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Polysilane Synthesis by Catalytic Disproportionation of Alkoxydisilanes

Keiji KABETA, Shigeru WAKAMATSU, and Takafumi IMAI*
Research and Development Center, Toshiba Silicone Co., Ltd., 133 Nishishinmachi, Ohta, Gunma 373

Network polysilanes with methyl, phenyl, and ethoxy groups (Mw 530 - 7000) were prepared by a catalytic disproportionation reaction of methylethoxydisilanes in the presence of phenylethoxysilanes. Hexyl or cyclohexyl groups were also incorporated into polysilanes when corresponding alkoxysilanes were employed. Reaction of pentamethylethoxydisilane clarified a mechanism of the reaction.

Recent interests have been focused on unusual properties of polysilanes. They are expected to be used as preceramics, conducting materials, photoconductor, nonlinear optical materials, *etc.*[1] Preparation of polysilanes, however, is almost limited to the Wurtz-type coupling of organochlorosilanes, therefore an alternative and convenient process for polysilanes has been strongly desired. Anionic polymerization of masked disilenes,[2] dehydrogenative coupling of hydrosilanes,[3] ring opening polymerization of cyclic oligosilanes[4a,b] are examples of promising approaches. Catalytic disproportionation reaction of alkoxydisilanes is also promising for a preparation of network polysilanes.[5]

The disproportionation reaction of 1,1,2,2-tetramethyldimethoxydisilane catalyzed by sodium methoxide was studied to give cyclic or linear oligosilanes by Nagai *et al.*[6a,b] It is considered that one of the silyl group cleaved from disilane was converted to silyl anion[7] and introduced into oligosilanes and another was transformed to dimethyldimethoxysilane in the reaction. Watanabe *et al.* recently published a synthesis of polysilanes by this method in obtaining silicon carbide ceramics.[5]

Methylalkoxydisilanes, starting materials of the reaction, are readily available as a by-product in the industrially operated direct synthesis for methylchorosilanes. Therefore a method for introducing other substituents into the polysilane is expected to provide for versatility of polymer properties and effective utilization of wastes. Here we report the first convenient method for obtaining substituted network polysilanes from methylethoxydisilanes by a catalytic disproportionation reaction in the presence of some ethoxysilanes.

Disproportionation reactions of three methylethoxydisilanes (**1a** - **1c**) were catalyzed by sodium ethoxide in the presence of equimolar amount of four ethoxysilanes (**2a** - **2d**) to give substituted polysilanes, respectively (Eq. 1). In a typical experiment, 1,2-dimethyltetraethoxydisilane (**1c**, 2.0 g, 7.5 mmol) and phenyltriethoxysilane (**2b**, 1.8 g, 7.5 mmol) were added to a mixture of sodium ethoxide (52 mg, 0.75 mmol) and 5 cm^3 of dried diglime. The reaction mixture was then heated for 27 h at 150 °C under nitrogen atmosphere with monitoring remaining disilane by GC (SE30). The reaction mixture turned yellow just after the heating. After the disilane disappeared completely, insoluble sodium ethoxide was filtered off and the filtrate was added to an absolute ethanol. Subsequent filtration of precipitated solid and drying *in vacuo* gave white powder. In cases that solids were not precipitated, the ethanol solutions were concentrated at 150 °C

under reduced pressure to obtain polymeric products by removing by-product methylethoxysilanes and unreacted phenylsilanes. The results are summarized in Table 1.

$$Me_nSi_2(EtO)_{6-n} + R_mSi(OEt)_{4-m} \xrightarrow[\text{diglyme}]{\text{NaOEt (10 mol\%)}} \text{(Me, EtO, R) polysilane} \quad (1)$$

1a n = 4; **1b** 3; **1c** 2

2a R = Ph, m = 2; **2b** Ph, 1; **2c** Hex, 1; **2d** CyclohexylMeSi(OEt)$_2$

3a - **3h**

Table 1. Disproportionation Reactions in the Presence of Alkoxysilanes

Disilane	Silane	Conditions	Polysilane	Yield/%	Mw(Mw / Mn)[a]	R :	Me :	OEt[b]	Product
1a	**2a**	150 °C, 23 h	**3a**	31	530 (1.1)	40	40	20	oil
1a	**2b**	150 , 22	**3b**	32	620 (1.2)	33	37	30	oil
1b	**2a**	150 , 22	**3c**	57	710 (1.1)	36	50	14	oil
1b	**2b**	150 , 27	**3d**	26	720 (1.1)	18	58	24	oil
1c	**2a**	150 , 18	**3e**	61	3300 (1.6)	17	52	31	solid
1c	**2b**	150 , 27	**3f**	52	7000 (1.5)	15	72	12	solid
1c	**2c**	150 , 23	**3g**	31	6000 (1.7)	29	33	38	solid
1c	**2d**	150 , 21	**3h**	35	4500 (1.2)[c]	21	29	50	solid

a) Measured by GPC (vs. polystyrene standards). b) Ratios of substituents on the silicon atoms were determined by ^{1}H NMR.[8] R is phenyl group for **3a** - **3f**, hexyl for **3g**, and cyclohexyl for **3h**. c) Three peaks were observed. Other peaks; Mw(Mw / Mn) 1550 (1.0), 840 (1.0).

