

Solid-state structure and condensation reaction of (triphenylmethyl)silanetriol

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Abstract

(Triphenylmethyl)silanetriol [**1**, (Ph₃C)Si(OH)₃] was obtained in 98% yield by the hydrolysis of (triphenylmethyl)trichlorosilane with ice-water in diethyl ether. Single crystal of [**1** · acetone] for X-ray crystallographic determination was grown from a saturated acetone solution. In the single crystal X-ray structure analysis, the silanetriol **1** crystallizes in the centrosymmetric triclinic space group with two independent molecules in the asymmetric unit. Two independent molecules of the silanetriols **1** interact with each other and with acetones by intermolecular hydrogen bondings. Such hydrogen-bonding interactions lead to a one-dimensional columnar polymeric tube. Finally, this tube interacts with others to make sheets alternating hydrophobic organic part and hydrophilic hydroxy groups of the molecules **1** and the oxygen of acetones arranged regularly. The silanetriol **1** is very stable compound in solution and in solid states at room temperature, but decomposed in the presence of KOH, and undergoes a condensation reaction with dicyclohexylcarbodiimide (DCC) as strong dehydrating agent to give polysiloxane. The silanetriol **1** reacts with trimethylchlorosilane to give three type siloxane products (Ph₃C)Si(OH)_{3-n}(OSiMe₃)_n (*n* = 1, 2, 3). The number (*n*) of silylation of hydroxy groups on the silanetriol **1** increase with increasing the mol ratio of trimethylchlorosilane used.

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1. Introduction

Much attention has been paid to synthetic approaches to silanepolyols, which can be used as models for studies on the building block of silica [1,2]. Especially silanetriols, which are unstable compounds, can be useful precursors for the synthesis of silsesquioxanes, ladder polymers, and metallosilsesquioxanes [2a,3–5]. Since stable *c*-hexylsilanetriol was first isolated and characterized by single crystal X-ray structure analysis in 1982 [6], some stable silanetriols bearing a bulky sub-

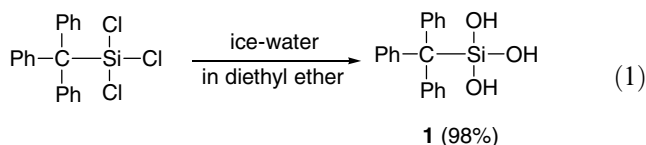
stituent have been isolated and studied for their structures and properties [7–18]. A bulky substituent on the silicon of silanetriol makes OH groups on the silicon stabilized for self-condensation reaction. Recently (triphenylmethyl)trichlorosilane containing a bulky substituent on the silicon was synthesized from the Friedel–Crafts reaction of (trichloromethyl)trichlorosilane with excess benzene [19] and hydrolyzed with water in organic solvent to give (triphenylmethyl)silanetriol (**1**) [8] in good yield. As a continuing study on the chemistry of silanetriol **1**, we conducted the systemic studies on its solid-state structure, thermal properties, and condensation reactions. In this paper, we wish to report these results in details.

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2. Results and discussion

2.1. Solid-state structure and thermal property of (triphenylmethyl)silanetriol

(Triphenylmethyl)trichlorosilane was hydrolyzed with crash ice-water in diethyl ether to give the stable silanetriol **1** in 98% yield (Eq. (1)). The silanetriol **1** was obtained in higher yield in diethyl ether solvent than that in THF [8].



The silanetriol **1** was purely isolated as colorless crystals by cooling a concentrated diethyl ether solution. Single crystals of the compound **1** suitable for X-ray crystallographic determination could be obtained from a concentrated THF solution [8] and an acetone at $-20\text{ }^{\circ}\text{C}$, respectively. The crystallographic data of compound **1** and acetone are summarized in Table 1.

