Polysilane Dendrimer. Synthesis and Characterization of $[2,2\text{-}(Me_3Si)_2Si_3Me_5]_3SiMe$

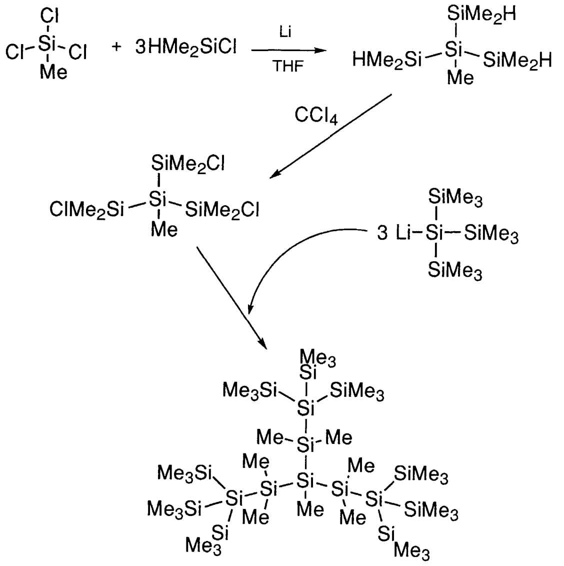
Hiroshi Suzuki,* Yoshinori Kimata, Shin Satoh, and Akira Kuriyama
Tsukuba Research Laboratory, Toagosei Co., Ltd., 2 Ohkubo, Tsukuba, Ibaraki 300-33

(Received December 26, 1994)

The entitled compound was synthesized by using a step-growth polymerization technique and its molecular structure was determined by X-ray crystallography. This dendrimer showed a distinct UV absorption maximum at 264 nm and exhibited two very feeble fluorescence maxima at 320 nm and 400 nm.

Polysilanes are an interesting class of photo-electronic materials which exhibit excitonic UV absorption and photoluminescence.[1] This behavior is attributed to delocalized electronic states derived from σ-conjugated silicon-silicon bonds in the polymer backbone. It was confirmed that the photo-electronic properties of polysilanes are influenced by the dimensionality of the silicon backbone structure. For example, 1-dimensional polysilanes (linear polysilanes) show strong photoluminescence in the ultraviolet around 350 nm.[1-3] On the other hand, 3-dimensional polysilanes (network polysilanes), which consist of a random backbone structure, exhibit weak photoluminescence in the visible region.[4,5]

Polysilane dendrimers will attract much attention as organosilicon clusters of well-defined nanostructures. These molecules are ideal systems for studying how physical properties depend on the σ-conjugated silicon architecture. Unique properties and potential new applications are also possible from this novel class of polysilanes. There have been several reports regarding the synthesis of polysilane dendrimers.[6,7] We also have successfully synthesized the same type of the first generation polysilane dendrimer, $[2,2\text{-}(Me_3Si)_2Si_3Me_5]_3SiMe$, (**1**) using a step-growth polymerization technique according to the following scheme and investigated the optical properties of this dendrimer **1**. The synthesis and characterization of the polysilane dendrimer **1** is described below.



1

$(ClMe_2Si)_3SiMe$[8] (1.63 g, 5 mmol) was dissolved in 100 mL of toluene, to which a THF solution of 15 mmol of $(Me_3Si)_3SiLi$[9] was slowly added at 0 °C. After stirring for 40 h, the reaction mixture was filtered to remove the salts. Organic solvents were distilled under reduced pressure and the volatile by-products were removed by sublimation. To the yellow semisolid residue was added 50 mL of methanol. The precipitated white solids were filtered from the methanolic solution giving 440 mg (11.5% yield) of **1**, mp 248-252 °C, which was soluble in common solvents such as benzene, toluene, xylene, n-hexane, $CHCl_3$, and THF and insoluble in CH_3OH, CH_3CN, and acetone.

We have obtained crystals of **1** for X-ray diffraction analysis.[12] The crystal structure is illustrated in Figure 1. The Si(1)-Si(2), Si(2)-Si(3), and Si(3)-Si(4)(average) bond lengths are 2.384, 2.424, and 2.362 Å, respectively, which are longer than that of tetrakis(trimethylsilyl)silane.[13] The dihedral angles of Si(1)-Si(2)-Si(3)-Si(4), Si(2)-Si(1)-Si(5)-Si(6), and Si(5)-Si(1)-Si(2)-Si(3) are 31.9°, 62.0°, and 182.6°, respectively, which show the silicon skeleton of **1** is twisted to minimize the van der Waals energy between methyl groups.