In the reactions, oily oligosilanes **3a** - **3d** of Mw 530 - 720 were formed from the reaction of **1a** or **1b** in the presence of phenylsilanes **2a** or **2b**, respectively. Whereas soluble white powdery polysilanes **3e** and **3f** of Mw 3300 - 7000 were obtained when **1c** was employed. Triethoxysilane **2b** always gave polysilanes of larger molecular weight than diethoxysilane **2a**. Because both Si-Si bond and Si-OEt bond are potential crosslink point in the polysilane framework, it is understandable that numbers of ethoxy groups in disilanes and silanes affected the molecular weight of polysilanes. Molecular weight of the products were strongly dependent on what ethoxydisilane was used in this case. Relative number of phenyl groups on the silicon atoms increased from 15 to 40% with decreasing molecular weight of polysilane, which means that disilanes with more ethoxy groups gave the polysilanes with less phenyl groups. Reactivity of **1c** would be greater than phenylsilanes, while the reactivity of **1a** would not be so different from phenylsilanes. Consequently **1c** would have high tendency to react by itself, and therefore a smaller amount of phenyl substituent was incorporated into the polysilanes.

UV-Vis absorption spectra of **3a** - **3f** are shown in Fig. 1. Oligosilanes **3a** - **3d** did not have absorptions over 320 nm, but higher molecular weight **3f** and **3e** absorbed at longer wavelength. Absorption of **3f** reached to 400 nm and indicated a network polysilane framework of **3f**.[9] Absorption of **3e** showed a readily apparent absorption maximum at 302 nm compared with that of **3f**, which may suggest that **3e** has a longer linear segment in the framework.

Disproportionation reactions in the presence of **2c** or **2d** also gave polysilanes with corresponding substituents, respectively. Molecular weight and the numbers of introduced alkyl groups for the products are summarized in Table 1. UV-Vis spectra of **3g** and **3h** were similar to those of **3e** and **3f.**

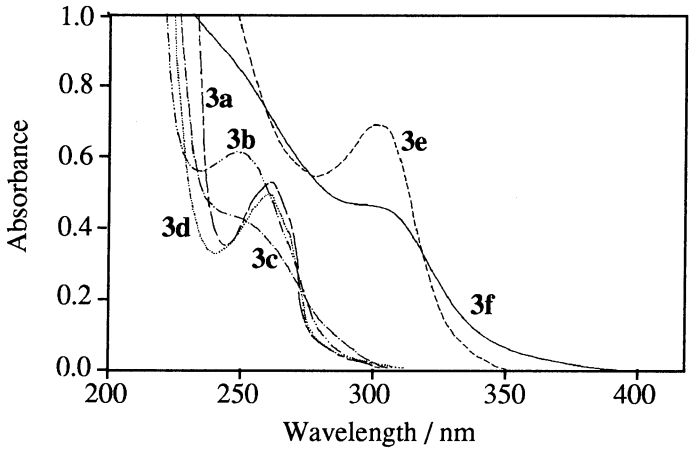


Fig. 1. UV-Vis absorption spectra of **3a** - **3f** (1.0 g dm^{-3} in tetrahydrofuran).

^{29}Si NMR and IR of the products were measured in order to obtain structural information. For example, **3g** showed two of large broad signals centered at -62 and -53 ppm and small broad signals from -40 through 10 ppm in ^{29}Si NMR (CP-MAS) spectrum and IR absorption bands at 1080 (Si-OEt) and 1250 (Si-Me) cm^{-1}. ^{29}Si NMR signals of -62 and -53 were considered to be ascribed to hexyl- and methylsilyne units[9] and hexylethoxy- and methylethoxysilylene units, respectively. It was difficult to evaluate the extent of siloxane bond in the polysilanes, which could be formed from the reactions, because IR absorption of siloxane bond was to be observed at the same region of Si-OEt bond.

Disproportionation reaction of pentamethylethoxydisilane (**1d**) was then carried out in order to investigate the mechanistic aspect of this reaction. Reaction of **1d** was catalyzed by 10 mol% of sodium ethoxide and 10 mol% of hexamethylphosphoric triamide (HMPA) at 70 °C. The reaction did not proceed without HMPA. The reaction turned out to give permethylated linear oligosilanes mainly with small amount of cyclic oligosilanes by ^{1}H NMR and GC-MS analyses. Relative GC area ratio is shown in Table 2. Linear octamethyltrisilane was formed most abundantly and the amount reduced exponentially with increasing Si atom numbers.