The ORTEP plot of [**1** · acetone] determined by the single crystal X-ray structure analysis and the selected

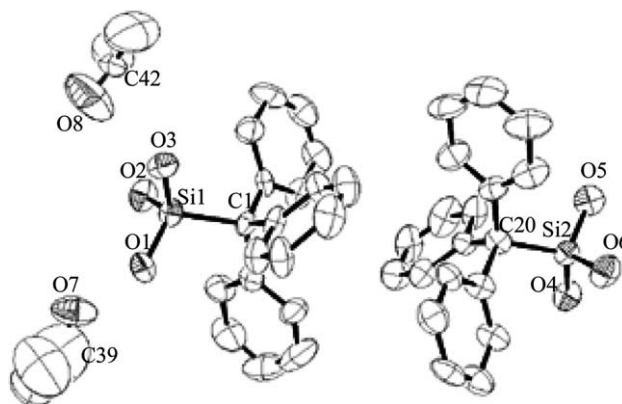


Fig. 1. Molecular structure of the two crystallographically independent molecules of the silanetriol **1** and acetone (thermal ellipsoids shown at 50% probability level). Selected bond lengths (Å) and angles (deg): Si(1)–O(1) 1.627(6); Si(1)–O(2) 1.621(6); Si(1)–O(3) 1.613(6); Si(1)–C(1) 1.946(7); Si(2)–O(4) 1.617(6); Si(2)–O(5) 1.634(6); Si(2)–O(6) 1.632(7); Si(2)–C(20) 1.900(8); O(7)–C(39) 1.27(5); O(8)–C(42) 1.110(12); O(1)–Si(1)–O(2) 108.8(3); O(1)–Si(1)–O(3) 108.9(4); O(2)–Si(1)–O(3) 109.5(3); O(1)–Si(1)–C(1) 110.6(3); O(2)–Si(1)–C(1) 109.8(3); O(3)–Si(1)–C(1) 109.2(3); O(4)–Si(2)–O(5) 109.0(3); O(4)–Si(2)–O(6) 109.4(3); O(5)–Si(2)–O(6) 108.3(4); O(4)–Si(2)–C(20) 111.4(4); O(5)–Si(2)–C(20) 109.0(3); O(6)–Si(2)–C(20) 109.6(4).

bond lengths and bond angles for the silanetriol **1** is depicted in Fig. 1.

The molecule **1** crystallizes in the centrosymmetric triclinic space group with two independent molecules in the asymmetric unit. In Fig. 1, the lengths of Si–O bonds in the two molecules range from 1.613 to 1.634 Å. The bond lengths of Si(1)–C(1) and Si(2)–C(20) are 1.946 and 1.900 Å, respectively. The bond angles for O–Si–O and O–Si–C in the two molecules range from 108.3 to 109.5° and from 109.0 to 111.4°, respectively. These are comparable to those found in *t*-BuSi(OH)₃ [15] and (Me₃)₃CSi(OH)₃ [18]. The solid-state packing diagram and hydrogen-bonded network structure of the silanetriol **1** and acetone are predicted in Fig. 2. Two independent molecules of the silanetriol **1** interact each other by the intermolecular hydrogen bondings to form a dimeric-unit as shown in a circle of Fig. 2. Such a dimeric-unit interacts with two acetones by the intermolecular hydrogen bondings. Such hydrogen-bonding interactions lead to a one-dimensional columnar polymeric tube. Finally, such a tube interacts with others to make sheets alternating hydrophobic organic part and hydrophilic hydroxy groups of the molecules **1** and oxygens of acetones arranged regularly as shown in Fig. 2. The distances of O(1)–O(4) and O(2)–O(5) bonds of the dimeric unit formed by the hydrogen bondings between two independent molecules are 2.865 and 2.870 Å, respectively, which are within the normal O–O bond distances for the hydrogen bondings (2.70–3.16 Å) of the silanetriols [2b]. The O(1)–O(7), O(3)–O(8), O(5)–O(8), and O(6)–O(7) bond distances of the intermolecular hydrogen-bondings formed between the dimeric

Table 1
Crystallographic data for the silanetriol **1**

Compound	(1 · acetone) × 2
Empirical formula	C ₄₄ H ₄₈ O ₈ Si ₂
Formula weight	761.00
Temperature (K)	293(2)
Wave length (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Unit cell dimensions	
<i>a</i> (Å)	8.850(2)
<i>b</i> (Å)	9.654(2)
<i>c</i> (Å)	12.662(2)
α (°)	86.51(2)
β (°)	86.730(10)
γ (°)	70.93(2)
Volume (Å ³)	1019.8(4)
<i>Z</i>	1
Density, calcd. (g/cm ³)	1.239
Absorption coefficient (mm)	0.139
<i>F</i> (000)	404
Crystal size (mm)	0.2 × 0.2 × 0.3
θ range for data collection (deg)	1.61–24.97
Index ranges	0 < = <i>h</i> < = 10 –10 < = <i>k</i> < = 11 –14 < = <i>l</i> < = 15
Reflections collected/unique	3082/2870 [<i>R</i> _{int} = 0.0132]
Completeness to 2 θ (%)	80.1
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3082/15/499
Goodness-of-fit on <i>F</i> ²	1.145
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0540, <i>wR</i> ₂ = 0.1478
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0545, <i>wR</i> ₂ = 0.1489

