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Synthesis and Characterization of New Polysiloxane Starburst Polymers

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ABSTRACT: New, highly branched polysiloxane starburst polymers were synthesized starting from tris[(phenyldimethylsiloxy)dimethylsiloxy]methylsilane and bis[(phenyldimethylsiloxy)methylsiloxy]dimethylsilanol as the initiator core (G0-Ph) and the building block, respectively. In this case, the phenylsilane moiety was a synthon of *N*,*N*-diethylaminosilane, which was a suitable electrophilic silicon species. The phenylsilane of G0-Ph was converted to the (*N*,*N*-diethylamino)silane (G0-DEA) via the corresponding bromosilane (G0-Br) generated by the reaction of G0-Ph with bromine. Next, the silanol of the building block was reacted with the aminosilane of G0-DEA, yielding the first generation polymer (G1-Ph), which contained twice the amount of phenylsilyl groups in the exterior layer than did G0-Ph. The higher generation polymers could be builtup by repeating the same reactions. Thus, the third generation polymer (G3-Ph) possessed 24 phenylsilyl groups. G0-Ph and G1-Ph were purified by vacuum distillation, whereas G2-Ph and G3-Ph were purified by preparative gel permeation chromatography (GPC). The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of all the starburst polymers were consistent with the proposed structures. The Mark–Houwink constants K and α, calculated from the relationship between the molecular weight and intrinsic viscosity of the polymers, were found to be 4.7×10^{-3} and 0.21, respectively. The molecular weight of the polymers of all generations measured by GPC using polystyrene standards was proportional to their size based on the Corey–Pauling–Koltun (CPK) model.

Introduction

Starburst polymers are constructed from various initiator cores, upon which concentric branched layers are builtup with geometric processes. They allow precision control of the molecular size as well as disposition of desired functionalities and are expected to be applied as a microsphere that consists of one molecule. Tomalia and co-workers[2] showed that "cascade synthesis", which consisted of the stepwise mathematical growth of the branches to yield the multibranched macromolecules, was useful for the preparation of starburst "dendrimers".[2] For example, they prepared starburst polyamido–amine dendrimers[3] starting from ammonia as the initiator core, followed by the Michael addition of the core to methyl acrylate, and then amidation with ethylenediamine, yielding the zero generation compound (G0). Next, G0 was reacted with methyl acrylate through the Michael reaction, and the subsequent amidation with ethylenediamine, giving the first generation molecule (G1) possessing six amino functions at the exterior layer. When this procedure was repeated, the starburst dendrimer of the tenth generation (G10) was obtained, which had a molecular weight of 700 091 with 3072 amine groups at the exterior layer. Another example of the starburst dendrimers was demonstrated in the polyether system, where the starburst polymers were synthesized by combination of the Williamson either synthesis and the protection–deprotection reaction of bicyclic orthoesters.[3] Newkome and his group also independently reported the synthesis of the multiarmed polyethers named "arborols", where the exterior hydroxyl groups were converted to tosylates, and then the tosylates were reacted with the sodium salt of tris(ethoxycarbonyl)methane to afford a new generation polymer.[5] The exterior hydroxyl groups were generated by the reduction of the esters. Starburst polysiloxanes were reported by Rebrov et al.,[6] and very recently by Masamune and his co-workers.[7] In addition, Frechet presented a concept of convergent approach to prepare dendritic polyethers.[8]

In this paper, we describe the synthesis of new highly branched starburst polymers consisting of polysiloxane units. A siloxane bond is generally formed by the reaction of a compound having electrophilic silicon species (Si$^+$) with a nucleophilic silanol. Since the building block in the present work has both silanol and Si$^+$ species, one of the functions must be protected to avoid self-condensation. Protection of the Si$^+$ was selected instead of protection of the silanol in the present work. The synthetic strategy is shown in Scheme I. The reaction started from the core possessing a synthon of Si$^+$ such as halosilane, alkoxysilane, and aminosilane (the masked Si$^+$ equivalents, which are unreactive with nucleophiles). Next, the building block having both Si$^+$ synthon and silanol was reacted with the

