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Preparation of Carbosilane Dendrimers with Perfluorosilane Branches

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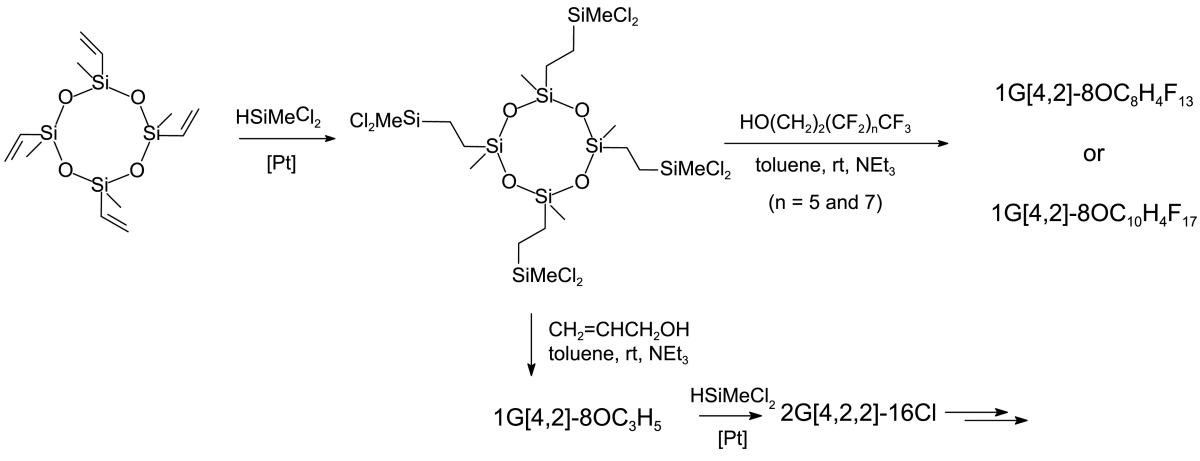
Perfluororosilanes[1] are highly stable compound, which used in a wide range of applications to heat resistance, impermeable to chemicals, sliding properties, electric characteristics and it has been also exhibit special repellency to water.[2-7] In addition, the measurement of wetting property and hydrophobic coating by the use of perfluorosilane film on metal oxide surface are widly studied.[1] And as a related subject, dendrimers are well defined macromolecule composed a focal point, it has unified and applicable nummerous end groups.[8] This report presents the preparation of carbosilane dendrimers having peripheral groups replaced by fluorinated functions as a characteristic peripheral branches. These dendrimers expects that show a new characteristic presisonal properties as a hydrophobic matter. Fluorinated alkyl branches having $F_3C(CF_2)_7(CH_2)_2O$-(Heptadecafluoro-1,1,2,2-tetrahydro-1-decanoxy; HDFD) and $F_3C(CF_2)_5(CH_2)_2O$-(Tridecafluoro-1,1,2,2-tetrahydro-1-octanoxy (TDFO) functions were used.

The carbosilane dendrimers that was began cyclic siloxane core and developed to high generation with Si-O-C branches on the periphery were published as previous reports.[8,9] These dendrimers were prepared by divergent synthetic methods using hydrosilation of vinyl rest on siloxane core ((MeSi-$(CH=CH_2)O)_4$; 1,3,5,7-tetramethyl-1,3,5,7-tetravinyl-2,4,6,8-tetraoxacyclooctane) with methyldichlorosilanes ($MeSiHCl_2$). The resulting compound **1G[4,2]-8Cl** with eight Si-Cl bonds on the periphery yields nearly quantitative, determined by NMR. The reaction followed by the addition of fluorinated alcohol $F_3C(CF_2)_7(CH_2)_2OH$ or $F_3C(CF_2)_5(CH_2)_2OH$ formed to **1G[4,2]-8OC$_{10}$H$_4$F$_{17}$** and **1G[4,2]-8OC$_8$H$_4$F$_{13}$** under dried basic toluene medium which obtained with high yields (65-95%). For the preparation of 1st generation with eight allyloxy groups **1G[4,2]-8OC$_3$H$_5$** was prepared by the addition of allylalcohol to **1G[4,2]-8Cl**. The skeleton of growing generations are prepared by the use of iterative alcoholysis and hydrosilation as the preparation of 1st generation **1G[4,2]-8OC$_3$H$_5$** (Scheme 1).

