# Polysilane Dendrimers[1]

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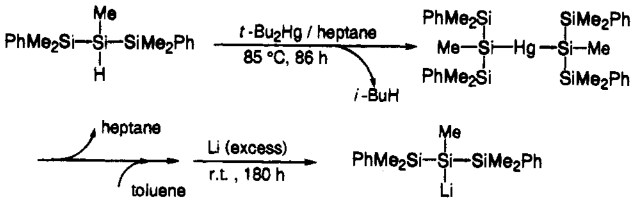
Dendrimers with a regular, three-dimensional, tree-like structure have attracted much attention as well-defined macromolecules.[2] Polysilane dendrimers containing Si atoms connected to three or four other Si atoms should be quite interesting in relation to linear one-dimensional polysilanes.[3,4] Despite several attempts at the synthesis of polysilane dendrimers, the molecular weight distribution and uniformity of branching could not be strictly controlled.[5,6] We wish to report the structurally defined synthesis of polysilane dendrimers up to the second generation with a molecular weight of 1832.9.

2-Lithio-1,3-diphenylpentamethyltrisilane, $PhMe_2SiMeSi(Li)SiMe_2Ph$ (**1a**), was used as a key intermediate for the synthesis of polysilane dendrimers. The lithium reagent **1a** was prepared and isolated as highly inflammable yellow crystals by the reaction of bis(1,3-diphenylpentamethyltrisilanyl)mercury and lithium in 80% yield (Scheme 1).[7,8]

A divergent method for polysilane dendrimer synthesis is shown in Scheme 2. First, $PhMe_2SiCl$ was reacted with silyllithium **1a** in toluene to give quantitatively colorless crystals of **2a** possessing a core and three branching points for a polysilane dendrimer. Then, the resulting **2a** was treated with 3 equiv of trifluoromethanesulfonic acid in dichloromethane followed by the reaction with **1a** in toluene to yield the first generation **3a** in 43% yield as a viscous oil.[9]

**Scheme 1**



**1a**

In order to simplify the NMR spectra, permethyl-substituted polysilane dendrimers were synthesized by use of 2-lithioheptamethyltrisilane, $Me_3SiMeSi(Li)SiMe_3$ (**1b**).[8] Thus, treatment of **3a** with 6 equiv of trifluoromethanesulfonic acid in dichloromethane followed by the reaction with **1b** in hexane/toluene resulted in the formation of the second generation **4** in 29% yield as colorless crystals (Scheme 2). The permethyl-substituted polysilane dendrimer **3b** was also prepared as colorless crystals.[10] It should be pointed out that the reactions in toluene or hexane proceed very cleanly to give the coupling products without any scrambling or redistribution reaction.

Polysilane dendrimers were successfully separated and purified by a gel permeation chromatography instrument equipped with a recycling system. As expected, the $^1H$ and $^{13}C$ NMR spectra of **4** gave eight different proton and carbon signals.[11] The $^{29}Si$ NMR showed seven resonances: the core Si atom at −62.3 (1 Si), the adjacent $SiMe_2$ at −26.7 (3 Si), the next adjacent SiMe at −64.8 (3 Si), the exterior $SiMe_2$ at −30.0 (6 Si), the outermost SiMe at −80.1 (6 Si), and the peripheral $SiMe_3$ at −11.3 (6 Si) and −11.4 ppm (6 Si). Assignments of these $^{29}Si$ resonances were made on the basis of peak intensities. The two methyl groups due to the outermost $SiMe_2$ are diastereotopic: 0.37 and 0.39 ppm for $^1H$ NMR and 1.92 and 2.21 ppm for $^{13}C$ NMR. As a result, two signals of the peripheral $SiMe_3$ can be observed: 0.13 and 0.15 ppm for $^1H$ NMR, 0.93 and 1.02 ppm for $^{13}C$ NMR, and −11.3 and −11.4 ppm for $^{29}Si$ NMR.