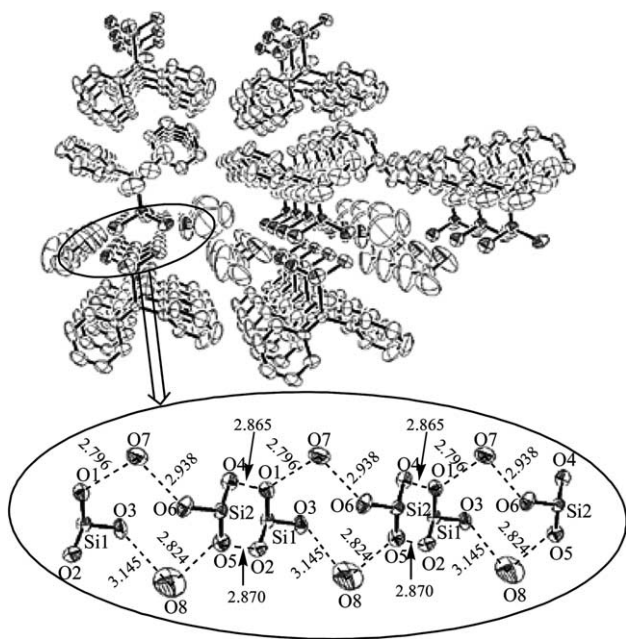


Fig. 2. Packing diagram of the silanetriol **1** and acetone (H-bonded network structure in a circle). For clarity, all carbon and hydrogen atoms are not shown in the circle.

units and acetones are 2.796, 3.145, 2.824, and 2.938 Å, respectively. The average O–O bond distance (2.8675 Å) of the former (the dimeric unit) is stronger than that (2.9258 Å) of the latter (between **1** and acetones).

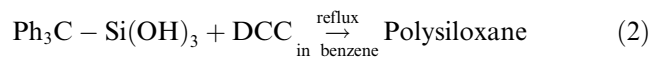
The packing diagram of [**1** · acetone] is different to that of [**1** · THF] as shown in Fig. 3 [8]. The packing diagram of **1** containing THF shows that the molecule **1** interacts with other two molecules and an acetone by the intermolecular hydrogen bondings as shown in a box. The O(1)–O(2) and O(2)–O(1) distances of the intermolecular hydrogen bondings formed between the two hydroxy-groups on the silanetriols are the same 2.898 Å and the distance of O(3)–O(3) is relatively long 3.083 Å. The distances of O(2)–O(4) and O(4)–O(3) of the intermolecular hydrogen bondings formed between a THF and the two silanetriols are 2.772 and 3.052 Å, respectively. Hydrogen-bonding networks of the silanetriols formed in an up and down fashion lead to one-dimensional wires. Such wires make sheets alternating hydrophobic organic part and hydrophilic hydroxy-groups on the silicon and oxygen at THF. The sheets are regularly arranged as shown in Fig. 3. Earlier known silanetriols showed a variety type of network structures: (a) a double-sheet structure in $C_6H_{11}Si(OH)_3$ [6] and $t\text{-BuSi(OH)}_3$ [15] where the molecules arrange in a head-to-head with hydrophobic alkyl groups and tail-to-tail fashion with hydrophilic OH groups alternating sheets, (b) a discrete hexameric cage structure with hydrogen-bonded silanetriols such as $(Me_3)_3SiSi(OH)_3$ [16] and $(Me_3)_3CSi(OH)_3$ [18], (c) a discrete tetrameric cage structure with hydrogen-bonded silanetriols as $[C_5H_4(SiMe_3)]Si(OH)_3$ [12], and etc. [8].