The procedures, hydrosilation and addition of fluorinated functions on the dendritic periphery have been well controlled by NMR spectroscopic determination. The observation of disappearance of vinyl signals between 5.1-5.3 ppm and appearance of characteristic methylsiloxane signal by hydrosilation process near 0.0-0.3 ppm was clearly determined. The fluorinated dendrimers **nG[4]-8nOC$_{10}$H$_4$F$_{17}$**, and **nG[4]-8nOC$_8$H$_4$F$_{13}$** was purified by column chromatography which can be removed dendrimers with hydrolyzed branches, free fluorinated alcohol and solvated salts in reaction medium. The yields of the prepared dendrimers have been obtained almost quantitatively in hydrosilation procedure and alcoholysis in general very high but some lower yield than hysrosilation procedure because the chromatographic purification methods brought reduced the yields. The spectroscopic measurement of reaction medium showed almost quantitatively which means the both reactions were well progressed. The analyses of MALDI mass spectra and elemental analysis made it possible to obtain the purity and unified properties. The MALDI mass analysis of the fluorinated dendrimers were not observed the molecular peaks.



Scheme 1. Preparative methods of perfluorosilane dendrimers.

Table 1. GPC data of carbosilane dendrimers with perfluorosilane groups

Name of Dendrimers	Formula	Mw (calcd.)	GPC	
			rt (min)[a]	PDI (Mw/Mn)
1G[4,2]-8$OC_{10}H_4F_{17}$	$C_{96}H_{72}F_{136}O_{12}Si_8$	4226	19.250	1.007 (25385/25193)
2G[4,2,2]-16$OC_{10}H_4F_{17}$	$C_{208}H_{176}F_{272}O_{28}Si_{16}$	8740	18.067	1.010 (32080/31735)
3G[4,2,2,2]-32$OC_{10}H_4F_{17}$	$C_{432}H_{384}F_{544}O_{60}Si_{32}$	17769	16.823	1.008 (33986/33713)
4G[4,2,2,2,2]-64$OC_{10}H_4F_{17}$	$C_{880}H_{800}F_{1088}O_{124}Si_{64}$	35827	15.683	1.006 (40675/40122)
1G[4,2]-8$OC_8H_4F_{13}$	$C_{80}H_{72}F_{104}O_{12}Si_8$	3425	16.767	1.010 (39350/38334)
2G[4,2,2]-16$OC_8H_4F_{13}$	$C_{176}H_{176}F_{208}O_{28}Si_{16}$	7140	16.502	1.008 (43236/42893)
3G[4,2,2,2]-32$OC_8H_4F_{13}$	$C_{368}H_{384}F_{416}O_{60}Si_{32}$	14569	16.250	1.010 (43706/43181)
4G[4,2,2,2,2]-64$OC_8H_4F_{13}$	$C_{752}H_{800}F_{832}O_{124}Si_{64}$	29460	15.924	1.006 (49648/48760)