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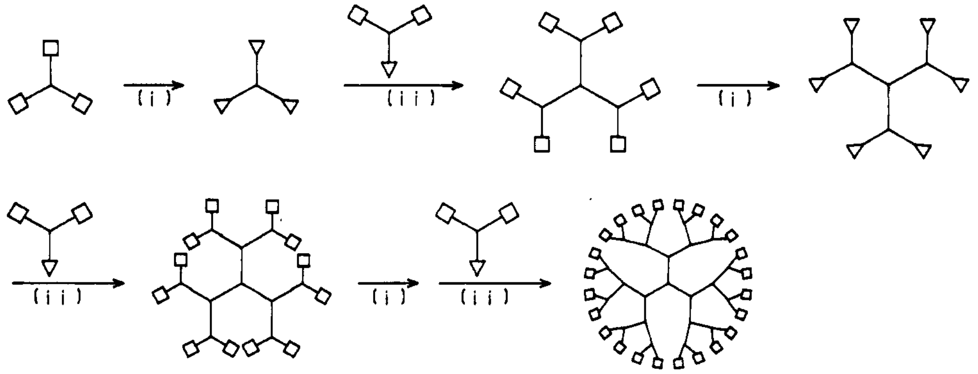
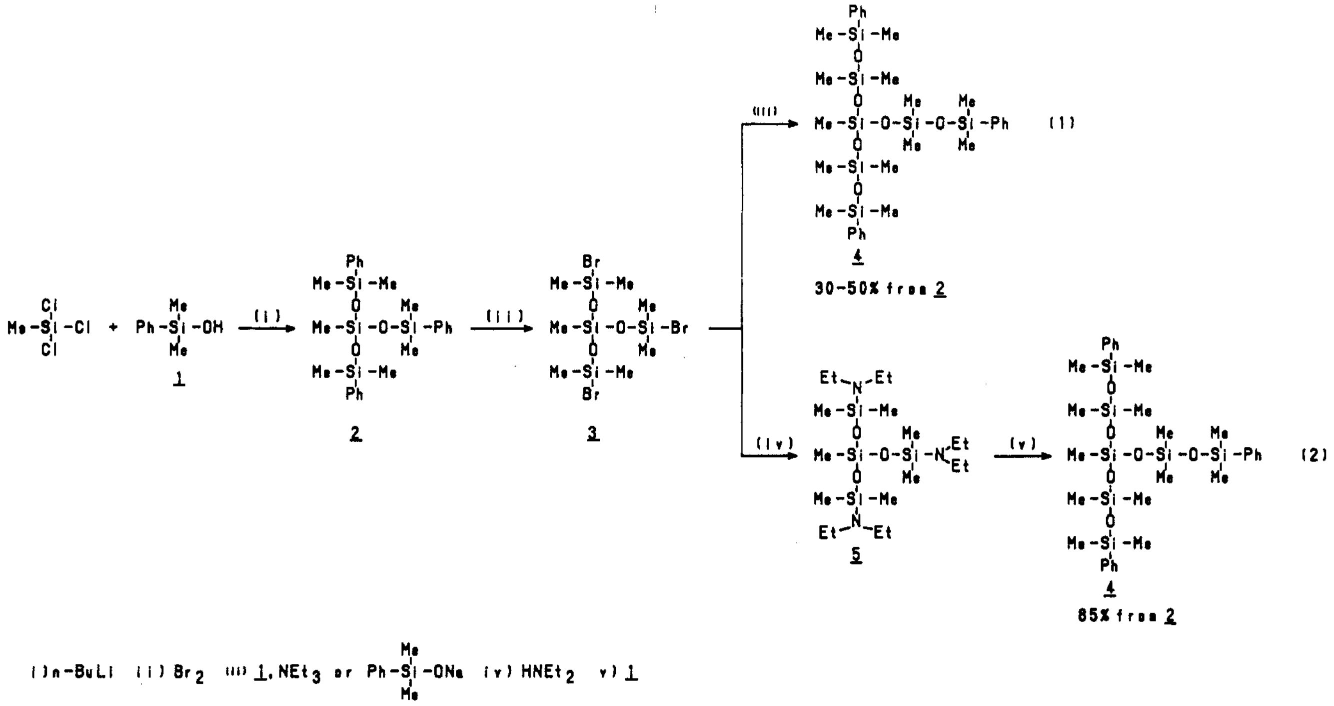
Scheme I



Scheme II



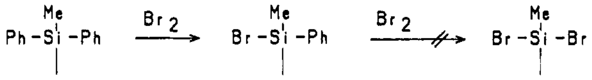
core leading to the formation of a siloxane bond. The exterior Si$^+$ units were again generated after the formation of the siloxane bond and then reacted with the silanol moiety of the building block. The polysiloxane starburst polymers were synthesized by repeating these reactions.

Results and Discussion

Siloxane-Forming Reaction. There are several synthons of Si$^+$ [9] such as ethoxycarbonylmethylsilanes,[10] allylsilanes,[11] and phenylsilanes,[12] which are converted to halosilanes by the reaction with hydrogen halides, halogens, or acyl halides. For the generation of halosilanes from the synthons, the combination of phenylsilane and bromine was selected in this study.

