# Convergent Synthesis of Siloxane Starburst Dendrons and Dendrimers via Hydrosilylation

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ABSTRACT: New highly branched starburst dendrons and dendrimers containing siloxane linkages were convergently synthesized via hydrosilylation. Allyl cyanide and allylbis[4-(hydroxydimethylsilyl)phenyl]-methylsilane were used as the starting material and building block, respectively. The allyl group was a synthon of (*N,N*-diethylamino)silane, which was a suitable electrophilic silicon species. The starburst dendrons and dendrimers were constructed starting at the point which became the periphery of the molecule. The hydrosilylation of allyl cyanide with chlorodimethylsilane was carried out, followed by amination with diethylamine, and the resultant aminosilane was reacted with the building block to yield the first-generation dendron (G1) possessing two cyano groups. The next-generation dendron (G2) could be built up in a similar manner, as the hydrosilylation of the allyl group of G1 with chlorodimethylsilane, amination, and reaction with the building block. By repeating the procedure, G2, G3, and G4 dendrons possessing 4, 8, and 16 cyano groups were synthesized, respectively, which were purified by silica gel column chromatography. $^1$H and $^{13}$C NMR spectra were consistent with the structure of these dendrons. The molecular weights based on standard polystyrene measured by GPC were somewhat higher than those of the calculated values, and the narrow molecular weight distribution indicated the starburst polymers were reasonably pure. The Mark-Houwink constants $K$ and $\alpha$, calculated from the relationship between the molecular weight and the intrinsic viscosity of the polymers, were found to be $1.33 \times 10^{-3}$ and 0.45, respectively. The spherical starburst dendrimer was synthesized by the reaction of the aminosilane intermediate of G3 with tris[4-(hydroxydimethylsilyl)phenyl]-methylsilane having three reactive hydroxy groups. The glass transition temperatures ($T_g$) of these polymers were from −61 to +36 °C, where the larger generation molecule had higher $T_g$.

## Introduction

Starburst dendrimers are molecules with a highly branched structure and have been prepared by "cascade synthesis",[1] which consists of repeating a series of stepwise reactions to achieve geometrical growth of branches. They allow precise control of the molecular size, as well as disposition of desired functionalities,[2] and are expected to assume a nanosphere (i.e., between 1.0 and 10 nm in diameter) consisting of one molecule.[3] The preparation of starburst dendrimers has been demonstrated in polyamido-amine[4] and polyether systems[5] by Tomalia and his co-workers. The former was prepared through Michael addition and amination and the latter by a combination of Williamson ether synthesis and a protection-deprotection reaction using bicyclic orthoesters.

Previously, we reported the synthesis of starburst polysiloxane from the initiator core containing three phenylsilyl groups.[6] The electrophilic silicon species were generated by the reaction of phenylsilane at the terminal position of the core molecule with bromine, followed by amination with diethylamine. The reaction of this silylamine species with a silanol containing phenylsilyl groups yielded the first-generation compound with six phenylsilyl groups. By repeating this procedure, the starburst polysiloxane of the third generation was obtained, which had a molecular weight of 8236 with 24 phenylsilyl groups at the periphery of the polymers. The starburst polysiloxane dendrimers were also reported by Masamune and his co-workers.[7]

These synthetic efforts toward the dendritic macromolecule involved a divergent growth methodology. In these cases, the molecules grew from the central core to the outside direction by successive stepwise activation and condensation which multiplied the number of branches. A problem with this strategy is that the reaction points existing at the peripheral position always multiplied with the number of branches. So, chain expanding reactions with very high efficiency are required to avoid the occurrence of structural defects.

Recently, Frechet reported a unique synthetic method of dendritic polyethers using a convergent approach in which the molecules were constructed starting at a point that becomes the periphery of the molecules.[8] The general concept of the convergent approach is shown in Scheme I. First, the unreactive group (□) of the starting molecule was converted to the reactive group (▽). Next, the building block having two reactive groups (△) and one unreactive group (□) was reacted with it. The reactive group (▽) in the new generation was again generated from the unreactive group (□) and then reacted with the reactive group of the building block. The starburst dendrimers were convergently synthesized by repeating these steps. Thus, since the starburst dendrimers grew to the inside direction from the peripheral position in the convergent synthesis, the number of points reacting with the building unit is usually constant, which is only 1 in most cases.

In this paper, we describe the convergent synthesis of new highly branched starburst dendrons and dendrimers which were constructed by siloxane linkages. As mentioned above, the siloxane bond is formed by the reaction of the electrophilic silicon species and silanol. Selection of the synthon of such reactive functions is generally important in starburst synthesis. In the present work, hydrosilylation of chlorosilane to the terminal olefin was employed as the key step, where the formation of a new silicon-carbon bond, as well as the generation of chlorosilane, electrophilic silicon species, was achieved at the same time. Next, siloxane bond formation was carried out by the reaction of aminosilane which was derived from chlorosilane and the building block which had two silanol units and one terminal olefin unit.

## Results and Discussion

Siloxane bonds are generally prepared by the reaction between silanol and electrophilic silicon species such as

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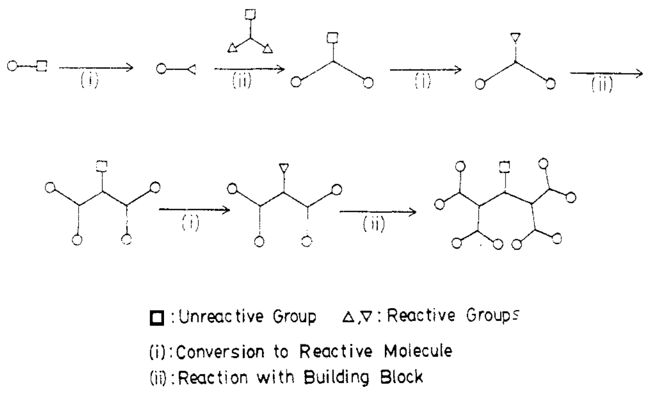
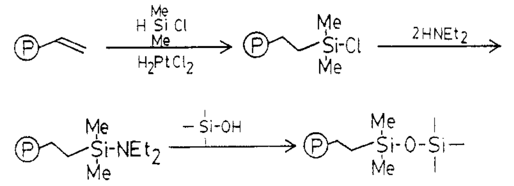
**Scheme I**