In the 1H NMR spectra of solution of the silanetriol **1**, the proton resonance of OH on the silanetriol **1** was shifted from 6.45 in DMSO- d_6 to 5.63 in acetone- d_6 to 4.38 ppm in acetonitril- d_3 solvent, indicating that the chemical shift of OH on the silanetriol **1** depends on organic solvents used in NMR studies. These results are consistent with the basicity of solvent, making stronger hydrogen bonding with the OH group of **1** at stronger basicity [20,21]. The proton resonance of OH on the silanetriol **1** in DMSO- d_6 appeared at lower field than that of $t\text{-BuSi(OH)}_3$ (5.50 ppm [15]), (1-trimethylsilyl)cyclopenta-2,4-dienylsilanetriol (5.76 ppm [12]), pentamethylcyclopenta-2,4-dienylsilanetriol (5.67 ppm [13]), and 9-methylfluoren-9-yl)silanetriol (6.12 ppm [9]).

The thermal property of the silanetriol **1** was studied by a TGA and DSC techniques. The powders of **1** were dried at 30 °C for 24 h under vacuum and then applied for the studies of TGA and DSC under the condition of flowing air and nitrogen (44 mL/min), respectively. In both cases, the data of TGA and DSC were very similar each other. TGA data of **1** was disclosed to be stable up to 180 °C without the loss of mass, then the decomposition rapidly preceded above 180 °C in the nitrogen atmosphere as shown in Fig. 4. About 600 °C, 81.1% of weight loss reached, 18.9% of residue was remained until up to 1000 °C. It means that silica (SiO_2) was formed by decomposing all organic part of **1** off. Endothermic phenomena was maximized at 192 °C in DSC.

2.2. Polymerization reaction of silanetriol **1**

Generally, it is well-known that simple silanetriols are easily polymerized by self-condensation to give polysiloxanes. Thus the self-condensation reaction of **1** was carried out by varying reaction conditions such as reaction catalyst, solvent, and temperature. Among some reactions, the silanetriol **1** was polymerized to give poly(triphenylmethyl)siloxane when 1,3-dicyclohexylcarbodiimide (DCC) was used as a dehydrate agent to (Eq. (2)). The results are summarized in Table 2.



As shown in Table 2, the compound **1** is stable up to the reflux temperature of acetone or benzene. Unreacted silanetriol **1** was recovered without self-condensation when an acetone and a benzene solution of the silanetriol **1** were refluxed for 24 h, respectively. When NaOH was used as a catalyst for a self-condensation, triphenylmethane was obtained in 96% yield as a decomposed compound along with insoluble silicate, suggesting that the cleavage reaction of Si–C bond in the presence of strong base catalyst occurred. When DCC, which is known as a good dehydrating agent, was used, the silanetriol **1** was polymerized to give only polysiloxanes through condensation reaction. These results showed