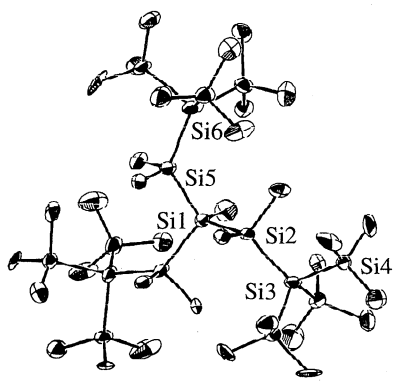


Figure 1. The crystal structure of **1**.

The ^{29}Si NMR signals of **1** are in the reasonable intensity ratio and can be assigned to the primary, secondary, tertiary, and quaternary signals of δ = -8.76 (primary), -25.49 (secondary), -37.13 (tertiary), and -119.83 (quaternary) ppm, respectively. Although tertiary silicon is generally observed between -60 and -90 ppm,[14] interestingly, the tertiary silicon of **1** was shifted considerably downfield.

The UV absorption spectrum of **1** in hexane showed a distinct absorption maximum at 264 nm (ε= 3000, per Si unit), which looked like the spectrum of linear (1-dimensional) polysilanes (Figure 2). The dendrimer **1** contains tertiary and quaternary silicons and is considered to consist of 3-dimensional σ-conjugated silicon architecture, but the spectrum of **1** was obviously different from that of network (3-dimensional) polysilanes, which did not exhibit a distinct absorption maximum.

Interestingly, the absorption maximum of **1** (264nm) was almost identical to that of the linear heptasilane(266nm).[15] Although **1** has sixteen silicon atoms in the dendritic structure, the longest polysilane chain of this dendrimer consists of seven silicon atoms. Namely, the UV absorption maximum of **1** depended on the longest silicon chain length (=7) irrespective of the total number of silicon atoms.

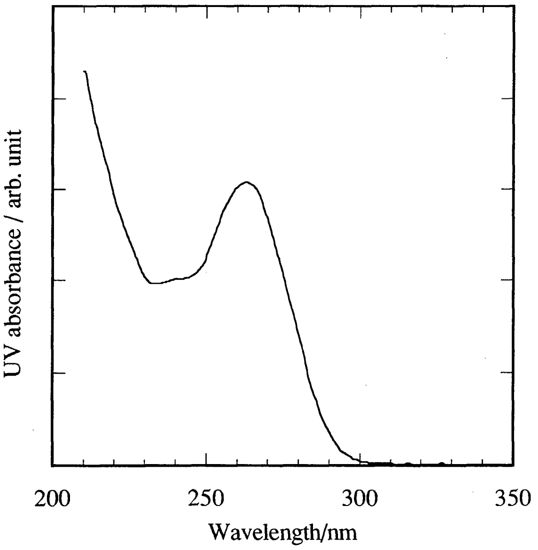


Figure 2. UV absorption spectrum of **1** in hexane.

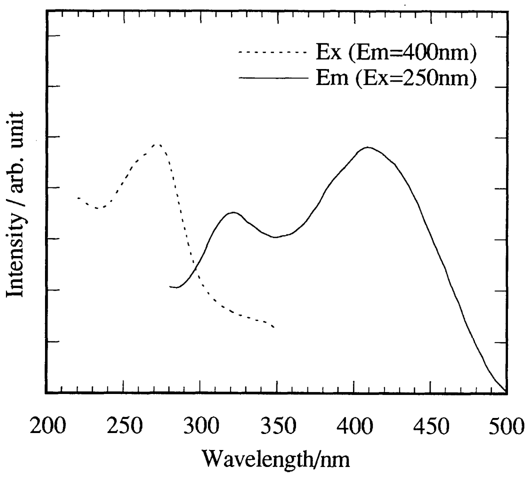


Figure 3. Emission and excitation spectra of **1** in hexane.