No molecular ion peaks appeared in the mass spectrum (DEI and FAB). However, $(M^+ - Me)$ ion peaks were observed in the range of 1813−1824 consistent with the $C_{63}H_{189}Si_{31}$ formula. The dendrimer **4** contains 31 silicon atoms and 30 Si−Si bonds. Its enhanced electronic properties include an extinction coefficient $\epsilon = 9.64 \times 10^4$ at $\lambda_{max} = 279$ nm, which is 2 times larger than that of **3b** ($\lambda_{max} = 269$ nm, $\epsilon = 4.91 \times 10^4$).

The structure of **4** was unambiguously confirmed by X-ray diffraction (Figure 1).[12] There are two independent molecules in the unit cell, and the crystal structure possesses a crystallographic 3-fold axis. The thermal motions associated with each arm increase with distance from the central silicon atom. The

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[1] Chemistry of Organosilicon Compounds. 323.

[2] For reviews, see: (a) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138. (b) Mekelburger, H.-B.; Jaworek, W.; Vogtle, F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1571. (c) Newkome, G. R.; Moorefield, C. N.; Baker,G. R. *Aldrichimica Acta* **1992**, *25*, 31. (d) Tomalia, D. A.; Durst, H. D. *Top. Curr. Chem.* **1993**, *165*, 192. (e) Tomalia D. A. *Aldrichimica Acta* **1993**, *26*, 91. (f) Frechet, J. M. J. *Science* **1994**, *263*, 1710.

[3] A part of this work was presented at the 41st Symposium on Organometallic Chemistry, Japan: Nanjo, M.; Sekiguchi, A.; Kabuto, C.; Sakurai, H. Abstract p 16 (1994).

[4] Dendrimers of siloxane and carbosilane are reported. Polysiloxane dendrimers: (a) Rebrov, E. A.; Muzafarov, A. M.; Papkov, V. S.; Zhdanov. A. A. *Dokl. Akad. Nauk SSSR* **1989**, *309*, 376. (b) Uchida, H.; Kabe, Y.; Yoshino, K.; Kawamata, A.; Tsumuraya, T.; Masamune, S. *J. Am. Chem. Soc.* **1990**, *112*, 7077. (c) Mathias, L. J.; Carothers, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 4043. (d) Morikawa, A.; Kakimoto, M.; Imai, Y. *Macromolecules* **1991**, *24*, 3469. Carbosilane dendrimers: (e) van der Made, A. W.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1400. (f) Zhou, L.-L.; Roovers, J. *Macromolecules* **1993**, *26*, 963. (g) Roovers, J.; Zhou, L.-L.; Toporowski, P. M.; van der Zwan, M.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1993**, *26*, 4324. (h) Seyferth, D.; Son, D. Y.; Rheingold, A. L.; Ostrander, R. L. *Organometallics* **1994**, *13*, 2682. (i) Knapen, J. W. J.; van der Made. A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. *Nature* **1994**, *372*, 659.

[5] Matyjaszewski, K.; Hrkach, J. XXVIth Organosilicon Symposium, Indianapolis, IN, 1993; Abstract F-3.

[6] While our work was in progress, we learned that a polysilane dendrimer with a longest chain of seven silicon atoms (total silicon atoms: 16) had been prepared. Lambert, J. B.; Pflug, J. L.; Stern, C. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 98. We thank Professor Lambert for sending us a preprint .

[7] Compound **1a**: yellow crystals; $^1H$ NMR ($C_7D_8$, $\delta$) 0.23 (s, 3 H, SiMe), 0.47 (s, 6 H, Ph*Me*MeSi), 0.53 (s, 6 H, PhMe*Me*Si), 7.05–7.14 (m, 6 H, ArH), 7.37 –7.40 (m, 4 H, ArH); $^{13}C$ NMR ($C_7D_8$, $\delta$) −11.12, 0.16 (Ph*Me*MeSi), 0.25 (PhMe*Me*Si), 128.5, 129.4, 133.0, 147.2; $^{29}Si$ NMR ($C_7D_8$, $\delta$) −123.3, −9.7; $^7Li$ NMR ($C_7D_8$, $\delta$) −0.54.

[8] The crystal structure of **1a** will be reported elsewhere. For the preparation of **1b** and the molecular structure of $(Me_3SiSiMe_2Li)_4$, see: Sekiguchi, A.; Nanjo, M.; Kabuto, C. Sakurai, H. Submitted for publication in *Organometallics*.