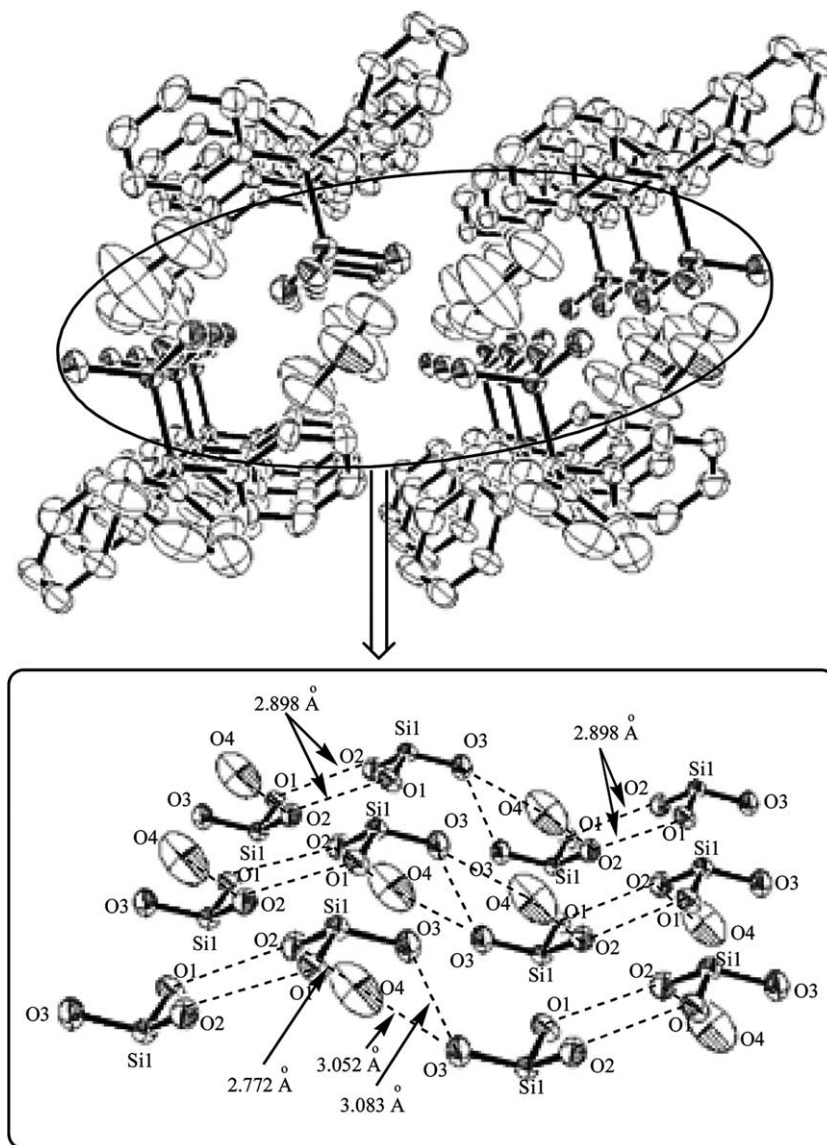


Fig. 3. Packing diagram of **1** · THF and H-bonded network structure in a box (indicating O1–O3 for three oxygens of **1** and O4 for the oxygen of THF). For clarity, all carbon and hydrogen atoms are not shown in the box.

that the silanetriol **1** is very stable in neutral medium, but undergo self-condensation in the presence of strong dehydrating agent.

2.3. Reaction of **1** with trimethylchlorosilane

In order to test the reactivity of the hydroxy-groups on the silanetriol **1**, the reaction with trimethylchlorosilane, which is known as a good silylating agent, was carried in the presence of pyridine as a HCl scavenger out at the reflux temperature of ethyl ether. The silanetriol **1** reacts slowly with trimethylchlorosilane to give three kinds of silylated products: monosilylated product, 1,1-dihydroxy-1-(triphenylmethyl)-3,3,3-trimethyldisiloxane (**2a**); disilylated product, 1-hydroxy-1-trimethylsiloxy-1-triphenylmethyl-3,3,3-trimethyldisiloxane (**2b**); three silylated product, 1,1-bis(trimethylsiloxy)-1-triphenyl-

methyl-3,3,3-trimethyldisiloxane (**2c**). The higher silylated products increase with increasing the ratio of $(\text{CH}_3)_3\text{SiCl}$ and **1** in the reaction. These results are summarized in Table 3.

As shown in Table 3, the ratio of three products **2a–c** obtained from the silylation of the silanetriol **1** with trimethylchlorosilane depends on the mol ratio of both **1** and trimethylchlorosilane. In a 24 h reaction of 1:1 mixture of **1** with trimethylchlorosilane, the monosilylated and disilylated products were obtained in 69% and 14% yields with an 83% consumption of **1**. When **1** reacted with 2 equiv of trimethylchlorosilane for 48 h to give the three products **2a**, **2b**, and **2c** in 52%, 46%, and 2% yields. The compound **1** reacted with 3.3 equiv of trimethylchlorosilane to afford the three products **2a**, **2b**, and **2c** in 1%, 81%, and 19%. The results suggest that the reactivity of **1** is not good due to the

