G*n*-*m*PA and G*n*P-*m*Cl ($n = 1$–5, $m = 9$, 27, 18, 36, 72 and 144) type dendrimers

Dendrimers [a]		MeSi	CH_2	CH=C	C≡C	Ph (ppm)
G0 [b]	^1H	0.36 (s, 18H, G0)				7.70 (s, 3H, G0)
	^{13}C	−2.87 (G0)				136.37, 139.97 (G0)
G1P-9Cl	^1H	0.36 (s, 18H, G0)	1.02 (m,6H) 1.30 (m, 6H)			7.64 (s, 3H, G0)
	^{13}C	−3.54 (G0)	6.79, 17.75			136.32, 139.61 (G0)
G1-9PA	^1H	0.33 (s, 18H, G0)	1.09 (m, 12H)			7.78 (s, 3H, G0) 7.21–7.58 (m, 45H, G1)
	^{13}C	−3.37 (G0)	7.41, 9.76		87.18 106.77	136.99, 139.61 (G0), 122.28, 128.21, 129.11, 132.21 (G1)
G2P-27Cl	^1H	0.08 (s, 18H, G0)	−0.21 (m, 6H) 0.37 (m, 6H)	6.40 (s, 9H, G1)		7.46 (s, 3H, G0), 6.96–7.30 (m, 45H, G1)
	^{13}C	−3.82 (G0)	6.83, 8.05	149.05, 154.87 (G1)		137.12, 139.27 (G0), 128.21, 128.35, 128.59, 138.23 (G1)
G2-27PA	^1H	−0.20 (s, 18H, G0)	0.35 (m, 12H)	6.84 (s, 9H, G1)		7.52 (s, 3H, G0), 7.02–7.50 (m, 135H, G1,G2)
	^{13}C	−3.47 (G0)	7.44	149.01, 155.17 (G1)	87.32 107.32	127.89, 128.08, 128.45, 142.20 (G1), 122.28, 128.18, 129.10, 132.20 (G2)
G2P-18Cl	^1H	0.06 (s, 18H, G0) 0.68 (s, 27H, G2P)	−0.20 (m, 6H) 0.41 (m, 6H)	6.26 (s, 9H, G1)		7.46 (s, 3H, G0), 6.95–7.27 (m, 45H, G1)
	^{13}C	−3.69 (G0) 4.53 (G2P)	7.08, 8.11	147.23, 157.52 (G1)		137.26, 139.29 (G0), 127.74, 128.08, 128.37, 140.45 (G1)
G2-18PA	^1H	−0.10 (s, 18H, G0) 0.38 (s, 27H, G2)	0.26 (m, 12H)	6.50 (s, 9H, G1)		7.53 (s, 3H, G0), 7.08–7.43(m, 135H, G1,G2)
	^{13}C	−3.56 (G0) −0.92 (G2)	6.63 7.81	147.12 157.54 (G1)	89.22 107.46	127.77, 128.01, 128.19, 143.24 (G1), 122.59, 128.15, 128.78, 132.00 (G2)
G3P-36Cl	^1H	−0.05 (s, 18H, G0) −0.76 (s, 27H, G2) 0.63 (s, 54H, G3P)	−0.27 (m, 12H)	5.90 (s, 9H, G1), 6.43 (s, 18H, G2)		7.43 (s, 3H, G0) 6.77–7.19 (m, 135H, G1,G2)
	^{13}C	−3.10 (G0,G2) 4.50 (G3P)	8.18	144.82,161.91 (G1), 146.55, 157.28 (G2)		137.36, 139.16 (G0), 126.60, 127.64, 144.34 (G1), 127.48, 128.11, 128.11, 140.04 (G2)
G3-36PA	^1H	−0.2 (s, 18H, G0) −0.7 (s, 27H, G2) 0.31 (s, 54H, G3)	−0.23 (m, 12H)	5.89 (s, 9H, G1) 6.54 (s, 18H, G2)		7.46 (s, 3H, G0) 6.83–7.36 (m, 315H, G1–G3)
	^{13}C	−2.82 (G0, G2) −0.96 (G3)	8.18	144.97, 162.91(G1), 145.72, 158.00 (G2)	89.21 107.46	125.27, 127.62, 128.03, 142.86 (G1, G2), 122.56, 128.18, 128.83, 132.01 (G3)
G4P-72Cl	^1H	−0.68 (s, 27H, G2) −0.78 (s, 54H, G3) 0.59(s, 108H, G4P)	−0.21 (m, 12H)	5.80 (s, 9H, G1) 5.97(s, 18H, G2) 6.39 (s, 36H, G3)		7.40 (s, 3H, G0) 6.48–7.25 (m, 315H, G1–G3)
	^{13}C	−3.30 (G0,G2,G3) 4.48(G4P)	8.09	143.79, 162.00 (G1,G2),146.18, 157.26 (G3)		137.12, 138.87 (G0), 126.40, 127.62, 143.50 (G1,G2), 127.44, 128.06, 128.06, 139.94 (G3)
G4-72PA	^1H	−0.65 (s, 27H, G2) −0.79 (s, 54H, G3) 0.31 (s, 108H, G4)	−0.30 (m, 12H)	5.98(s, 9H, G1) 6.49 (s, 18H, G2) 6.59 (s, 36H, G3)		7.52 (s, 3H, G0), 6.70–7.36 (m, 675H, G1–G4)
	^{13}C	−3.10 (G0,G2,G3) −0.97 (G4)	9.00	144.53, 164.06 (G1, G2), 145.31, 158.08 (G3)	89.28 107.42	126.40, 127.59, 129.00, 142.77 (G1–G3), 122.55, 128.17, 128.83, 132.01 (G4)