[9] **3a**: $^1H$ NMR ($CDCl_3$, $\delta$) −0.38 (s, 3 H, SiMe), 0.14 (s, 18 H, $SiMe_2$), 0.19 (s, 9 H, SiMe), 0.24 (s, 18 H, Ph*Me*MeSi), 0.31 (s, 18 H, PhMe*Me*Si), 7.28–7.32 (m, 30 H, ArH); $^{13}C$ NMR ($CDCl_3$, $\delta$) −8.60, −7.11, −0.97 (Ph*Me*MeSi), −0.89 (PhMe*Me*Si), 1.63, 127.7,128.3, 134.0, 140.7; $^{29}Si$ NMR ($CDCl_3$, $\delta$) −79.0, −64.5, −29.1, −14.9; mass spectrum (DEI) *m/z* 1141−1144 $(M^+ - Me)$.

[10] **3b**: mp 153−153.5 °C; $^1H$ NMR ($CDCl_3$, $\delta$) 0.14 (s, 54 H), 0.17 (s, 9 H), 0.33 (s, 3 H), 0.36 (s, 18 H); $^{13}C$ NMR ($CDCl_3$, $\delta$) −10.09, −6.04, 0.97, 1.60; $^{29}Si$ NMR ($CDCl_3$, $\delta$) −80.4, −66.3, -30.0, −11.4; mass spectrum (EI) *m/z* 784 $(M^+)$.

[11] **4**: mp 139−140 °C; $^1H$ NMR ($CDCl_3$, $\delta$) 0.13 (s, 54 H), 0.15 (s, 54 H), 0.20 (s, 18 H), 0.37 (s, 18 H), 0.39 (s, 18 H), 0.40 (s, 9H), 0.44 (s, 18 H), 0.47 (s, 3 H); $^{13}C$ NMR ($CDCl_3$, $\delta$) −9.81 (6 C), −4.95 (3 C), −3.31 (1 C), 0.93 (18 C), 1.02 (18 C), 1.92 (6 C), 2.21 (6 C), 2.73 (6 C); $^{29}Si$ NMR ($CDCl_3$, $\delta$) −80.1 (6 Si), −64.8 (3 Si), −62.3 (1 Si), −30.0 (6 Si), −26.7 (3 Si), −11.4 (6 Si), −11.3 (6 Si); mass spectrum (DEI) *m/z* 1813−1824 $(M^+ - Me)$.

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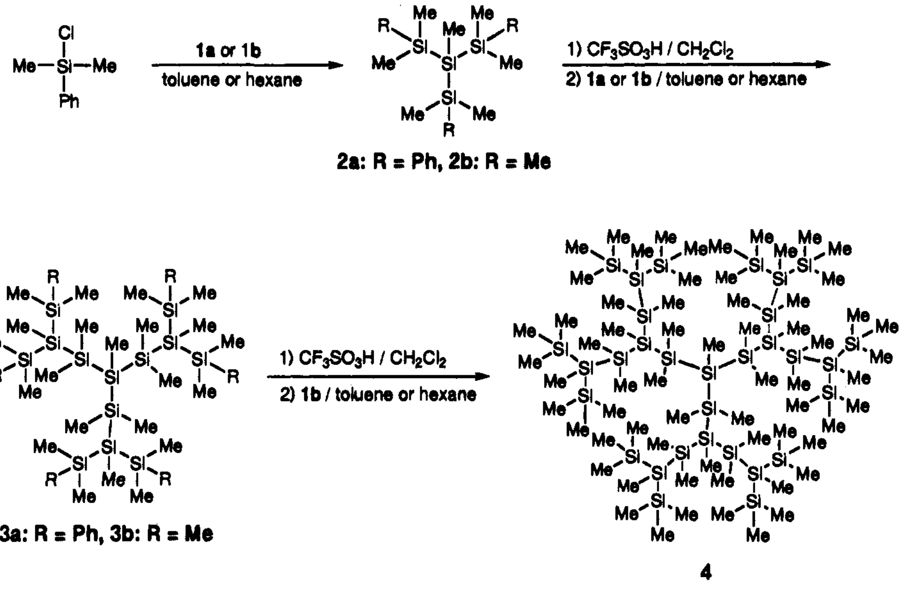
**Scheme 2**