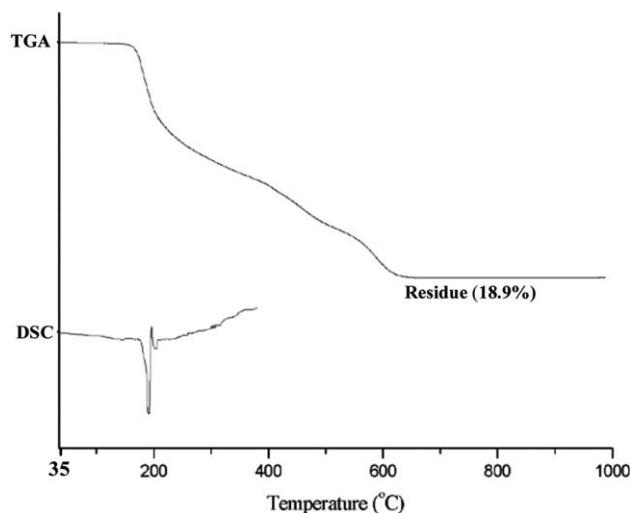


Fig. 4. Thermogram of TGA and DSC for the silanetriol **1** in the nitrogen atmosphere.

steric hindrance of bulky triphenylmethyl-substituent on the silicon.

The silylated products in the solution were characterized by NMR techniques. In ^1H NMR spectra, the proton-resonance signals of trimethylsilyl-group at the silylated products is shifted to up-field with increasing the numbers of silylation of the hydroxy groups on the silanetriol **1** with trimethylchlorosilane due to an increase of steric repulsion between a trimethylsilyl- and a bulky Ph_3C -group on the silicon atom. The typical protons resonances of the aromatic rings for the compounds **2a–c** are between 7.17 and 7.32 ppm. The mono-silylated compound **2a** appeared at 0.00 ppm with a singlet for the resonance of methyl-protons and at 2.89 ppm with a broad singlet for that of Si–OH, the disilylated compound **2b** at -0.02 and 2.56 ppm, respectively, the trisilylated compound **2c** at -0.04 ppm for the resonance of methyl-protons. In ^{13}C NMR spectra, the resonance signals of aliphatic-carbons for the compounds **2a**, **2b**, and **2c** appear at -1.27 , -1.32 , and -1.37 ppm for methyl-substituent and 53.94, 53.89, and 53.66 ppm for benzylic-carbon, suggesting that the chemical shifts are moved to up-field as their steric hindrance in-

Table 2
Self-condensation reaction of **1**

Reactant 1	Reaction conditions ^a			Products (%)	
	Cat.	Solvent	Time (h)	Polymer ^b (average molecular weights)	Other
100	–	Acetone	24	–	–
100	–	Benzene	24	–	–
–	NaOH	Benzene	72	–	96 ^c
–	DCC	Benzene	72	99 (5500)	–
–	DCC	Acetone	72	99 (12,400)	–

^a Reaction was carried out at the reflux temperature of solvent.

^b Percentage of polymer indicates the mol% of $\text{Ph}_3\text{CSiO}_{3/2}$ unit converted from **1**.

^c Triphenylmethane.

Table 3
Reaction of **1** with trimethylchlorosilane^a

Mol ratio of reactants	Reaction time (h)	Products (%)		
		2a	2b	2c
1.0 (17) ^b	24	69	14	–
2.0 (–)	48	52	46	2
3.3 (–)	48	1	81	19

^a Reaction of the silanetriol **1** with $(\text{CH}_3)_3\text{SiCl}$ was carried out at the refluxing temperature of diethyl ether.

^b Unreacted **1** remained.

creases from **2a**, **2b**, to **2c**. In the ^{29}Si NMR spectra of the compound **2a–c**, two kinds of silicon-resonance signals appeared at -5.63 and -63.36 ppm for SiMe_3 and SiCPh_3 of **2a**; at 4.40 and -73.39 ppm for those of **2b**; 3.17 and -84.14 ppm for those of **2c**, respectively.

In conclusion, the silanetriol **1** is very stable compound in solution and in solid states at room temperature, decomposed in the presence of KOH, and but undergoes condensation reaction in the presence of DCC as strong dehydrating agent to give polysiloxane. The compound **1** reacts with trimethylchlorosilane to give three type siloxane products $(\text{Ph}_3\text{C})\text{Si}(\text{OH})_{3-n}(\text{OSiMe}_3)_n$ ($n = 1, 2, 3$). The number (n) of silylation of hydroxy groups on the silanetriol **1** increase with increasing the mol ratio of trimethylchlorosilane used.