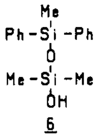
Typical Si$^+$ species for siloxane formation would be halosilanes and aminosilanes.[13] The reactivity of bromosilane and aminosilane was examined as shown in eqs 1 and 2 of Scheme II. The reaction of bromosilane 3, generated from phenylsiloxane 2 by treatment with bromine, with dimethylphenylsilanol (1) in the presence of triethylamine or the sodium siloxide of 1 afforded one siloxy unit extended phenylsiloxane 4 in a low yield of 30–50% (eq 1). On the other hand, compound 4 was obtained in 85% yield from (*N,N*-diethylamino)silane 5, which was quantitatively prepared by successive treatment of 2 with bromine and diethylamine (eq 2). Thus, (*N,N*-diethylamino)silanes were found to be suitable Si$^+$ species in the siloxane-forming reaction.

Scheme III



Selection of Initiator Core and Building Block. Tris[(phenyldimethylsiloxy)dimethylsiloxy]methylsilane (4) was employed as the initiator core (G0-Ph) having three phenylsilane-terminated disiloxane branches, which can minimize the steric hindrance in further reactions. Starting from methyltrichlorosilane, G0-Ph 4 was synthesized in four steps in 66% overall yield as shown in eq 2.

The building block required for the further reactions should be the compounds having one silanol and two phenylsilane units such as 6–8. Diphenylsilane 6 could not be converted to the desired dibromosilane by treatment with bromine as shown in Scheme III, because the electron density of the silicon atom probably was decreased drastically by the electron-withdrawing effect of the bromine atom, which was introduced by the first bromi-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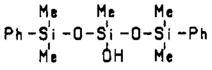
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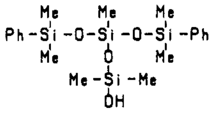
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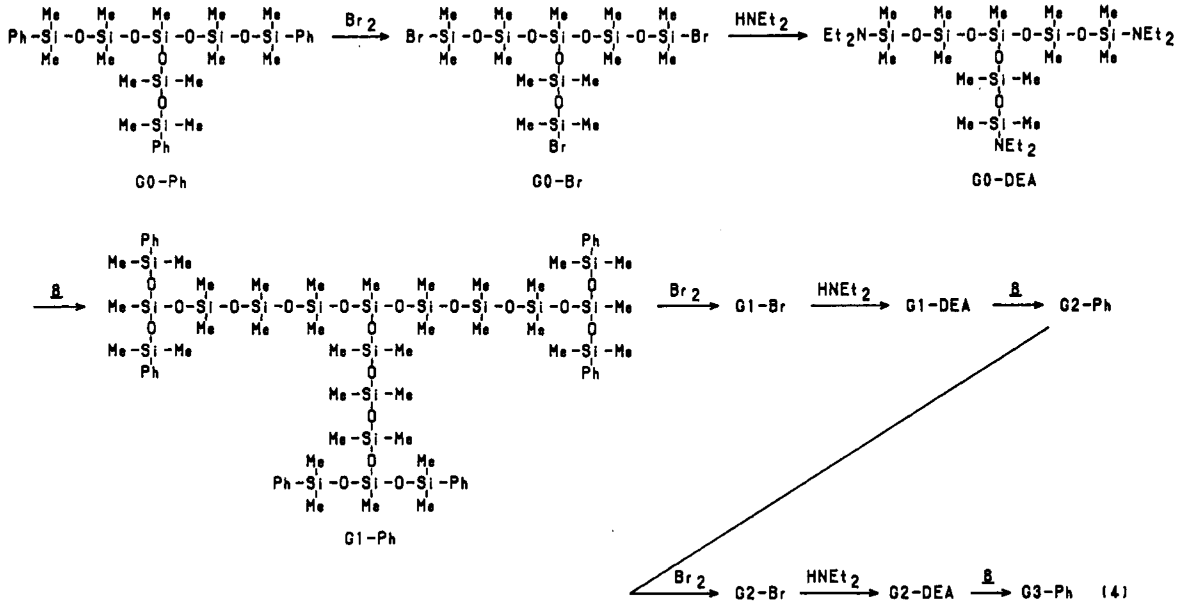
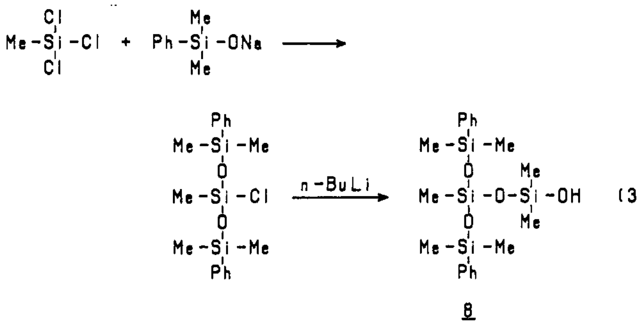
Scheme IV



nation of the diphenylsilane. Primary silanols such as **6** and **8** must be more reactive than secondary silanols such as **7** because of the steric hindrance around silanol groups. Thus, [bis(phenyldimethylsiloxy)methylsiloxy]dimethylsilanol (**8**) was selected to be the best silanol for the building block. Building block **8** was prepared as shown in eq 3 in 25% overall yield.