**Scheme II**



halosilanes or aminosilanes. Terminal olefins were selected as the synthon of electrophilic silicon species in this study.[9] Thus, halosilane species were conveniently generated from allyl groups by hydrosilylation with chlorodimethylsilane. We reported that the reaction of aminosilane with silanol was a more suitable siloxane bond-forming reaction compared with the use of chlorosilane,[6] even though one more reaction step was required to produce aminosilane. Scheme II shows the general concept of the chain extension procedure in the present work. The terminal olefins of the polymers were reacted with chlorodimethylsilane to obtain the chlorosilane-terminated polymers, which were converted to aminosilane species, and then new siloxane bonds were formed by reaction with the silanol of the building block.

The building block 1 for the present starburst dendrons should have one terminal olefin and two silanol groups. It was synthesized starting from *p*-dibromobenzene as shown in eq 1, whose overall yield was 16% starting from *p*-dibromobenzene. The building block 1 did not have sterically hindered silanol and could be purified by recrystallization.

The starburst dendrons and dendrimers in the present study were designed to have cyano functionality at the external position, which can be converted to other functional groups such as carboxylic acid and amine. Furthermore, the obtained polymer could be purified by silica gel column chromatography because of the affinity between the cyano group and silica gel.

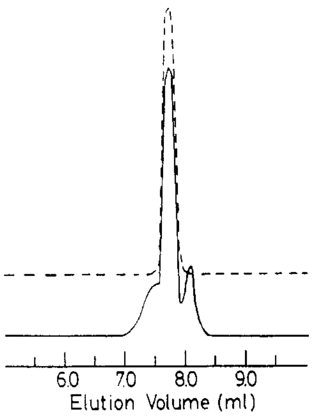
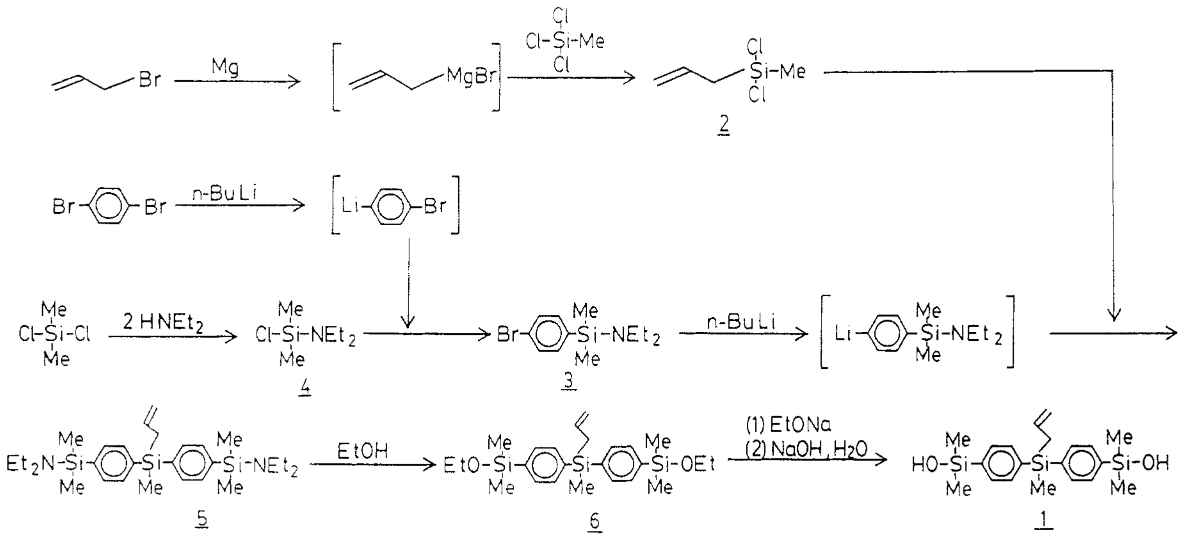
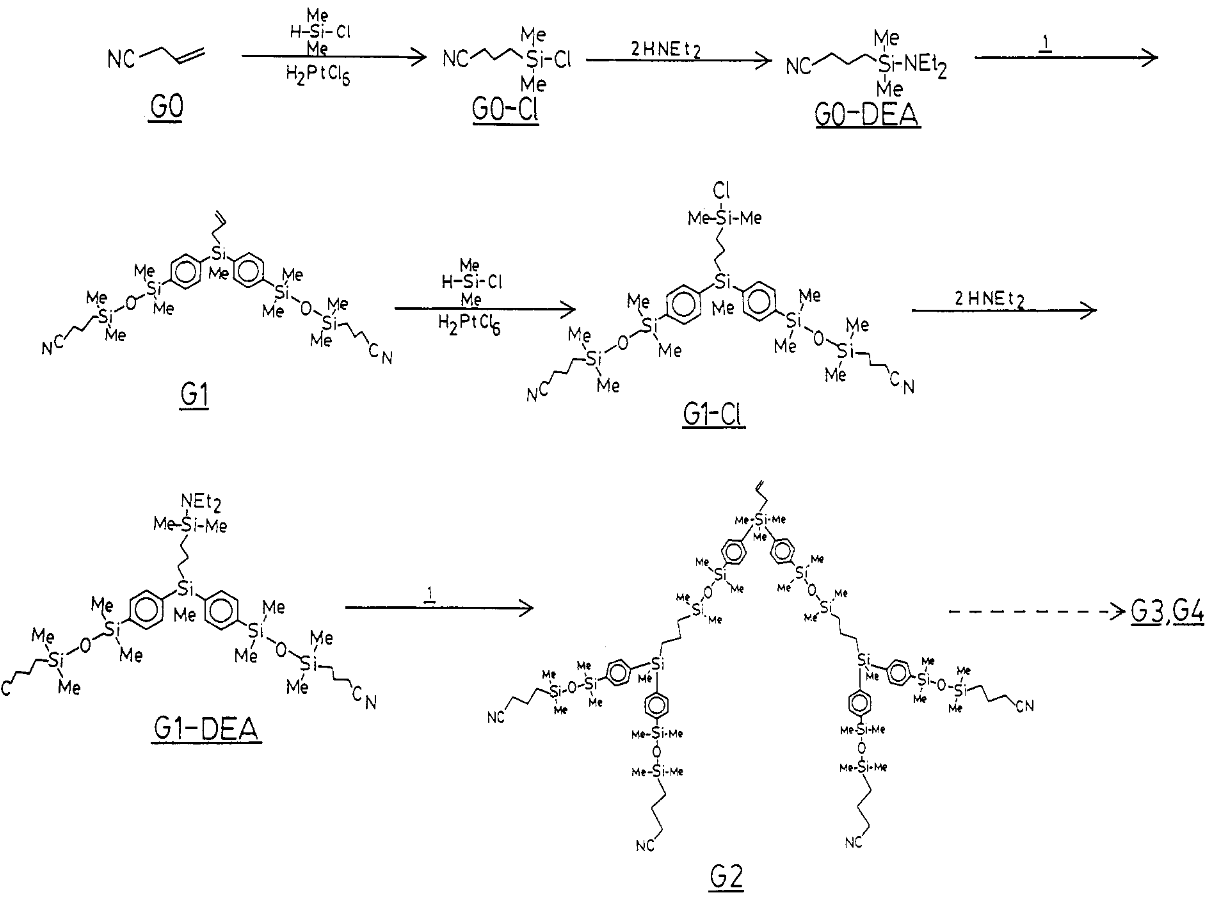