3. Experimental section

Trimethylchlorosilane and DCC were purchased from Gelest, Inc. and used without purification. TLC plate sheets coated with silica gel 60 F₂₅₄ from Merck. NMR spectra were recorded on a Varian Unity Plus 600 (FT, 600 MHz, ^1H ; 150 MHz for ^{13}C) spectrometer or Bruker Avance 300 spectrometer (300 MHz for ^1H ; 75 MHz for ^{13}C , for ^{29}Si) in acetone- d_6 and chloroform- d_1 solvents. The chemical shifts are given in ppm relative to the residual proton signal of the solvents. Melting points (uncorrected) were measured with a Mel-Temp II melting point apparatus using sealed capillary tubes. Thermogravimetric analysis was measured with a Universal V1 8M from TA Instruments. The

powder of the silanetriol **1** was dried at 30 °C for 24 h under vacuum and then applied for the studies of TGA and DSC. Temperature was increased to 1000 °C from the initial equilibrium temperature of 30 °C in the heating rate of 10 °C/min under the condition of flowing air and nitrogen (44 mL/min), respectively. Gel permeation chromatography (GPC) was carried out on a Waters Millipore gel permeation chromatograph with Ultrastaygel GPC column series (in sequence, 100, 500, 10³, and 10⁴ Å columns) using THF solvent as an eluant. Molecular weights were calibrated by polystyrene standards. HRMS (high-resolution mass (70 eV, EI) spectra) were performed by Korea Basic Science Institute, Seoul, Korea. (Triphenylmethyl)trichlorosilane was obtained by the reaction of benzene with (trichloromethyl)trichlorosilane in the presence of aluminum chloride [19].

3.1. Synthesis of (triphenylmethyl)silanetriol **1**

Into a stirring crush ice (50 g, 360 mmol) in diethyl ether (500 mL) in ice-water bath was added dropwise (triphenylmethyl)trichlorosilane (5.0 g, 13.2 mmol) in diethyl ether (100 mL) for 1 h. The reaction mixture was stirred at 0 °C for another 1 h and warmed up to room temperature. Then organic layer was separated, washed three times with distilled water (30 mL), concentrated, and crystallized to give (triphenylmethyl)silanetriol (**1**; 4.2 g, 98%) as crystalline solids. A single crystal [0.2 × 0.2 × 0.3 mm] of 1:1 mixture of two compounds **1** and acetone suitable for X-ray crystallographic determination was obtained from a solution of acetone at –30 °C.

Data for **1**: m.p. 192–3 °C dec.; ¹H NMR (300 MHz, acetonitril-d₃) δ 4.38 (s, OH, 3H), 7.14–7.30 (m, 15H, Ph-H); ¹H NMR (300 MHz, acetone-d₆) δ 5.63 (s, OH, 3H), 7.12–7.27 (m, 15H, Ph-H); ¹H NMR (300 MHz, DMSO-d₆) δ 6.45 (s, OH, 3H), 7.10–7.27 (m, 15H, Ph-H); ¹³C NMR (75 MHz, acetone-d₆) δ 55.16, 126.25, 128.70, 131.63, 147.92; ²⁹Si NMR (60 MHz, DMSO-d₆) δ –53.19; HRMS (EI, 70 eV) Calc. for C₁₉H₁₈O₃Si (M⁺) *m/z* 322.1025, Found *m/z* 322.1029; IR (KBr pellet): 3336 (s, OH), 1595, 1481, 1442, 947, 898, 811, 745, 705, 507 cm^{–1}.

3.2. Self-condensation reaction of silanetriol **1**

A solution of **1** (1.0 g, 3.1 mmol) and DCC (2.1 g, 10.2 mmol) in benzene (50 mL) was stirred at reflux temperature for 72 h. Then benzene was removed from a reaction mixture. Poly(phenylsiloxane) was extracted with *n*-hexane (20 mL × 3) from the reaction mixture. Then, 1,3-dicyclohexylurea was precipitated off in hexane solution. Poly(phenylsilsesquioxane)s (0.91 g) was obtained after hexane was removed. Data for poly(phenylsilsesquioxane)s: white solid, *R_f* = 0.55 (TLC, a 3:7 mixture of methylene chloride and hexane as eluant), *M_w* = 5,500, *M_w*/*M_n* = 1.30; IR (KBr pellet):

1089 cm^{–1} (strong band, Si–O–Si), ¹H NMR δ 6.50–7.50 (broad, Ph-H); ¹³C NMR δ 56.8 (broad, Si-C), 125.9, 128.3, 130.1, 143.3 (broad, phenyl-C). ²⁸Si NMR δ –82 (broad). The same reaction was carried out using acetone solvent (50 mL) at 50 °C for 72 h. This reaction gave poly(phenylsilsesquioxane)s with higher molecular weight (*M_w* = 12,400; *M_w*/*M_n* = 1.38).