Synthesis of Starburst Polymers. General synthetic procedure for the starburst polymers is shown in Scheme IV (eq 4). First, G0-Ph **4** was treated with excess bromine to generate bromosilane **9** (G0-Br). The unreacted bromine was removed by bubbling ethylene gas into the reaction mixture. Diethylamine was then added to this solution in order to obtain (*N*,*N*-diethylamino)silane **10** (G0-DEA). Attempts to isolate **9** and **10** failed, because these Si^+ compounds reacted with the surface of the glassware when they were concentrated in solution. The first generation polymer (G1-Ph) was obtained by the reaction of building block **8** with G0-DEA in carbon tetrachloride. Thus, a series of bromination, amination, and reaction with building block **8** was repeated twice more without isolation of both bromosilanes and aminosilanes to prepare the second and third generation polymers (G2-Ph and G3-Ph). All starburst polymers G1-Ph, G2-Ph, and G3-Ph were obtained as colorless oils, and the yields were 75%, 48%, and 32%, respectively. Core **4** (G0-Ph) and G1-Ph were purified by vacuum distillation, whereas pure G2-Ph and G3-Ph were isolated by preparative gel permeation chromatography (GPC). Although the crude G2-Ph showed a weight- to number-average molecular weight (M_w/M_n) of 1.68 due to the presence of a small amount of higher molecular weight impurities, as shown in Figure 1, the ratio was markedly reduced to 1.06 after purification, which meant that G2-Ph had a monodisperse molecular weight distribution. The behavior of the molecular weight distribution of G3-Ph was almost the same as that of G2-Ph. The higher molecular weight impurities might be produced by self-coupling reaction of G*M*-Br and/or G*M*-DEA (*M* is the generation number) by the action of a small amount of water in the solvent.

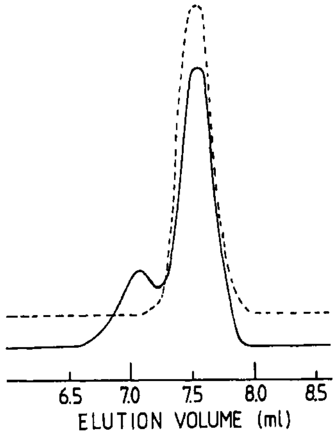
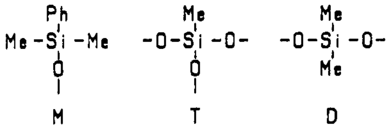


Figure 1. GPC curves of G2-Ph. Solid line: before purification by preparative GPC. Dotted line: after purification by preparative GPC.

Chart I



NMR Studies of Starburst Polymers. As illustrated in Chart I, the present starburst polymers had three different types of silicon atoms, which are located at the most exterior layer connected with phenyl groups (M type), at the branching point connected with three oxygen atoms (T type), and at the center of the chain connected with two oxygen atoms (D type).

The ^1H NMR spectra are shown in Figure 2. Three kinds of protons, i.e., aromatic protons, methyl protons bonded to the M-type silicon atoms, and methyl protons bonded to the D- and T-type silicon atoms were observed at 7.2–7.6, 0.3–0.4, and 0.05–0.15 ppm, respectively. The ratio of these protons agreed with the calculated values as shown in Table I. The fact that the peaks of the methyl