**Figure 1.** GPC curves of G3. Solid line: Crude G3. Dotted line: After purification using silica gel column chromatography.

A general synthetic procedure for the starburst dendrons is shown in eq 2. First, the hydrosilylation of chlorodimethylsilane to allyl cyanide (G0) afforded chloro(3-cyanopropyl)dimethylsilane (G0-Cl). Diethylamine was then added to the solution of G0-Cl to obtain (3-cyanopropyl)(diethylamino)dimethylsilane (G0-DEA). Attempts to isolate G0-DEA failed because the aminosilane was highly sensitive to the air moisture. The first-generation polymer (G1) was obtained by the reaction between G0-DEA and building block 1. Thus, a series of hydrosilylation, amination, and reaction with building block 1 was repeated three times to prepare the second-, third-, and fourth-generation polymers (G2, G3, and G4). The intermediates G1-Cl, G2-Cl, and G3-Cl could be isolated and identified by the NMR spectra. All pure starburst dendrons G1, G2, G3, and G4 were obtained as colorless oils with the final isolated yields of 80, 48, 41, and 17%, respectively. G1 was purified by vacuum distillation, whereas pure G2, G3, and G4 were isolated by silica gel column chromatography. Although, as shown in Figure 1, the crude starburst polymers showed relatively broad molecular weight distributions due to the presence of a small amount of higher and lower molecular weight impurities, the molecular weight distributions were remarkably reduced after chromatographic purification. Higher molecular weight impurities in the crude products might be produced by the self-coupling reaction of the



(1)



(2)

intermediates or the coupling reaction assisted by building block 1 of the hydroxy group of compound 7 which was produced by the reaction of building block 1 with G*X*-DEA (Scheme III), while lower molecular weight impurities might be unreacted G*X*-DEA.

Next, G3-DEA was reacted with tris[4-(hydroxydimethylsilyl)phenyl]methylsilane (8) instead of building block 1 to afford new polymer G3-3 which had a $M_w$ of 12 820 and 24 cyano groups in the exterior position (Scheme IV).

As illustrated in Chart I, the silicon atoms in the present starburst polymers were classified into five different species, B, Mme, Mmi, Mpe, and Mpi. The $^1$H NMR spectra are shown in Figure 2. In G1, six kinds of protons, i.e., aromatic protons, allyl protons, methylene protons, methyl protons bonded to the B type silicon atoms, methyl protons bonded to the Mpe type silicon atoms, and methyl protons bonded to the Mme type silicon atoms, are observed. Methyl protons bonded to Mpi type silicon atoms and Mmi type silicon atoms besides the above six kinds of protons were recognized at 0.3 and 0.1 ppm in G2, G3, G4, and G3-3. The ratio of integration of these protons agreed with the calculated values as shown in Table I. The fact that the peaks of the methyl protons bonded to Mme and Mpe type silicon atoms were observed as singlet peaks in all compounds suggested that the present starburst dendrons had the proposed structure.

All carbons of cyano, phenyl, allyl, methylene, and methyl bonded to the different types of silicon atoms could be distinguished in the $^{13}$C NMR spectra (Figure 3). These carbons were clearly separated in G1 and G2, whereas they were relatively unclear in G3, G4, and G3-3. The peaks of methyl carbons of Mpe and Mme type silicon atoms at 0.9 and 0.4 ppm were observed as sharp singlets. That implied high purity of these polymers.

Table II summarizes the results of molecular weight measurements of the starburst dendrons. The $M_n$ values obtained by the GPC measurement were higher than those of the $F_w$ (formula weights) in G1, G2, G3, and G4, whereas the relationship was opposite in G3-3. This fact may be caused by the shape of G3-3, which had the more spherical structure compared with other polymers. The Mark–Houwink constants $K$ and $\alpha$ of the present starburst dendrons were calculated to be $1.33 \times 10^{-3}$ and 0.45, respectively. The relationship between the intrinsic viscosity and the $F_w$ is shown in Figure 4. The $\alpha$ value of 0.45 was larger than the value of the previous siloxane starburst polymers[4] (0.21) prepared by the divergent method.

The glass transition temperautres ($T_g$) of the starburst polymers were determined by differential scanning calorimetry (DSC) as shown in Figure 5. The higher generation polymers showed higher $T_g$'s. This suggests that the movement of each chain in the starburst polymers is more restricted in the higher generation polymers.