3.3. Condensation reaction of **1** with trimethylchlorosilane

Into a solution of **1** (200 mg, 0.62 mmol) in diethyl ether (10 mL) in the presence of pyridine (50 mL (49 mg), 0.62 mmol) as a HCl scavenger was added dropwise trimethylchlorosilane (67 mg, 0.62 mmol). A mild exothermic reaction accompanied by the formation of triethylamine · hydrochloride salt occurred. The reaction mixture was allowed to warm up to reflux temperature and stirred for one day. The insoluble salt, which had formed, was filtered off. The filtrate was concentrated by evaporation under vacuum to give 250 mg of reaction mixture, consisted of a mixture of 1,1-dihydroxy-1-triphenylmethyl-3,3,3-trimethyldisiloxane (**2a**), 1-dihydroxy-1-trimethylmethyl-1-triphenylmethyl-3,3,3-trimethyldisiloxane (**2b**) in 69% and 14% yields. The 1:2 and 1:3.3 reactions of **1** and trimethylchlorosilane were carried out under the same reaction condition above, respectively. These results are summarized in Table 2. Data for **2a**, ¹H NMR (300 MHz, CDCl₃) δ 0.00 (s, 9H, SiCH₃), 2.89 (br. s, 2H, Si–OH), 7.17–7.32 (m, 15H, phenyl-H). ¹³C NMR (75 MHz, CDCl₃) δ –1.27 (SiC₃), 53.94 (benzylic-C), 125.99, 128.19, 130.20, 145.34 (phenyl-C). ²⁹Si NMR (60 MHz, CDCl₃) δ 5.63 (SiMe₃), –63.36 (SiCPh₃). HRMS (EI, 70 eV) Calc. for C₂₂H₂₆O₃Si₂ (M⁺) *m/z* 394.1420, Found *m/z* 394.1423. Data for **2b**, ¹H NMR (300 MHz, CDCl₃) δ –0.02 (s, 18H, Si–CH₃), 2.56 (br. s, 2H, Si–OH), 7.17–7.32 (m, 15H, phenyl-H). ¹³C NMR (75 MHz, CDCl₃) δ –1.32 (SiC₃), 53.89 (benzylic-C), 125.80, 127.94, 130.37, 145.72 (phenyl-C). ²⁹Si NMR (60 MHz, CDCl₃) δ 4.40 (Si Me₃), –73.39 (SiCPh₃). HRMS (EI, 70 eV) Calc. for C₂₅H₃₄O₃Si₃ (M⁺) *m/z* 466.1816, Found *m/z* 466.1814. Data for **2c**, ¹H NMR (300 MHz, CDCl₃) δ –0.04 (s, 27H, SiCH₃), 7.18–7.29 (m, 15H, phenyl-H). ¹³C NMR (75 MHz, CDCl₃) δ –1.37 (SiC₃), 53.66 (benzylic-C), 125.52, 127.72, 130.54, 146.00 (phenyl-C). ²⁹Si NMR (60 MHz, CDCl₃) δ 3.17 (SiMe₃), –84.14 (SiCPh₃). HRMS (EI, 70 eV) Calc. for C₂₈H₄₂O₃Si₄ (M⁺) *m/z* 538.2211, Found *m/z* 538.2210.

3.4. X-ray crystallography

All X-ray data were collected on a Siemens SMART CCD area detector with graphite monochromated Mo K radiation (0.71073 Å) source at ambient temperature or at –100 °C.

Unit cell dimensions were based on 25 well-centered reflections by using a least-squares procedure. During the data collection, three standard reflections monitored after every hour did not reveal any systematic variation in intensity. The structures were solved by the SHELXS-97 [22], followed by successive difference Fourier synthesis. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. All calculations were carried out on a personal computer with use of SHELXS-97 and SHELXL-97. Crystal parameters and procedural information corresponding to data collection and structure refinement were given in Table 1.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 249439 for compound **1**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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