On the other hand, the fluorescence spectrum was obviously different from that of linear polysilanes. Figure 3 shows the fluorescence spectrum of **1** in a dilute hexane solution ($1.7\mathrm{x}10^{-5}$ mol of **1** dm^{-3}). The dendrimer **1** exhibited two very feeble broad emission maxima at 320 nm and 400 nm and did not exhibit a strong emission which is usually observed for linear polysilanes. It is considered that the visible fluorescence similar to network polysilanes is due to the high dimensionality of the silicon backbone structure. The quantum yield of **1** (<0.1%) could not be exactly determined, but it was less than that of network polysilanes (0.2-0.3%). The reason of this low quantum yield is not clear but might be attributed to the regularity branched silicon architecture.

This research was performed under the management of the Japan High Polymer Center as part of the Industrial Science and Technology Frontier Program supported by the New Energy and Industrial Technology Development Organization. The authors are grateful to Dr. M. Shiro of Rigaku Co. for X-ray analysis.

Reference and Notes

1 R. D. Miller and J. Michl, *Chem. Rev.*, **89**, 1359 (1989).
2 L.A. Harrah and J. M. Zeigler, *Macromolecules*, **20**, 601 (1987).
3 J. M. Zeigler, *Chem. Phys. Lett.*, **145**, 75 (1988).
4 P. A. Binancoi, F. Schilling, and T. W. Weidman, *Macromolecules*, **22**, 1967 (1989).
5 K. Furukawa, M. Fujino, and N. Matsumoto, *Macromolecules*, **23**, 3423 (1990).
6 J. B. Lambert, J. L. Pflug, and C. L. Stern, *Angew. Chem. Int. Ed. Engl.*, **34**, 98 (1995).
7 M. Nanjo, A. Sekiguchi, C. Kabuto, and H. Sakurai, presented at The Sendai International Symposium on The Frontiers of Organosilicon Chemistry, Sendai, Japan, 1994, Abstr., 162.
8 $(HMe_2Si)_3SiMe$[10] (8.0 g) was dissolved in 92.2 g of CCl_4 under dry argon. The solution was heated to reflux temperature. After 40 h, the organic solvent was removed under reduced pressure and 7.1 g (60% yield) of $(ClMe_2Si)_3SiMe$ was obtained by distillation under vacuum, bp 80 °C/0.1 mmHg.
9 $(Me_3Si)_3SiLi$ was prepared from $(Me_3Si)_4Si$ essentially according to the literature procedure,[11] except that a 5% excess of $(Me_3Si)_4Si$ over methyllithium was employed.
10 To a mixture of 7.9 g (1.14 g-atom) of lithium wire and 200 mL of THF was added a mixture of 25.4 g (170 mmol) of $MeSiCl_3$ and 53.0 g (560 mmol) of HMe_2SiCl at 10 °C. After stirring for 24 h, the reaction mixture was filtered to remove the salts. The organic solvent was removed by distillation and 12.5 g (33.3% yield) of $(HMe_2Si)_3SiMe$ was obtained by distillation under reduced pressure, bp 48 °C/1 mmHg.
11 H. Gilman and C. L. Smith, *J. Organomet. Chem.*, **8**, 245 (1967).
12 Crystal data for **1** at 296 K with CuKα(λ=1.54178 Å) radiation: crystals from THF over 5 days, formula=$C_{34}H_{102}Si_{16}$, FW=960.55, colorless prismatic, space group $P6_3$(#173), a=26.248(4), c=16.293(9) Å, V=9721(4) Å^3, Z=6, d=0.984 gcm^{-3}. Some nonhydrogen atoms were anisotropically refined while the rest were isotropically refined. The final cycle of full-matrix least-squares refinement was based on 2839 observed reflections [I > 3.00(I)] from 4998 unique data points (5382 collected) and 432 variable parameters. R=0.092, Rw=0.106.
13 The Si-Si bond length of $(Me_3Si)_4Si$ is 2.361 Å ; G. Klebe, J. W. Bats, and K. Hensen, *J. Chem. Soc., Dalton Trans.*, 1 (1985).
14 D. A. Stanislawski and R. West, *J. Organomet. Chem.*, **204**, 295 (1981).
15 R. West, *J. Organomet. Chem.*, **300**, 327 (1986).