## Experimental Section

$^1$H and $^{13}$C NMR spectra and IR spectra were recorded on a JEOL FX-900 FT-NMR spectrometer and a Jasco FT/IR-5000 spectrophotometer, respectively. Gel permeation chromatography (GPC) was performed with an apparatus using a Shodex analytical column KF8025 and tetrahydrofuran (THF) as the eluent.

**Measurement of Viscosities.** Specific viscosities $\eta_{sp}$ were measured at various concentrations $C$ using an Ostwald-type capillary viscometer in THF at 30 °C. Figure 6 shows the relationship between reduced viscosity $\eta_{sp}/C$ and concentration $C$. The intrinsic viscosities $\eta = (\eta_{sp}/C)_{c=0}$ of each generation polymer were obtained from Figure 6 and are summarized in Table II.

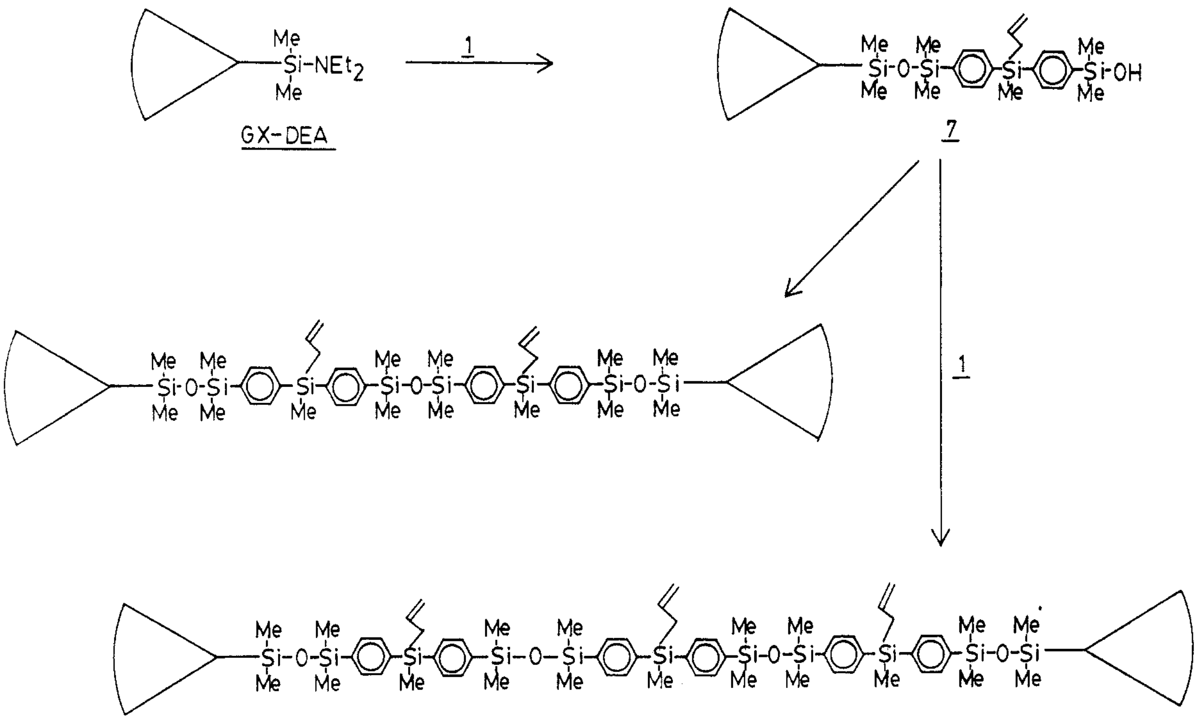
**Allyldichloromethylsilane (2).** To a solution of 89.7 g (0.6 mol) of trichloromethylsilane in 400 mL of dry ether was added dropwise a solution of allylmagnesium bromide that was prepared from 60.5 g (0.5 mol) of allyl bromide and 12.2 g (0.5 mol) of magnesium in 150 mL of ether at 5 °C. After the solution was stirred for 1 h, the precipitated magnesium salts were filtered under nitrogen. The solvent was evaporated, and the residue

**Table I**
**Integration in $^1$H NMR Spectra of Starburst Polysiloxanes**

| | aromatic[a] | | allyl[b] | | methylene[c] | | B[d] | | Mpe[d] | | Mpi[d] | | Mme[d] | | Mmi[d] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | calc[e] | fnd[f] | calc[e] | fnd[f] | calc[e] | fnd[f] | calc[e] | fnd[f] | calc[e] | fnd[f] | calc[e] | fnd[f] | calc[e] | fnd[f] | calc[e] | fnd[f] |
| G1 | 8 | 8.0 | 5 | 5.1 | 12 | 12.0 | 3 | 2.9 | 12 | 11.8 | | | 12 | 11.8 | | |
| G2 | 24 | 24.0 | 5 | 5.0 | 36 | 35.7 | 9 | 8.9 | 24 | 23.3 | 12 | 11.7 | 24 | 23.3 | 12 | 11.7 |
| G3 | 56 | 56.0 | 5 | 4.9 | 84 | 84.3 | 21 | 20.5 | 48 | 47.6 | 36 | 35.2 | 48 | 47.6 | 36 | 35.2 |
| G4 | 120 | 120.0 | 5 | 4.9 | 180 | 179.6 | 45 | 43.2 | 96 | 94.7 | 84 | 82.6 | 96 | 94.7 | 84 | 82.9 |
| G3-3 | 180 | 180.0 | | | 270 | 274.4 | 66 | 65.0 | 144 | 144.8 | 126 | 125.1 | 144 | 144.8 | 126 | 125.1 |

[a] Aromatic protons. [b] Allyl protons. [c] Methylene protons. [d] Methyl protons bonded to the B, Mpe, Mpi, Mme, and Mmi type silicon atoms. [e] Calculated integration. [f] Found integration.