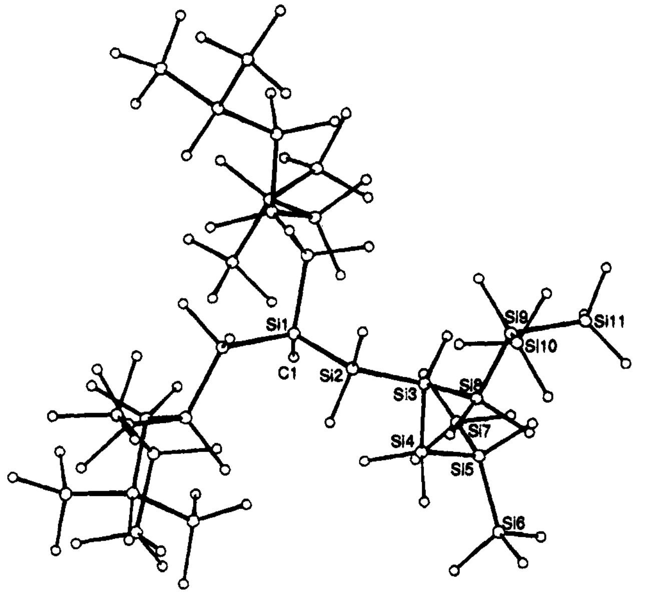


**Figure 1.** ORTEP drawing of polysilane dendrimer **4**. Silicon and carbon atoms are shown isotropically for clarity. Torsion angles (deg): C1–Si1–Si2–Si3 39.4, Si1–Si2–Si3–Si4 80.4, Si1–Si2–Si3–Si8 164.4, Si2–Si3–Si4–Si5 157.8, Si8–Si3–Si4–Si5 86.0, Si2–Si3–Si8–Si9 84.0, Si4–Si3–Si8–Si9 157.7, Si3–Si4–Si5–Si6 149.5, Si3–Si4–Si5–Si7 88.7, Si3–Si8–Si9–Si10 99.6, Si3–Si8–Si9–Si11 139.9.

longest chain has 11 silicon atoms. The conformations of the hexasilane chain for Si1–Si2–Si3–Si4–Si5–Si6 and Si1–Si2–Si3–Si4–Si5–Si7 are C-T-T and C-T-C (C, cis; T, trans), respectively.[13] Those of the other chains, Si1–Si2–Si3–Si8–Si9–Si10 and Si1–Si2–Si3–Si8–Si9–Si11, are T-C-C and T-C-T, respectively. Polysilane dendrimer **4** is the largest pure synthetic polysilane hitherto known.

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**Supplementary Material Available:** Details of X-ray experiments, atomic parameters, anisotropic temperature factors, and lists of distances and angles for **4** (20 pages); observed and calculated structure factors (29 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[12] Crystal data of **4**: MF = $Si_{31}C_{64}H_{192}$, MW = 1832.87, trigonal; $a = b = 22.887(6)$ Å, $c = 32.124(8)$ Å, $V = 14578(7)$ Å$^3$, space group $P\bar{3}1c$, $Z = 4$, $D_c = 0.835$ g/cm$^3$. A total of 5027 reflections with $F_o > 2\sigma(F_o)$ and $\sin\theta/\lambda < 0.55$ was used in the refinement. The number of effective reflections was reduced because of the large thermal motions of the peripheral atoms, and therefore the constraint refinement was applied; first only non-hydrogen atoms anisotropically to give an $R$-factor of 0.13 and next only hydrogen atoms isotropically to give an $R$-factor of 0.11. Finally only non-hydrogen atoms were again refined including the refined hydrogen atoms, and then the $R$-factor was dropped to 0.0996 ($R_w$ = 0.0978).

[13] The conformations are roughly classified as cis (C) and trans (T) by torsional angles of 0–90° and 90–180°, respectively.