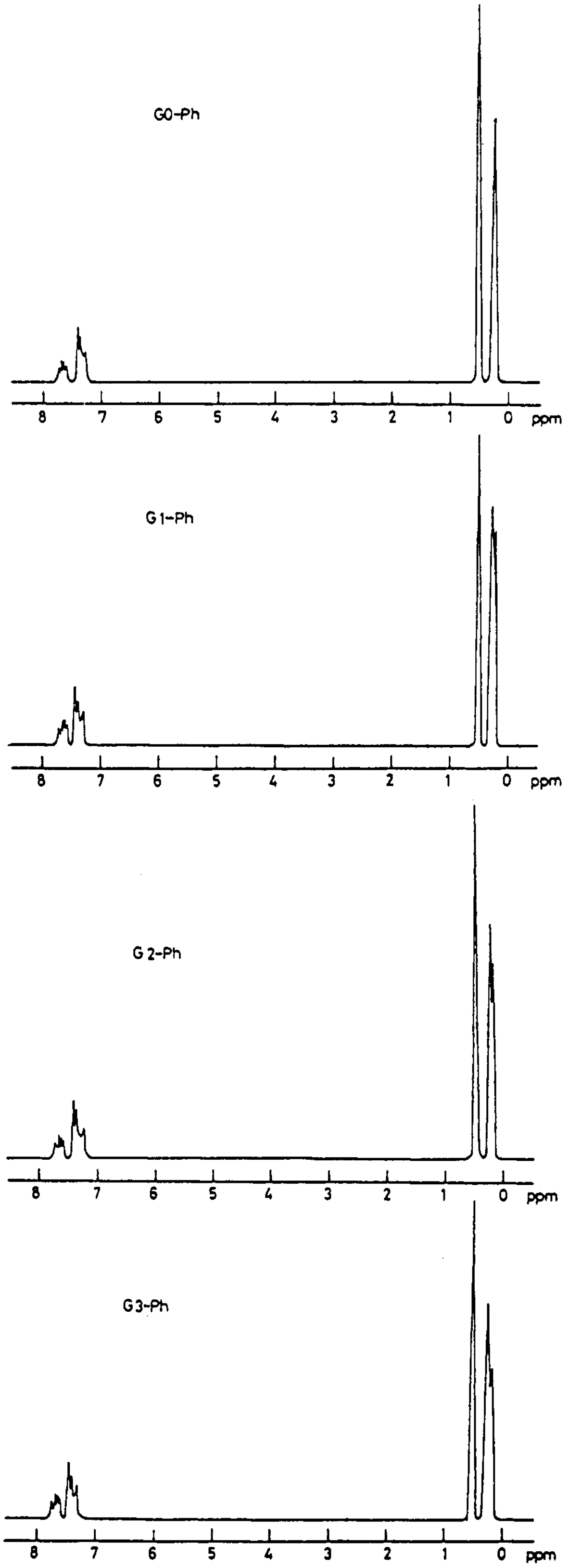


Figure 2. ^{1}H NMR spectra of G0-Ph, G1-Ph, G2-Ph, and G3-Ph measured in $CDCl_3$.

protons bonded to the M-type silicon atoms were observed as a singlet peak in G0-Ph as well as all the higher generation polymers suggested that the present starburst polymers had the proposed structures.

In ^{13}C NMR spectra (Figure 3), three kinds of methyl carbons, attached to the M-, D-, and T-type silicon atoms could be distinguished. These carbons were clearly separated in G0-Ph and G1-Ph, but were not clear in G2-Ph and G3-Ph. The peak of the methyl carbon of M-type

Table I
Ratio of Integration in ^{1}H NMR Spectra of Starburst Polysiloxanes

	aromatic[a]		M[b]		D + T[b]	
polymer	calc[c]	fnd[d]	calc[c]	fnd[d]	calc[c]	fnd[d]
G0-Ph	1	1	1.2	1.21	1.4	1.39
G1-Ph	1	1	1.2	1.16	2.2	2.23
G2-Ph	1	1	1.2	1.19	2.6	2.62
G3-Ph	1	1	1.2	1.22	2.8	2.82

[a] Aromatic protons. [b] Methyl protons bonded to the M-, D-, and T-type silicon atoms. [c] Calculated ratio of integration. [d] Found ratio of integration.

Table II
Ratio of Number of Signals in ^{29}Si NMR Spectra of Starburst Polysiloxanes

	M[a]		D[a]		T[a]	
polymer	calc[b]	fnd[c]	calc[b]	fnd[c]	calc[b]	fnd[c]
G0-Ph	1	1	1	1	1	1
G1-Ph	1	1	3	3	2	2
G2-Ph	1	1	5	mult[d]	3	3
G3-Ph	1	1	7	mult[d]	4	4

[a] Number of signals of M-, D-, and T-type silicon atoms. [b] Calculated number. [c] Found number. [d] Duplicated multiplet signal.

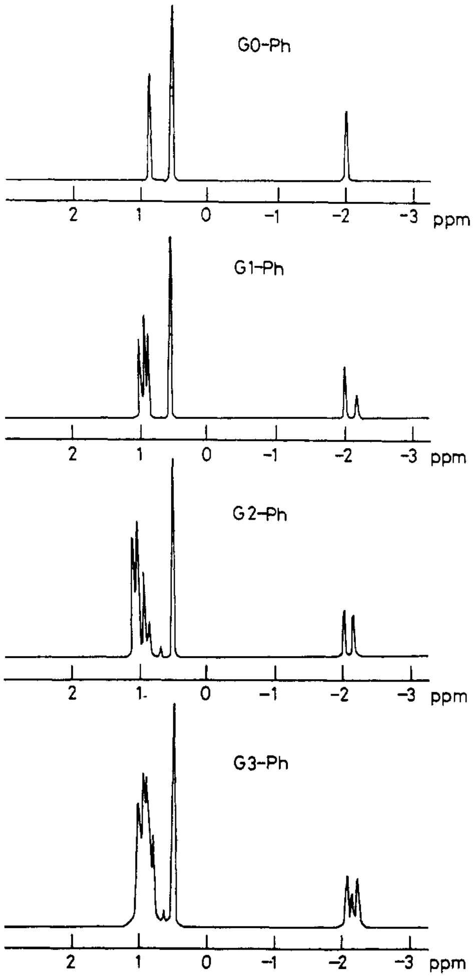


Figure 3. ^{13}C NMR spectra of G0-Ph, G1-Ph, G2-Ph, and G3-Ph measured in $CDCl_3$.

silicons observed at 0.6 ppm was a sharp singlet, and that implied high purity of these polymers.