**Scheme III**



**Scheme IV**

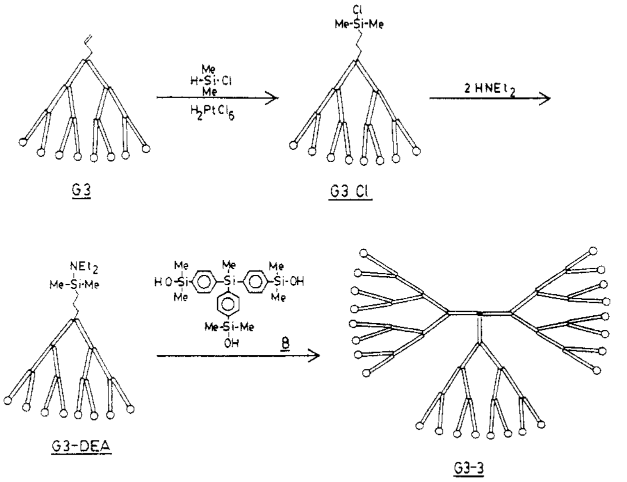
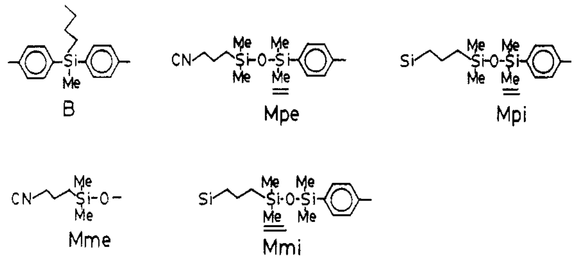


**Chart I**



was distilled to afford pure allyldichloromethylsilane (2). Yield: 37.2 g (48%). Bp: 113–119 °C. $^1$H NMR (CDCl$_3$, ppm): 6.15–5.50 (m, 1 H), 5.32–4.95 (m, 2 H), 2.10 (d, 2 H), 0.8 (s, 3 H).

**(4-Bromophenyl)(diethylamino)dimethylsilane (3).** To a solution of 64.5 g (0.5 mol) of dichlorodimethylsilane in 1.2 L of dry ether was added dropwise a solution of 73.1 g (1.0 mol) of diethylamine in 200 mL of ether at 20 °C. After the solution was stirred for 1 h, the precipitated diethylamine hydrochloride was filtered under nitrogen. The solvent was evaporated, and the residue was distilled in vacuo to afford pure chloro(diethylamino)-dimethylsilane (4). Yield: 60.2 g (80%). Bp: 45–48 °C (16 mmHg). $^1$H NMR (CDCl$_3$, ppm): 2.74 (q, 4 H), 0.88 (t, 6 H), 0.45 (s, 6 H).

A solution of (4-bromophenyl)lithium that was prepared from 103.8 g (0.44 mol) of *p*-dibromobenzene and 275 mL of butyllithium (1.6 N hexane solution) in 500 mL of ether was added to a solution of 60.2 g (0.4 mol) of 4 in 150 mL of ether at 20 °C, and the mixture was stirred for 5 h. The precipitate was filtered under nitrogen. After evaporation of the solvent, pure (4-bromophenyl)(diethylamino)dimethylsilane (3) was distilled in vacuo. Yield: 89.2 g (78%). Bp: 80–85 °C (0.5 mmHg). $^1$H NMR (CDCl$_3$, ppm): 7.60–7.40 (m, 4 H), 2.74 (q, 4 H), 1.02 (t, 6 H), 0.45 (s, 6 H). $^{13}$C NMR (CDCl$_3$, ppm): 139.5, 136.0, 135.0, 130.8, 40.4, 16.2, −1.0.

**Allylbis[4-[(diethylamino)dimethylsilyl]phenyl]methylsilane (5).** A solution of [4-[(diethylamino)dimethylsilyl]phenyl]-lithium that was prepared from 85.8 g (0.30 mol) of 3 and 190 mL of butyllithium (1.6 N hexane solution) in 200 mL of ether was added to a solution of 23.3 g (0.15 mol) of 2 in 50 mL of ether at 20 °C, and the mixture was stirred for 5 h. The precipitate was filtered under nitrogen. After evaporation of the solvent, pure allylbis[4-[(diethylamino)dimethylsilyl]phenyl]methylsilane (5) was distilled in vacuo. Yield: 43.2 g (58%). Bp: 195–205 °C (0.5 mmHg). $^1$H NMR (CDCl$_3$, ppm): 7.60–7.40 (m, 8 H),