Table 1 (*Continued*)

Dendrimers [a]		MeSi	CH_2	CH=C	C≡C	Ph (ppm)
G5P-144Cl	^1H	−0.78 (s, 189H, G2–G4), 0.59 (s, 216H, G5P)	−0.29 (m, 12H)	6.40 (s, 54H, G2, G3), 6.61 (s, 72H, G4)		6.72–7.60 (m, 678H, G0–G4)
	^{13}C	−1.81 (G0,G2–G4) 4.52 (G5P)	6.36	143.63, 159.09 (G1–G3), 146.11, 157.27 (G4)		125.90–140.10 (G0–G4)
G5-144PA	^1H	−0.80 (s, 189H, G2–G4), 0.31 (s, 216H, G5)	−0.41 (m, 12H)	6.30–8.05 (m, 135H, G1–G4) [a]		6.30–8.05 (m, 1398H, G0–G5)
	^{13}C	−3.63 (G0,G2–G4), −0.90 (G5)	9.00	141.36–166.81 (G1–G4)	89.18 107.27	121.36–140.00 (G0–G5)

[a] Small signals in inner shell are omitted.

[b] Vinyl groups in G0: ^1H; 5.7–6.4 (m, 9H), and ^{13}C: 132.72, 138.0 ppm.

eration. Fig. 1 shows a composite of the calculated molecular weight and retention time on SEC for G1-9PA to G5-144PA. A significant feature of the chromatographs is the presence of a small shoulder at the lower-molecular-weight site in the fifth generation that could be a toluene moiety, but the small shoulder was not observed in lower generations. The polydispersity Mw/Mn remained unchanged in value in going from G1-9PA to G5-144PA (Mw/Mn estimated between 1.1 and 1.2; see Table 2). Therefore, by the use of MALDI-TOF, UV and SEC attachments, the molar mass of the phenylethynyl-group-containing dendrimers was grossly overestimated.

3. Experimental

All reactions were carried out under a dried N_2 atmosphere. THF was dried by sodium benzophenone ketyl, while solvents such as toluene were dried and distilled from sodium metal. The NMR spectra were recorded on a Bruker AC-200 spectrometer. The UV spectra were measured by an HP 8452A diode array UV–vis spectrophotometer. For GPC, a combination of PL columns 10^3, 10^4, 10^5 was employed and THF was used as a solvent. Elemental analysis and MALDI mass spectroscopy (Kratos Kompackt MALDI 2) were performed by the Pusan and Taejon Branches of the Korean Basic Science Institute.

3.1. G0

A mixture of 10.80 g (34.30 mmol) of 1,3,5-tribromobenzene and 17.4 g (144.20 mmol) of dimethylchlorovinylsilane dissolved in 50 ml THF was slowly added to 5.7 g (234.37 mmol) of Mg in 25 ml THF. Subsequently, the reaction mixture was stirred for 2 days. The THF was then removed under reduced pressure and the salt was precipitated in pentane and filtered off. The prepared compounds were chro-

Table 2
Mass, EA, UV and SEC data of the prepared dendrimers

Gn	Formula	Mw by mass (Found/Calc.)	EA in% (Found/Calc.)	UV λ_{max} (nm) ($\varepsilon_{max} \times 10^5$)	SEC Rt (in min), PD (Mw/Mn) [a]
G0	$C_{18}H_{3}0Si_3$	330/330.69	C; 65.31/65.38 H; 9.16/9.14		
G1-9PA	$C_{90}H_{78}Si_6$	1350/1328	C; 80.07/81.39 H; 5.89/5.92	283 (1.49)	Rt; 16.93, PD (1.24)
G2-18PA	$C_{243}H_{204}Si_{15}$	3609/3545	C; 81.55/82.32 H; 5.70/5.80	284 (4.99)	Rt; 16.44, PD (1.18)
G2-27PA	$C_{306}H_{222}Si_{15}$	4354/4320	C; 84.69/85.07 H; 5.19/5.18	283 (8.16)	Rt; 16.12, PD (1.22)
G3-36PA	$C_{549}H_{456}Si1_{33}$	8048/7980	C; 81.55/82.32 H; 5.77/5.76	285 (10.85)	Rt; 15.72, PD (1.24)
G4-72PA	$C_{1161}H_{960}Si_{69}$	/16850	C; 81.19/82.76	287 (20.95)	Rt; 14.97, PD (1.14)
G5-144PA	$C_{2385}H_{1968}Si_{141}$	/34590	H; 5.85/5.74	287 (29.84)	Rt; 14.36, PD (1.18)

[a] Retention time, PD: polydispersity.