[a]rt: Retention time

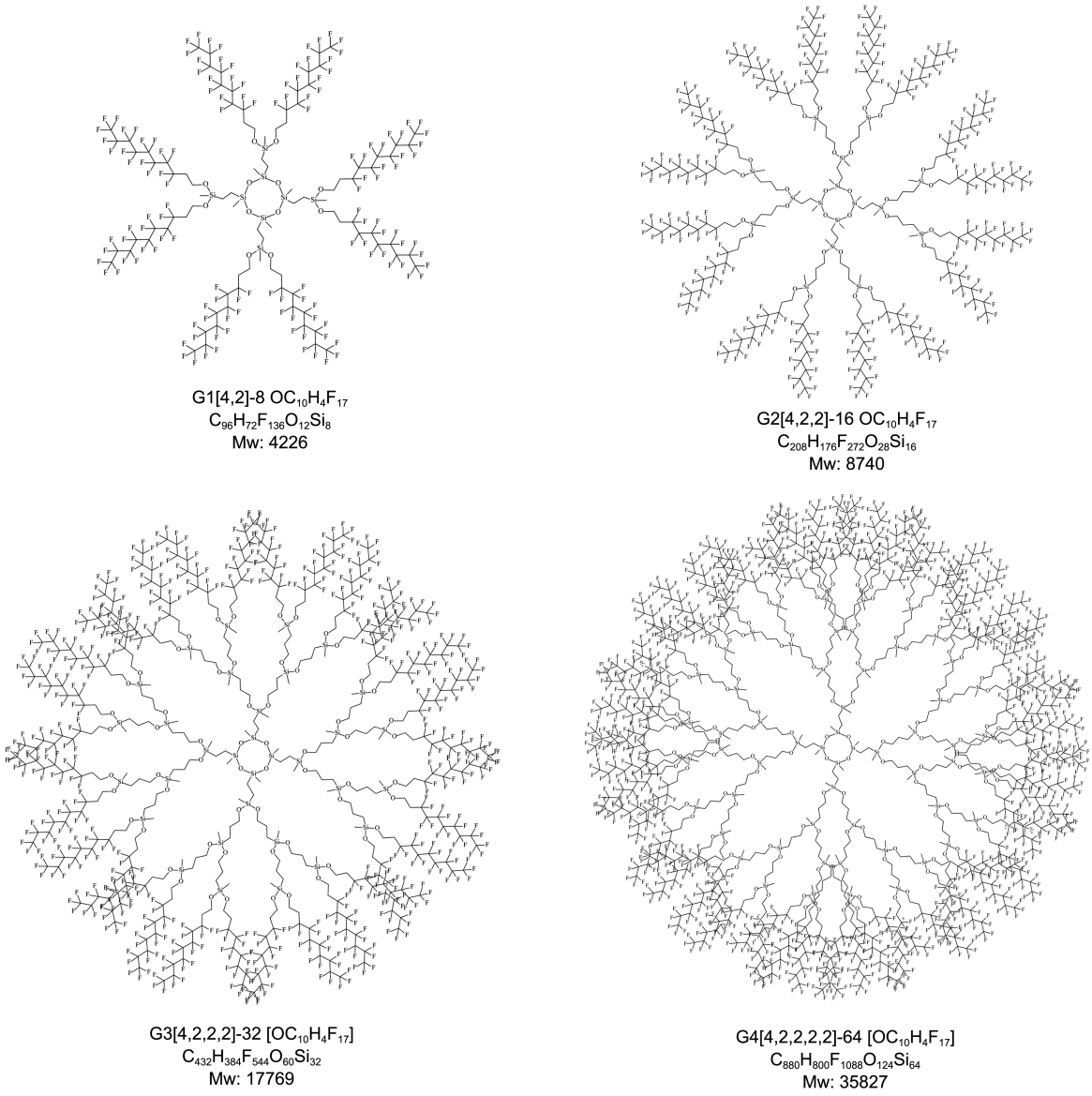


Figure 1. Schematic view of 1st to 4th generation of carbosilane dendrimers with $OC_{10}H_4F_{17}$ perfluoro-peripheral functions.

Because, as we suppose it were hanged of the matrix stability against the laser beam on the measurement procedure. The analysis of GPC (Gel Permeation Chromatography) of fluorinated dendrimers **nG[4]-8n$OC_{10}H_4F_{17}$**, and **nG[4]-8n$OC_8H_4F_{13}$** have very low, regular and consistent polydispersity index values (1.005-1.010). The retention times of them show regular patterns according to increasing the generations of them, which means no structural defects of the

dendrimers and their unified structures. The dendrimers **nG[4]-8nOC$_{10}$H$_4$F$_{17}$**, and **nG[4]-8nOC$_8$H$_4$F$_{13}$** were well characterized (Table 1).

The synthetic methods of the preparation of siloxane type dendrimers were published as previous papers,[8,9] but we would like to write a sample methods for the preparation of fluorinated dendrimers as following examples: the first generation **1G[4,2]-8Cl** with 8 Si-Cl bonds has been prepared by hydrosilation of **0[G4]-4vinyl** with the excess of dichloromethylsilane as neat or the reflux condition of toluene. The growing generations of dendrimers with Si-Cl bonds are prepared by the same methods as mentioned above. The preparation of Si-HDFD and Si-TDFO bonds on dendritic periphery were use of the reaction with Si-Cl containing dendrimers and fluorinated alcohols HDFD-OH and TDFO-OH of under basic toluene. The detailed characteristic data are described in reference.[10] Hydrosilation products of the core moieties are identified by NMR spectroscopy by recognized the decreasing characteristic double bonds peaks and alkoxysilyl moieties of forming β-silylated branches (-OCH$_2$(CH$_2$)$_2$SiCl$_3$) in an anti-Markovnikov direction. The hydrosilation of the allylic groups of the core moiety in nonpolar toluene solvent were performed with high yields, but unsuitable results such as the ring opening and polymerization of THF were obtained when the reaction progressed in THF medium. Allyloxy groups were introduced onto the terminal Si atoms of dendrimers by the reaction of the chlorosilanes with allylalcohol in the presence of NEt$_3$ as acid scavenger. The purification of these dendrimers is very critical to get each generations as unimolecular dendrimers with no defects of their functional groups. All of hydrosilation and alcoholysis are performed in high yields due to the simplicity of the reactions. The purification methods of dendrimers were reported in many articles,[8,9] meanwhile simple column chromatography of the carbosilane dendrimers with mixed solvents gave highly purified products in good yields.