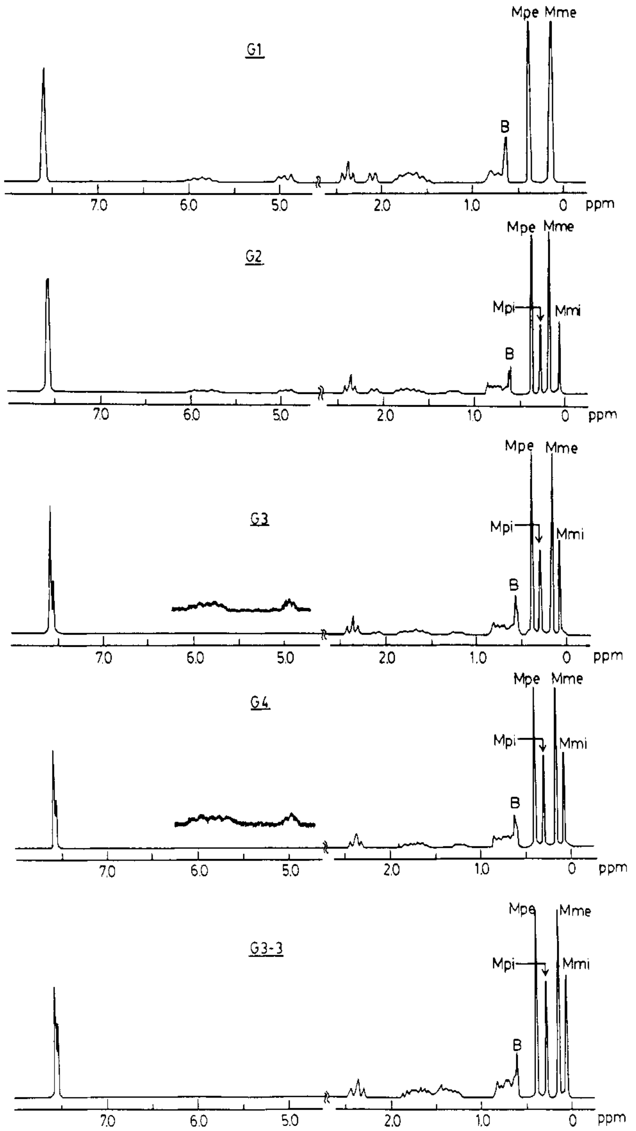


**Figure 2.** $^1$H NMR spectra of G1, G2, G3, G4, and G3-3 measured in $CDCl_3$.

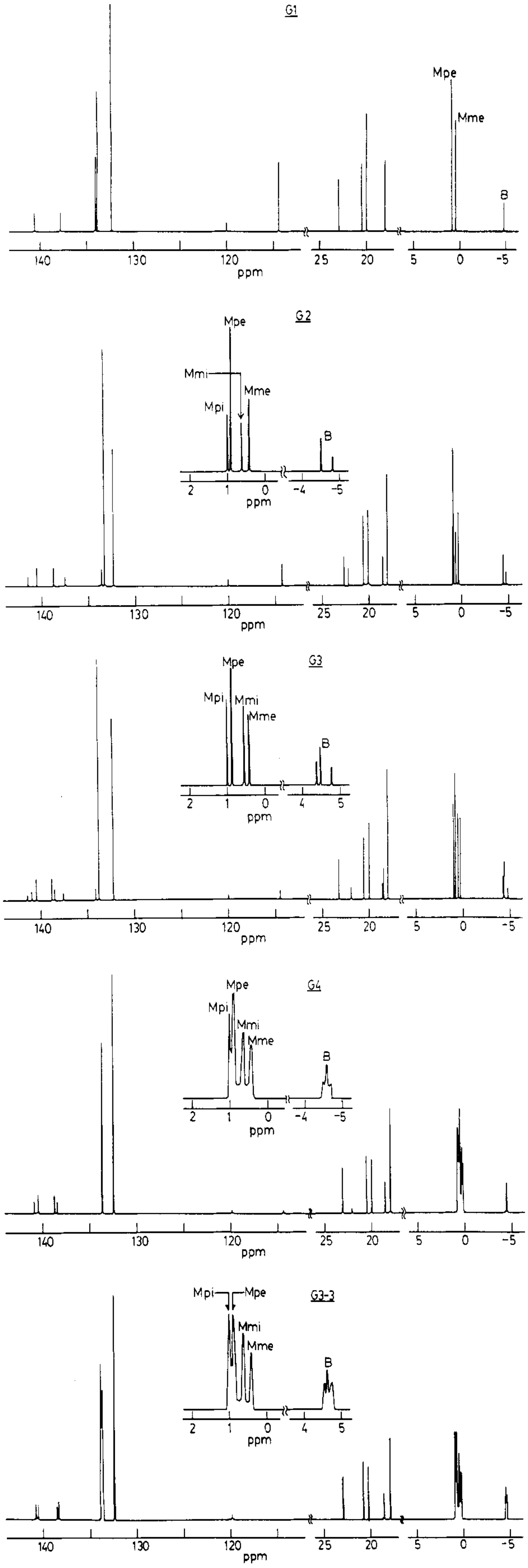


**Figure 3.** $^{13}$C NMR spectra of G1, G2, G3, G4, and G3-3 measured in $CDCl_3$.

6.15–5.50 (m, 1 H), 5.32–4.95 (m, 2 H), 2.74 (q, 8 H), 2.10 (d, 2 H), 1.02 (t, 12 H), 0.55 (s, 3 H), 0.30 (s, 12 H). $^{13}$C NMR ($CDCl_3$, ppm): 136.8, 134.5, 133.5, 133.0, 132.4, 114.2, 40.4, 22.1, 16.2, −1.0, −5.0.

**Allylbis[4-(ethoxydimethylsilyl)phenyl]methylsilane (6).** In a flask, 43.2 g (0.087 mol) of **5** was added to 50 mL of ethanol at 20 °C, and the solution was stirred for 0.5 h. After evaporation of the solvent, pure allylbis[4-(ethoxydimethylsilyl)phenyl]methylsilane (**6**) was distilled in vacuo. Yield: 36.9 g (96%). Bp: 185–195 °C (0.5 mmHg). $^1$H NMR ($CDCl_3$, ppm): 7.60–7.40 (m, 8 H), 6.15–5.50 (m, 1 H), 5.32–4.95 (m, 2 H), 3.72 (q, 4 H), 2.10 (d, 2 H), 1.20 (t, 6 H), 0.55 (s, 3 H), 0.30 (s, 12 H). $^{13}$C NMR ($CDCl_3$, ppm): 136.8, 134.5, 133.5, 133.0, 132.4, 114.2, 68.9, 18.2, −1.0, −5.0.

**Allylbis[4-(hydroxydimethylsilyl)phenyl]methylsilane (1).** **1** was prepared in reference to the synthesis of 1,3,5-tris(hydroxydimethylsilyl)benzene.[10] In a flask, 33.2 g (0.075 mol) of **6** was added to the ethanol solution of sodium ethoxide that was prepared from 105 mL of dry ethanol and a piece of sodium, and the mixture was stirred for 5 min. Then, the mixture was added to the solution prepared from 9.8 g of sodium hydroxide, 8.4 mL of water, and 59.5 mL of methanol at 20 °C. After the solution was stirred for 1.25 h, the mixture was poured into the saturated aqueous solution of $KH_2PO_4$ (87.2 g). The precipitate was isolated and the aqueous layer was extracted twice with 100 mL of ether. The combined extract was dried with anhydrous magnesium sulfate. After evaporation of the solvent, allylbis[4-(hydroxydimethylsilyl)phenyl]methylsilane (**1**) was obtained as crystals, which were recrystallized from hexane. Yield: 17.2 g (59.3%). Mp: 97.5–99.0 °C. $^1$H NMR ($CDCl_3$, ppm): 7.60–7.40 (m, 8 H), 6.15–5.50 (m, 1 H), 5.32–4.95 (m, 2 H), 2.80 (s, 2 H), 0.55 (s, 3 H), 0.30 (s, 12 H). $^{13}$C NMR ($CDCl_3$, ppm): 136.8, 134.5, 133.5, 133.0, 132.4, 114.2, −1.0, −5.0.