Table 3
Reaction conditions

Dendrimers	Reactants g (mmol) G*n*/G*n*P + HsiMe$_n$Cl$_{3-n}$ /LiC≡CPh	Reaction conditions h/°C/solvents/cat.	Yield g (mmol, %)	Remarks [a]
G1P-9Cl	4.25 (12.85) G0 + 12.07 (89.16) of HSiCl$_3$	19 h/RT/neat/Pt in C [b]	8.72 (11.83, 92)	White solid
G1-9PA	7.00 (9.49) of G1P-9Cl + 95 ml (95) LiC≡CPh	7 h/reflux/THF	11.10 (8.36, 88)	Yellow solid
G2P-27Cl	2.91 (2.19) G1P-9PA + 6.30 (46.51) of HSiCl$_3$	24 h/reflux/toluene/Pt in C [b]	4.90 (1.92, 89)	Yellow solid
G2-27PA	3.50 (1.37) of G2P-27Cl + 45 ml (45) LiC≡CPh	7 h/reflux/THF	5.28 (1.22, 89)	Yellow solid
G2P-18Cl	5.22 (3.93) G1P-9PA + 8.45 (73.45) of MeHSiCl$_2$	12 h/reflux/toluene/Pt in C [b]	8.43 (3.56, 91)	Yellow solid
G2-18PA	8.43 (3.56) of G2-18Cl + 75 ml (75) LiC≡CPh	7 h/reflux/THF	11.00 (3.10, 87)	Yellow solid
G3P-36Cl	4.76 (1.34) G2-18PA + 6.01 (52.24) of MeHSiCl$_2$	24 h/reflux/toluene/Pt in C [b]	6.35 (1.13, 84)	Yellow solid
G3-36PA	6.35 (1.13) of G3-36Cl + 50 ml (50) LiC≡CPh	7 h/reflux/THF	8.03 (1.01, 89)	Yellow solid
G4P-72Cl	1.83 (0.22) G3-36PA + 2.34 (20.34) of MeHSiCl$_2$	24 h/reflux/toluene/Pt in C [b]	2.40 (0.19, 86)	Yellow solid
G4-72PA	2.40 (0.19) of G4-72Cl + 25 ml (25) LiC≡CPh	17 h/reflux/THF	2.97 (0.18, 89)	Yellow solid
G5P-144Cl	0.80 (0.047) G4-72PA + 1.68 (14.69) of MeHSiCl$_2$	24 h/reflux/toluene/Pt in C [b]	1.02 (0.04, 85)	Yellow soild [c]
G5-144PA	0.88 (0.035) of G5-144Cl + 8 ml (8) LiC≡CPh	21 h/reflux/THF	1.07 (0.03, 88)	Yellow solid [d]

[a] All prepared dendrimers are soluble in organic media such as toluene, chloroform and acetone etc.

[b] The hydrosilation catalyst Pt–C is formed using 10% Pt in activated carbon and the reaction is carried out neat or in toluene solution.

[c] Soluble in organic media such as toluene, chloroform and acetone.

[d] Viewed as a main peak and toluene peaks as trace peaks in the NMR spectrum.

matographed on silica gel with pentane (obtained 8.4 g). The sample contained about 10% of 1,3-disubstituted benzene derivatives. The byproduct could be evaporated by vacuum distillation (58°C at 10^{-1} Torr). The product G0 was obtained as a clear liquid (6.8 g, 20.50 mmol, 60%) (see Tables 1 and 2 for characterization).

3.2. General procedure for the preparation of GnP-mCl type dendrimers: G1P-9Cl

A mixture of 4.25 g (12.85 mmol) of G0, 12.00 g (89.16 mmol) of HSiCl$_3$ and a hydrosilation catalyst (Pt–C, 10% content on activated carbon) was stirred for 19 h. The excess trichlorosilane was removed by vacuum distillation. The catalyst was filtered off and the volatile components were removed by vacuum distillation, leaving 8.72 g (11.83 mmol, 92%) as a white precipitate. Further purification was not available because of the compound's sensitivity to moisture. The compound was found to consist of only one dendrimer via NMR spectroscopy (see Tables 1 and 2 for the characterization and reaction conditions for other models).

3.3. General procedure of the preparation of Gn-mPA type dendrimers: G1-9PA

A lithium phenylacethylide solution in THF (95 ml (95 mmol)) was slowly added to 7.00 g (9.49 mmol) of G1P-9Cl in 50 ml THF. After the addition was finished, the reaction mixture was refluxed for 7 h. Volatile components were removed under reduced pressure, leaving a yellow precipitate and a salt that precipitated in toluene and was subsequently filtered off. The prepared compounds were chromatographed on silica gel with chloroform as eluent. The product G1-9PA was obtained as yellow–brown crystals (11.10 g, 8.36 mmol, 88%) (see Tables 1–3 for the characterization and reaction condition for other models.

Acknowledgements

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