Table 2. Relative GC Area Ratio for the Products in the Reaction of Pentamethylethoxydisilane

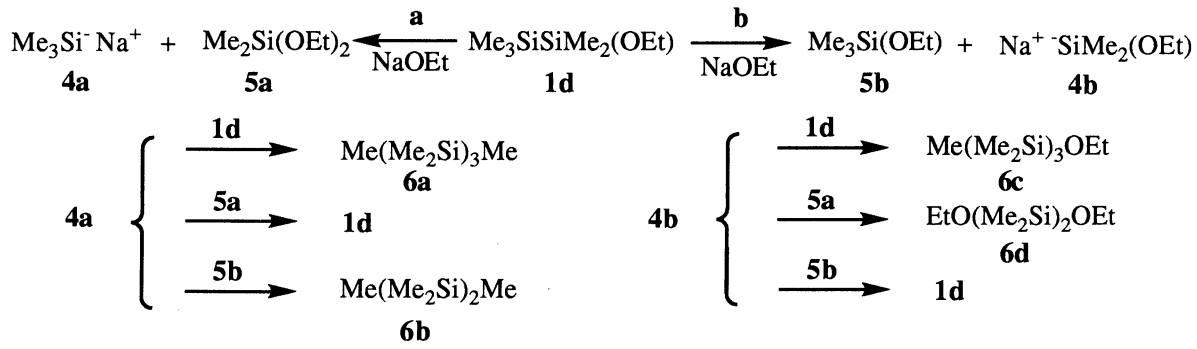
n[a]	2	3	4	5	6	7	8	9	10	11	c-5[b]	c-6[b]	c-7[b]
Area ratio	3	100	55	31	17	9	5	3	1	trace	2	18	trace

a) $Me(Me_2Si)_nMe$. b) Cyclic compounds. $(Me_2Si)_n$.

We propose a possible mechanism for the reaction of pentamethylethoxydisilane shown in Scheme 1. Disilane **1d** was cleaved in two ways **a** or **b** to give either **4a** and **5a** or **4b** and **5b**. Then silyl anions **4a** and **4b** were reacted with **1d**, **5a**, or **5b** to give **6a** - **6d** or **1d**. Permethylated oligosilanes **6a** and **6b** were no longer reactive in this conditions. But **6c** and **6d** were further reacted with other silyl anions or cleaved by sodium ethoxide. Eventually all ethoxyoligosilanes were converted to unreactive permethylated oligosilanes. Cyclic oligosilanes could be formed from **6d**.

Reactions of disilanes **1a** - **1c** in the presence of ethoxysilanes **2a** - **2d** were thought to proceed in a similar manner. Silyl anions cleaved from **1a** - **1c** attacked not only disilanes and methylethoxysilanes but **2a** - **2d** to give disilanes with phenyl, hexyl, or cyclohexyl groups along with methylethoxydisilanes and trisilanes

at the beginning of the reactions. Then newly formed substituted disilanes were reacted with silyl anions or cleaved by sodium ethoxide to give other substituted disilanes or trisilanes. The catalytic reactions proceeded and polysilanes with phenyl, hexyl, or cyclohexyl groups were formed finally.



Scheme 1. Proposed reaction mechanism for the reaction of pentamethyldisilane.

In conclusion, we disclose that many kinds of substituted polysilanes could be prepared by the one pot disproportionation reaction of easily available methylalkoxydisilanes with a wide variety of substituted alkoxysilanes. The disproportionation reactions in the presence of other alkoxysilanes are now in progress.

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8) **3f**: ^{1}H NMR ($CDCl_3$): δ 0.1 - 1.0 (m, Si-CH_3), 1.1 - 1.6 (m, O-C-CH_3), 3.5 - 4.2 (m, O-CH_2-C), 6.8 - 7.9 (m, Ph). ^{1}H NMR spectra for **3a** - **3e** are similar to that for **3f** except for the signal intensities. **3g**: ^{1}H NMR ($CDCl_3$): δ 0.2 (br. s, 26H, Si-CH_3), 0.4 - 0.6 (m, 15H, Si-CH_2-), 0.9 - 1.9 (m, 113H, other protons), 3.6 - 4.1 (m, 20H, O-CH_2-C); **3h**: ^{1}H NMR ($CDCl_3$): δ 0.1 (br. s, 12H, Si-CH_3), 0.7 - 1.9 (m, 32H, cyclohexyl), 1.2 (t, J = 7 Hz, 21H, O-C-CH_3), 3.8 (q, J = 7 Hz, 14H, O-CH_2-C).
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