**Table II**
**Molecular Weights and Related Values of Starburst Polysiloxanes**

| polymer | $F_w$[a] | $M_n$[b] | $M_w/M_n$ | $[\eta]$[c] |
|---|---|---|---|---|
| G1 | 636 | 1166 | 1.00 | 0.026 |
| G2 | 1774 | 2107 | 1.01 | 0.034 |
| G3 | 4050 | 4384 | 1.02 | 0.051 |
| G4 | 8602 | 10069 | 1.04 | 0.084 |
| G3-3 | 12820 | 100812 | 1.05 | 0.092 |

[a] Formula weight. [b] Measured by GPC based on standard polystyrene. [c] Intrinsic viscosity.

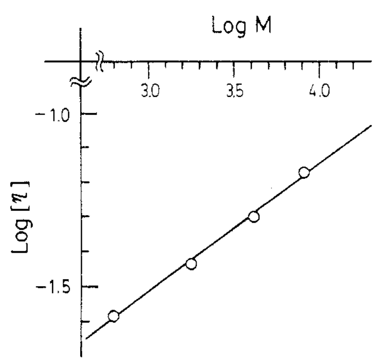


**Figure 4.** Relationship between intrinsic viscosity $\eta$ measured in THF and molecular weight $M$ (formula weight).

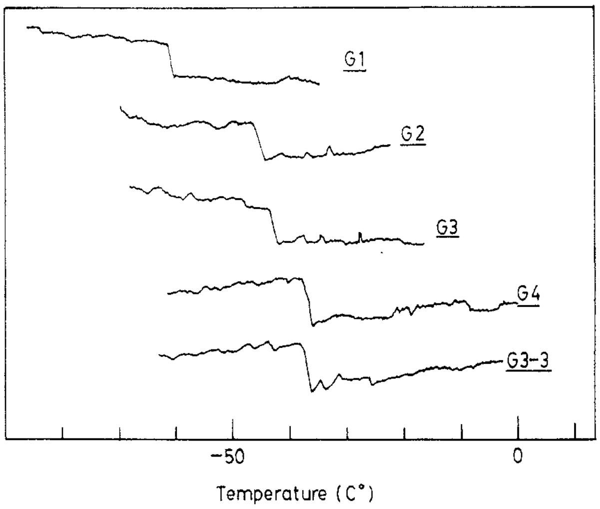


**Figure 5.** DSC curves of starburst dendrons.

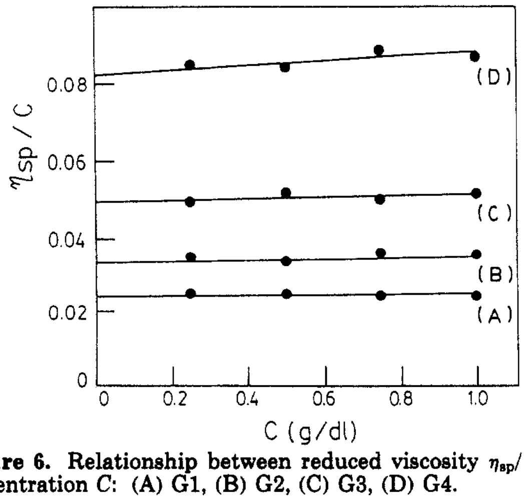


**Figure 6.** Relationship between reduced viscosity $\eta_{sp}/C$ and concentration $C$: (A) G1, (B) G2, (C) G3, (D) G4.

**Tris[4-(hydroxydimethylsilyl)phenyl]methylsilane (8).** Tris[4-(hydroxydimethylsilyl)phenyl]methylsilane (8) was synthesized in a similar manner to 1. A solution of [4-[(diethylamino)dimethylsilyl]phenyl]lithium that was prepared from 17.2 g (0.06 mol) of (4-bromophenyl)(diethylamino)dimethylsilane (3) and 38 mL of butyllithium (1.6 N hexane solution) in 40 mL of ether was added to a solution of 3.0 g (0.02 mol) of trichloromethylsilane in 20 mL of ether at 20 °C, and the mixture was stirred for 5 h. The precipitate was filtered under nitrogen. After evaporation of the solvent, pure tris[4-[(diethylamino)dimethylsilyl]phenyl]methylsilane was distilled in vacuo (Kugelrohr). Yield: 9.5 g (72%). Bp: 260–265 °C (0.5 mmHg). $^1$H NMR ($CDCl_3$, ppm): 7.60–7.40 (m, 12 H), 2.74 (q, 12 H), 1.02 (t, 18 H), 0.93 (s, 3 H), 0.42 (s, 18 H). $^{13}$C NMR ($CDCl_3$, ppm): 142.0, 136.7, 134.6, 133.3, 40.4, 16.1, -1.0, -3.2.

In a flask, 9.5 g (0.014 mol) of tris[4-[(diethylamino)dimethylsilyl]phenyl]methylsilane was added to 30 mL of ethanol at 20 °C, and the solution was stirred for 0.5 h. After evaporation of the solvent, pure tris[4-(ethoxydimethylsilyl)phenyl]methylsilane was distilled in vacuo (Kugelrohr). Yield: 8.0 g (98%). Bp: 240–245 °C (0.5 mmHg), $^1$H NMR ($CDCl_3$, ppm): 7.60–7.40 (m, 12 H), 4.72 (q, 6 H), 1.20 (t, 9 H), 1.19 (s, 3 H), 0.35 (s, 18 H). $^{13}$C NMR ($CDCl_3$, ppm): 139.4, 137.5, 134.7, 132.9, 58.9, 18.6, -1.6, -3.4.