The behavior in the ^{29}Si NMR spectra, shown in Figure 4, was almost the same as that in the ^{13}C NMR spectra. The peaks of the M-, D-, and T-type silicons were clearly separated, with reasonable chemical shifts. Table II shows the number of signals corresponding to M-, D-, and T-type

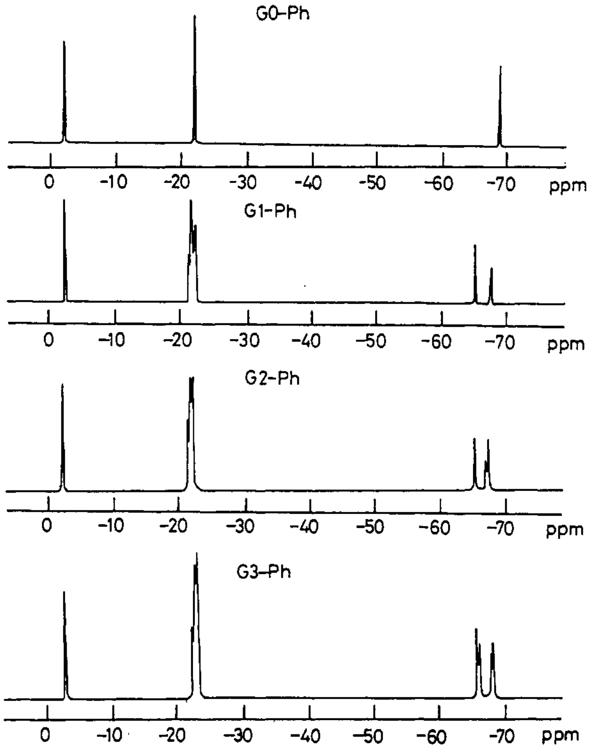


Figure 4. ^{29}Si NMR spectra of G0-Ph, G1-Ph, G2-Ph, and G3-Ph measured in $CDCl_3$.

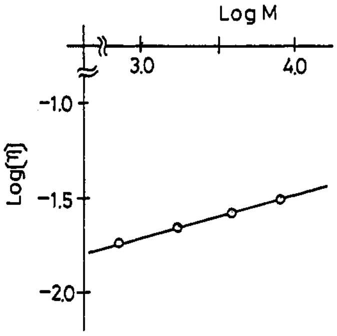


Figure 5. Relationship between intrinsic viscosity [η] measured in THF and molecular weight M (formula weight).

silicons considering the circumstance of each silicon atoms. Although the signal numbers of D-type silicons were not unclear because of their duplicated multiplet signals in G2-Ph and G3-Ph, the signal numbers of M and T were in good agreement with calculated values. The M-type silicons in the exterior layer were also observed as a sharp singlet at −2 ppm.

Characterization of Starburst Polymers. Figure 5 shows the relationship between the intrinsic viscosity and the calculated molecular weight (formula weight, F_w). The Mark–Houwink constants[14] K and α (eq 5) of the present

$$[\eta] = KM^{\alpha} \tag{5}$$

starburst polymers were calculated from this curve to be 4.7×10^{-3} and 0.21, respectively. The α values of 0.21 indicated that these polymers had a spherical structure.

The molecular weights and their distributions of G0-Ph, G1-Ph, G2-Ph, and G3-Ph, measured by GPC based on standard polystyrene, and the diameters (r) measured on the Corey–Pauling–Koltun (CPK) molecular model of the starburst polymers are listed in Table III. The observed M_n was smaller than the F_w except for G0-Ph, where the difference between M_n and F_w increased with increasing size of the polymers.

Table III
Molecular Weights and Related Values of Starburst Polysiloxanes

polymer	F_w[a]	M_n[b]	M_w/M_n	[η][c]	r,[d] nm
G0-Ph	718	878	1.01	0.0190	0.91
G1-Ph	1792	1613	1.06	0.0225	1.34
G2-Ph	3940	2792	1.06	0.0270	1.85
G3-Ph	8324	4819	1.14	0.0315	2.31

[a] Formula weight. [b] Measured by GPC based on standard polystyrene. [c] Intrinsic viscosity. [d] Diameter measured on CPK molecular model.

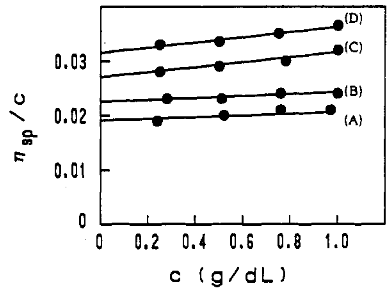


Figure 6. Relationship between reduced viscosity η_{sp}/c and concentration c. (A) G0-Ph, (B) G1-Ph, (C) G2-Ph, (D) G3-Ph.