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10. Selected data for prepared dendrimers: **1G[4,2]-8OC$_{10}$H$_4$F$_{17}$** (C$_{96}$H$_{72}$F$_{136}$O$_{12}$Si$_8$), materials were used 0.31 g (0.39 mmol) of **1G[4,2]-8Cl** and 1.52 g (3.28 mmol), 1*H*,1*H*,2*H*,2*H*-heptadecafluoro-1-decanol. Yield 1.50 g (0.36 mmol, 92%) of difficult moving jelly type material. GPC, PDI (Mw/Mn): 1.008 (42337/41962), Retention time: 16.61 min. ^{1}H-NMR (ppm, CDCl$_3$): δ 0.0-0.2 (s, 24H, SiMe, (G0-G1)), 0.45-0.72 (m, 16H, CH$_2$ (G0)), 2.29-2.45 (m, 16H, CH$_2$ (G1)), 3.88-4.05 (m, 16H, OCH$_2$ (G1)). **2G[4,2,2]-16OC$_{10}$H$_4$F$_{17}$** (C$_{188}$H$_{206}$F$_{202}$O$_{28}$Si$_{16}$), materials were used 0.30 g (0.16 mmol) of 2G[4,2,2]-16Cl and 1.21 g (2.61 mmol) of 1*H*,1*H*,2*H*,2*H*-heptadecafluoro-1-decanol. Yield: 1.24 g (0.14 mmol, 87%) of difficult flowing light jelly type material. GPC: PDI (Mw/Mn) = 1.005 (44084/43826), rt = 16.43 min. ^{1}H-NMR (ppm, CDCl$_3$): δ 0.0-0.15 (s, 48H, SiMe (G0-G2)), 0.5-0.65 (m, 16H, CH$_2$ (G0)), 1.78-1.92 (m, 16H, CH$_2$ (G1)), 2.27-2.41 (m, 16H, CH$_2$ (G1)), 3.53-3.71 (m, 32H, CH$_2$ (G2)), 3.86-4.02 (m, 48H, OCH$_2$ (G2)). **3G[4,2,2,2]-32OC$_{10}$H$_4$F$_{17}$** (C$_{432}$H$_{384}$F$_{544}$O$_{60}$Si$_{32}$), materials were used 0.36 g (0.09 mmol) of **3G[4,2,2,2]-32Cl** and 1.42 g (3.07 mmol) of 1*H*,1*H*,2*H*,2*H*-heptadecafluoro-1-decanol Yield: 1.36 g (0.08 mmol, 88%) of difficult flowing light jelly type material. GPC: PDI (Mw/Mn) = 1.007 (45169/44853), rt = 16.250 min. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 0.0-0.15 (s, 96H, SiMe (G0-G3)), 0.48-0.63 (m, 16H, CH$_2$ (G0)), 1.32-1.48 (m, 48H, CH$_2$ (G1-G2)), 1.48-1.63 (m, 48H, CH$_2$ (G1G2)), 2.27-2.4 (m, 64H, CH$_2$ (G3)), 3.58-3.7 (m, 48H, OCH$_2$ (G1G2)), 3.91-4.08 (m, 64H, OCH$_2$ (G3)). **4G[4,2,2,2,2]-64OC$_{10}$H$_4$F$_{17}$** (C$_{880}$H$_{801}$F$_{1087}$O$_{124}$Si$_{64}$), materials were used 0.32 g (0.04 mmol) of 4G[4,2,2,2,2]-64Cl and 1.17 g (2.51 mmol) of 1*H*,1*H*,2*H*,2*H*-heptadecafluoro-1-decanol. Yield: 1.13 g (0.03 mmol, 75%) of difficult flowing light jelly type material. GPC: PDI (Mw/Mn) = 1.006 (58063/57120), rt = 15.98 min. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 0.02-0.17 (s, 192H, SiMe (G0-G4)), 0.51-0.65 (m, 16H, CH$_2$ (G0)), 0.94-1.1 (m, 112H, CH$_2$ (G1-G3)), 1.58-1.73 (m, 112H, CH$_2$ (G1-G3)), 2.28-2.42 (m, 128H, CH$_2$ (G4)), 3.53-3.69 (m, 112H, OCH2 (G1-G3)), 3.94-4.08 (m, 128H, OCH$_2$ (G4)). **1G[4,2]-8OC$_8$H$_4$F$_{13}$** (C$_{80}$H$_{72}$F$_{104}$O$_{12}$Si$_8$), materials were used 0.22 g (0.29 mmol) of **1G[4,2]-8Cl** and 0.85 g (2.336 mmol) of 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol (CF$_3$(CF$_2$)$_5$-CH$_2$CH$_2$OH). Yield: 0.88 g (0.26 mmol, 90%) of white gel type difficult flowing liquid. GPC: PDI (Mw/Mn) = 1.02 (39350/38334), rt = 16.767 min. ^{1}H-NMR (ppm, CDCl$_3$): δ 0.14 (s, 12H, SiMe (G0)), 0.14-0.8 (m, 16H, CH$_2$ (G0)), 1.4 (s, 12H, SiMe (G1)), 1.80 (m, 16H, CH$_2$ (G1)), 3.79 (m, 16H, OCH$_2$ (G1)). **2G[4,2,2]-16 OC$_8$H$_4$F$_{13}$** (C$_{176}$H$_{176}$F$_{208}$O$_{28}$Si$_{16}$), materials were used 0.47 g (0.25 mmol) of **2G[4,2,2]-16Cl** and 1.47 g (4.03 mmol) of 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol. Yield: 1.17 g (0.16 mmol, 64%) of light yellow gel type difficult flowing liquid. GPC: PDI (Mw/Mn) = 1.008 (43236/42893), rt = 16.560 min. ^{1}H-NMR (ppm, CDCl$_3$): δ 0.0-0.36 (s, 36H, SiMe (G0-G2)), 0.36-0.8 (m, 16H, CH$_2$ (G0)), 1.78-187 (m, 16H, CH$_2$ (G1)), 2.26-2.48 (m, 16H, CH$_2$ (G1)), 3.6-3.82 (m, 32H, CH$_2$ (G2)), 3.82-4.2 (m, 32H, OCH$_2$ (G2)). **3G[4,2,2,2]-32OC$_8$H$_4$F$_{13}$** (C$_{368}$H$_{384}$F$_{416}$O$_{60}$Si$_{32}$), materials were used 0.39 g (0.09 mmol) of 3G[4,2,2,2]-32Cl and 1.47 g (4.04 mmol) of 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol. Yield: 0.98 g (0.07 mmol, 77%) of gel type difficult flowing liquid. GPC: PDI (Mw/Mn) = 1.01 (43706/43181), rt = 16.333 min. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 0.14 (s, 96H, SiMe (G0-G3)), 0.4-0.8 (m, 16H, CH$_2$ (G0)), 1.64-1.8 (m, 48H, CH$_2$ (G1-G2)), 2.18-2.57 (m, 48H, CH$_2$ (G1-G2)), 3.6-3.8 (m, 64H, CH$_2$ (G3)), 3.8-4.0 (m, 64H, OCH$_2$ (G3)). **4G[4,2,2,2,2]-64OC$_8$H$_4$F$_{13}$** (C$_{752}$H$_{800}$F$_{832}$O$_{124}$Si$_{64}$), materials were used 0.42 g (0.05 mmol) 4G[4,2,2,2,2]-64Cl and 1.30 g (3.58 mmol) of 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol. Yield: 1.18 g (0.04 mmol, 80%) of light yellow gel type difficult flowing liquid. GPC: PDI (Mw/Mn) = 1.006 (49648/48760), rt = 16.124 min. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 0.0-0.4 (s, 48H, SiMe (G0-G4)), 0.4-0.74 (m, 16H, CH$_2$ (G0)), 0.9-1.14 (m, 64H, CH$_2$ (G1-G3)), 1.5-1.68.