In a flask, 8.0 g (0.014 mmol) of tris[4-(ethoxydimethylsilyl)phenyl]methylsilane was added to the ethanol solution of sodium ethoxide that was prepared from 30 mL of dry ethanol and a piece of sodium, and the mixture was stirred for 5 min. Then, the mixture was added to the solution prepared from 2.8 g of sodium hydroxide, 2.4 mL of water, and 17.0 mL of methanol at 20 °C. After the solution was stirred for 1.25 h, the mixture was poured into the saturated aqueous solution of $KH_2PO_4$ (24.9 g). The precipitate was isolated, and the aqueous layer was extracted twice with 100 mL of ether. The combined extract was dried with anhydrous magnesium sulfate. After evaporation of the solvent, tris[4-(dimethylhydroxysilyl)phenyl]methylsilane (8) was obtained as crystals which were recrystallized from benzene. Yield: 4.5 g (65%). Mp: 186–187.5 °C. $^1$H NMR (DMSO-$d_6$, ppm): 7.70–7.30 (m, 12 H), 5.90 (s, 3 H), 0.80 (s, 3 H), 0.30 (s, 18 H). $^{13}$C NMR (DMSO-$d_6$, ppm): 143.2, 137.7, 135.2, 133.7, 1.8, -2.6.

**Chloro(3-cyanopropyl)dimethylsilane (G0-Cl).** A mixture of allyl cyanide (26.8 g, 0.4 mol), chloroplatinic acid (0.02 g), dimethylchlorosilane (37.8 g, 0.4 mol), and THF (40 mL) was charged into an ampule of 200-mL capacity. After freezing the mixture with liquid nitrogen, the ampule was sealed in vacuo. Then, the mixture was stirred at 60 °C for 6 h. The reaction mixture was cooled, and after removal of THF by distillation, the residue was distilled in vacuo to afford pure G0-Cl. Yield: 68.2 g (92%). Bp: 92–96 °C (18 mmHg). $^1$H NMR ($CDCl_3$, ppm): 2.38 (t, 2 H), 1.75 (m, 2 H), 0.90 (m, 2 H), 0.40 (s, 6 H). $^{13}$C NMR ($CDCl_3$, ppm): 119.2, 19.9, 19.6, 18.0. 1.4.

**First-Generation Dendron (G1).** To a solution of 25.8 g (0.16 mol) of G0-Cl in 200 mL of THF was added dropwise 23.4 g (0.32 mol) of diethylamine at 20 °C. The solution was stirred at room temperature for 10 min. Then, 30.9 g (0.08 mol) of building block 1 was added, and the mixture was stirred at 60 °C for 8 h. The mixture was diluted with 150 mL of ether and washed with 200 mL of water. After the organic solution was dried over anhydrous magnesium sulfate, the solvent was evaporated. The residue was distilled in vacuo (Kugelrohr) to afford pure G1. Yield: 40.7 g (80%). Bp: 185–190 °C (0.5 mmHg). $^1$H and $^{13}$C NMR spectra are shown in Figures 2 and 3, respectively.

**G1-Cl.** G1-Cl was prepared by the same procedure as that for the synthesis of G0-Cl starting from 25.4 g (0.04 mol) of G1. After evaporation of the solvent, the residue was distilled in vacuo (Kugelrohr) to afford pure G1-Cl. Yield: 27.8 g (95%). Bp: 270–275 °C (0.5 mmHg). $^1$H NMR ($CDCl_3$, ppm): 7.58 (m, 8 H), 2.42 (t, 4 H), 1.73 (m, 6 H), 1.25 (m, 2 H), 1.00 (m, 2 H), 0.78 (m, 4 H), 0.62 (s, 3 H), 0.42 (s, 6 H), 0.38 (s, 12 H), 0.15 (s, 12 H). $^{13}$C NMR ($CDCl_3$, ppm): 140.5, 138.5, 133.7, 132.3, 120.0, 23.4, 20.6, 20.2, 18.1, 17.9, 17.8, 2.0, 0.9, 0.4, -4.4.

**Second-Generation Dendron (G2).** G2 was prepared by the same procedure as that for the synthesis of G1 starting from 27.8 g (0.052 mol) of G1-Cl. Pure G2 was obtained by silica gel column chromatography eluted by $CHCl_3$. Yield: 22.0 g (48%). $^1$H and $^{13}$C NMR spectra are shown in Figures 2 and 3, respectively.

**Third-Generation Dendron (G3).** G3 was prepared by the same procedure as that for the synthesis of G1 starting from 23.0

g (0.013 mol) of G2. The completion of the hydrosilylation was indicated by the disappearance of olefin signals in the $^1$H and $^{13}$C NMR spectra of crude G2-Cl. Pure G3 was obtained by silica gel column chromatography eluted by methylene chloride. Yield: 10.8 g (41%). $^1$H and $^{13}$C NMR spectra are shown in Figures 2 and 3, respectively.

**Fourth-Generation Dendron (G4).** G2 was prepared by the same procedure as that for the synthesis of G1 starting from 8.10 g (2.0 mmol) of G3. The completion of the hydrosilylation was indicated by the disappearance of olefin signals in the $^1$H and $^{13}$C NMR spectra of crude G3-Cl. Pure G4 was obtained by silica gel column chromatography eluted by methylene chloride. Yield: 1.50 g (17%). $^1$H and $^{13}$C NMR spectra are shown in Figures 2 and 3, respectively.

**G3-3.** G3-3 was prepared by the same procedure as that for the synthesis of G1 starting from 7.29 g (1.8 mmol) of G3. Pure G3-3 was obtained by silica gel column chromatography eluted by methylene chloride. Yield: 0.75 g (9.7%). $^1$H and $^{13}$C NMR spectra are shown in Figures 2 and 3, respectively.

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