Conclusion

The starburst polymers based on the siloxane structure could be successfully prepared with the usual siloxane synthetic reaction between an electrophilic silicon species (Si^+) and the nucleophilic silanols, where the phenylsilane acts as the most suitable synthon of Si^+. As the present starburst polymers have phenylsilane units at the exterior position, some functional groups can be easily introduced via the generation of Si^+ species. One of the potential applications of the starburst polymers would be as drug carriers. Because of the harmless nature of polysiloxanes,[16] the present starburst polysiloxanes could be considered as promising drug microcarriers directly injected into the living body.

Experimental Section

^{1}H, ^{13}C, and ^{29}Si NMR spectra and IR spectra were recorded on a JEOL-FX-90Q FT-NMR spectrometer, and a Jasco FT/IR-5000 spectrometer, respectively. GPC was performed with an apparatus using a Shodex analytical column KF8025 and tetrahydrofuran (THF) as the eluent. In the case of preparative GPC, a Shodex GPC H-203 column was used with chloroform eluent.

Measurement of Viscosities. Specific viscosities η_{sp} were measured with the various concentration c by use of an Ostwald-type capillary viscometer in THF at 30 °C. Figure 6 shows the relationship between the concentration c and reduced viscosities $\eta_{red} = \eta_{sp}/c$. Intrinsic viscosities $[\eta] = (\eta_{sp}/c)_{c=0}$ of each generation were obtained from Figure 6 and shown in Table III.

Phenyldimethylsilanol (1). To a solution of 64.5 g (0.5 mol) of dichlorodimethylsilane in 1.2 L of dry ether was added dropwise 73.1 g (1.0 mol) of diethylamine in 200 mL of ether at 20 °C. After the solution was stirred for 1 h, precipitated diethylamine hydrochloride was filtered under nitrogen. The solvent was evaporated, and the residue was distilled in vacuo to afford pure (*N*,*N*-diethylamino)chlorodimethylsilane. Yield: 60.2 g (80%). bp: 48 °C (16 mmHg). ^{1}H NMR ($CDCl_3$, δ ppm): 2.74 (q, 4 H), 0.88 (t, 6 H), 0.45 (s, 6 H).

A solution of phenyllithium that was prepared from 69.8 g (0.44 mol) of bromobenzene and 6.1 g (0.88 mol) of lithium metal in 300 mL of ether was added to a solution of 60.2 g (0.4 mol) of (*N*,*N*-diethylamino)chlorodimethylsilane in 150 mL of ether at 20 °C, and the mixture was stirred for 5 h. The precipitate was filtered under nitrogen. After the solvent was evaporated, pure (*N*,*N*-diethylamino)phenyldimethylsilane was distilled in vacuo. Yield: 74 g (89%). bp: 65 °C (0.5 mmHg). ^{1}H NMR ($CDCl_3$, δ ppm): 7.30 (m, 5 H), 2.81 (q, 4 H), 0.88 (t, 6 H), 0.55 (s, 6 H).

To 400 mL of a 10% aqueous solution of acetic acid was added 72.5 g (0.35 mol) of (*N,N*-diethylamino)phenyldimethylsilane at 20 °C, and the mixture was stirred vigorously for 5 min. The organic layer was separated, and the aqueous layer was extracted twice with 100 mL of ether. The combined extract was washed with 400 mL of 5% aqueous sodium bicarbonate and dried with anhydrous magnesium sulfate. After evaporation of the solvent, dimethylphenylsilanol (1) was distilled in vacuo. Yield: 43 g (80%). bp: 63 °C (0.5 mmHg). ^{1}H NMR ($CDCl_3$, δ ppm): 7.30 (m, 5 H), 2.62 (br s, 1 H), 0.55 (s, 6 H). IR (neat, cm^{-1}): 3239, 3050, 2910, 1429, 1408, 1027, 789, and 700.

Tris(phenyldimethylsiloxy)methylsilane (2). To a solution of lithium phenyldimethylsiloxide that was prepared from 7.6 g (0.05 mol) of silanol 1 in 20 mL of THF and 31.3 mL of butyllithium (1.6 M hexane solution) was added a solution of 1.87 g (0.0125 mol) of methyltrichlorosilane. After the mixture was stirred for 4 h at room temperature, the lithium chloride formed was removed by filtration. The solvent of the filtrate was evaporated, and the residue was distilled in vacuo (Kugelrohr) to afford pure tris(phenyldimethylsiloxy)methylsilane (2). Yield: 5.1 g (82%). bp: 165 °C (0.5 mmHg). ^{1}H NMR ($CDCl_3$, δ ppm): 7.45 (m, 15 H), 0.35 (s, 18 H), 0.10 (s, 3 H). ^{13}C NMR ($CDCl_3$, δ ppm): 133.5, 129.5, 128.0, 0.9, −2.0.

Tris[(phenyldimethylsiloxy)dimethylsiloxy]methylsilane (G0-Ph) (4). To a solution of 5.0 g (0.01 mol) of phenylsiloxane 2 in 10 mL of carbon tetrachloride was added 5 mL of a 3 M solution of bromine in carbon tetrachloride, and the solution was stirred at room temperature for 30 min. Tris(bromodimethylsiloxy)methylsilane (3) was generated in this stage. The reaction vessel was filled with ethylene gas until the color of bromine disappeared. Next, 4.39 g (0.06 mol) of diethylamine was added to the reaction mixture at room temperature, and the mixture was stirred for 30 min to afford tris[(*N,N*-diethylamino)dimethylsiloxy]methylsilane (5). Finally, 6.08 g (0.04 mol) of silanol 1 was added to the solution of 5 at room temperature, and the mixture was stirred at 80 °C for 8 h. The mixture was diluted with 100 mL of ether and washed with 50 mL of water. After the organic solution was dried over anhydrous magnesium sulfate, the solvent was evaporated. Pure core 4 was distilled in vacuo (Kugelrohr) at 188 °C (0.5 mmHg). Yield: 6.01 g (81%). IR (neat, cm^{-1}): 3074, 2964, 1261, 1122, 1040, 799.

[Bis(phenyldimethylsiloxy)methylsiloxy]dimethylsilanol (8). To a solution of 19.7 g (0.13 mol) of methyltrichlorosilane in 150 mL of ether was added dropwise a solution of the sodium salt of silanol 1, which was prepared from 39.5 g (0.26 mol) of 1 and 6.0 g (0.26 mol) of sodium metal in 200 mL of ether. The mixture was stirred at room temperature for 2 h. After the sodium chloride formed was removed by filtration under nitrogen, the ether was evaporated, and the residue was distilled twice by fractional distillation to afford pure bis(phenyldimethylsiloxy)methylchlorosilane. Yield: 19.8 g (40%). bp: 128 °C (0.5 mmHg). ^{1}H NMR ($CDCl_3$, δ ppm): 7.35 (m, 10 H), 0.25 (s, 12 H), 0.20 (s, 3 H).

A solution of 15.6 mL of a 1.6 M solution of butyllithium in hexane was added to 2.3 g (0.025 mol) of dimethylsilanediol[17] in 20 mL of THF at −60 °C. To this solution was added 9.5 g (0.025 mol) of bis(phenyldimethylsiloxy)methylchlorosilane, and the mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with 100 mL of ether and washed with 100 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 building block 8. Yield: 6.8 g (63%). bp: 150 °C (0.5 mmHg). ^{1}H NMR ($CDCl_3$, δ ppm): 7.59 (m, 10 H), 0.45 (s, 12 H), 0.19 (s, 3 H), 0.15 (s, 6 H). ^{13}C NMR ($CDCl_3$, δ ppm): 133.4, 129.5, 128.0, 1.2, 0.9, −2.4. IR (neat, cm^{-1}): 3322, 3074, 2966, 1429, 1259, 1058, 832, 789, 700.

First Generation Polymer (G1-Ph). To a solution of 2.87 g (0.004 mol) of core 4 in 5 mL of carbon tetrachloride was added 6 mL of a 3 M solution of bromine in carbon tetrachloride. The solution was stirred at room temperature for 30 min. The excess bromine was quenched by filling the reaction vessel with ethylene gas. To the colorless solution was added 1.76 g (0.024 mol) of diethylamine dropwise at 20 °C. And then 6.98 g (0.016 mol) of silanol 8 was added and the mixture was stirred at 80 °C for 8 h. The mixture was diluted with 100 mL of ether and washed with 100 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-Ph. Yield: 5.38 g (75%). bp: 348 °C (2 × 10^{-4} mmHg).

Second Generation Polymer (G2-Ph). Second generation polymer, G2-Ph, was prepared by the same procedure as that for the synthesis of G1-Ph starting from 3.58 g (0.002 mol) of G1-Ph. Low molecular weight compounds in the crude product were distilled in vacuo at 330 °C (0.5 mmHg). Pure G2-Ph was obtained by preparative GPC. Yield: 5.85 g (74%) (before purification; M_w/M_n = 1.68) and 3.80 g (48%) (after purification; M_w/M_n = 1.06).

Third Generation Polymer (G3-Ph). Third generation polymer, G3-Ph, was prepared by the same procedure as that for the synthesis of G1-Ph starting from 3.94 g (0.001 mol) of G2-Ph. Purification was done as with G2-Ph. Yield: 6.92 g (84%) (before purification; M_w/M_n = 1.39) and 2.64 g (32%) (after purification; M_w/M_n = 1.14).

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