

Syntheses and Properties of Sila-Functional Oligosiloxanes—Linear and Cyclic Tetrasiloxanes with Methyl and Vinyl Groups—

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The syntheses of the titled oligosiloxanes by controlled hydrolysis of the corresponding isocyanatosilanes under vapor phase or in THF (or THF/ether) were investigated. The vapor phase hydrolysis of $RSi(NCO)_3$ (R = Me, Vinyl) with a water–1,4-dioxane vapor gave the disiloxanes $[R(OCN)_2Si]_2O$ in yields of 85% (R = Me) and 90% (R = Vinyl). Further vapor phase hydrolysis of the disiloxanes provided the linear tetrasiloxanes $NCO[SiR(NCO)O]_3SiR(NCO)_2$ in yields of 71% (R = Me) and 69% (R = Vinyl). The cyclotetrasiloxanes $[R(OCN)SiO]_4$ were synthesized in yields of 12% (R = Me) and 33% (R = Vinyl) or 24% (R = Me) and 58% (R = Vinyl) by hydrolysis of the disiloxanes or of the linear tetrasiloxanes in THF, respectively. On the other hand, the linear tetrasiloxanes $OCN[SiR(OPr^i)O]_3SiR(OPr^i)(NCO)$ were obtained in yields of 50% (R = Me) and 56% (R = Vinyl) by hydrolysis of $[R(OCN)(Pr^iO)Si]_2O$ prepared from $RSi(OPr^i)(NCO)_2$ under mild conditions in THF/ether, while the cyclic tetrasiloxanes $[R(Pr^iO)SiO]_4$ were afforded in the yield of 61–62% by hydrolysis of the disiloxanes under more severe conditions in THF.

Isocyanatosilanes are heterocumulene type pseudo-halides and are expected to be new chlorine-free chemical agents, since they produce cyanic acid instead of hydrogen chloride upon substitution with nucleophiles. Nowadays, the practical uses of isocyanatosilanes are widely developing in the industrial fields as vulcanizers and cross-linking agents for resins, surface treatment and coupling agents for organic and inorganic materials, and precursors for polysiloxanes. The application of isocyanatosilanes are based on the substitution or addition reaction with hydroxy and amino groups: The nucleophilic substitution reaction with alcohols and amines provides alkoxysilanes or aminosilanes,[1,2] while the addition reaction with amines forms silylureas[3,4] although the reaction competitively takes place with the substitution reaction depending on the structure and basicity of the amines.

A key factor when selectively synthesizing the substitution products by the reactions such as hydrolysis and alcoholysis is the reactivity of the sila-functional silanes which is reported to be in the order[5–7] $Et_3SiNCS < Et_3SiNCO < Et_3SiBr < Et_3SiCl$. The reactivity of isocyanatosilanes is lower than that of the corresponding halosilanes but higher than that of alkoxysilanes. The moderate reactivity of the isocyanato group, therefore, has resulted in the stepwise nucleophilic substitution reaction of $R_{4-n}Si(NCO)_n$ (R = Me, Ph; n = 1–4) with alcohols to form partially alkoxy substituted silanes[8,9] and even the silane with different alkoxy groups, *t*-butoxy(ethoxy)(isopropoxy)(methoxy)silane,[10] which suggests that the reaction can be applied to the selective synthesis of oligosiloxanes with a desirable structure.

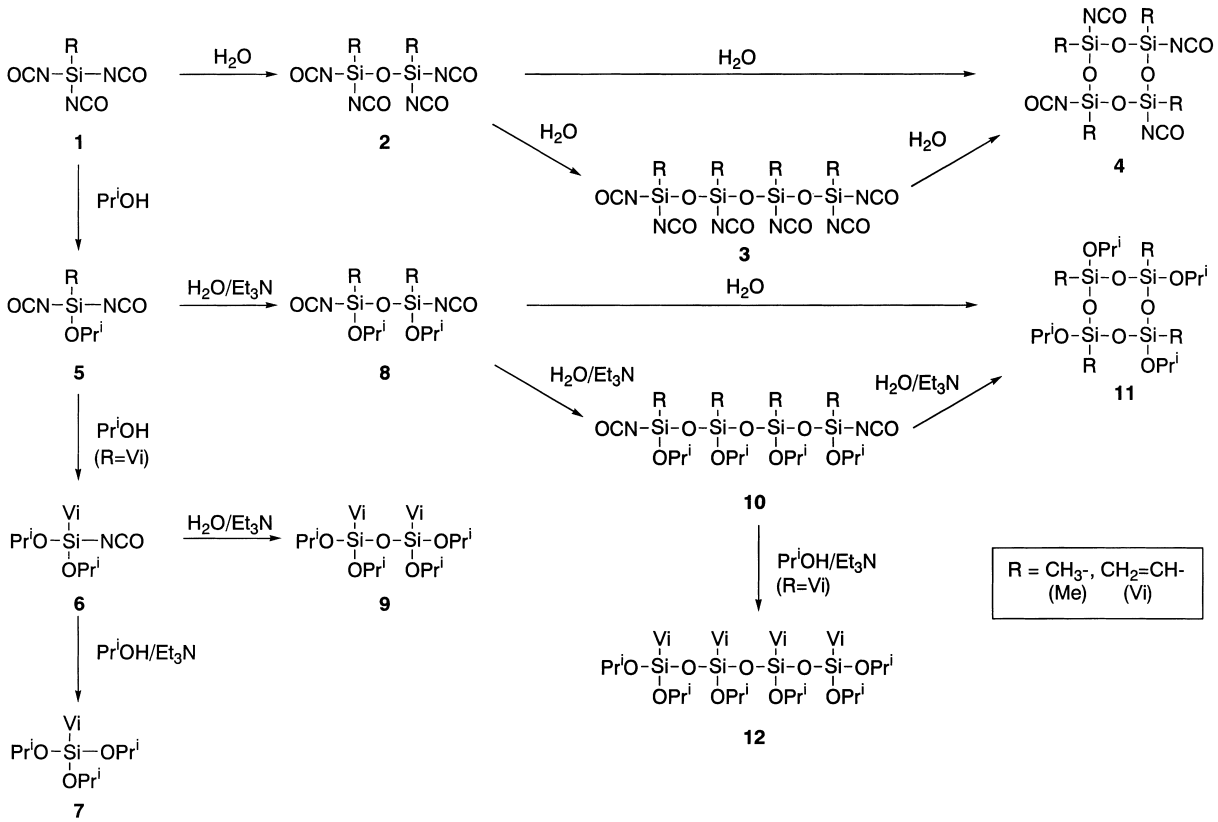
Several sila-functional oligosiloxanes have already been reported; these include $Cl_3Si(OSiCl_2)_nCl$ (n = 2–8),[11,12] $Cl_2SiR(OSiRCl)_nCl$ (R = Me, Et; n = 1–5),[13] $(OSiCl_2)_m$ (m = 3–6),[12] and $(OSiRCl)_m$ (R = Me, Et; m = 3–6).[13] These compounds were only determined by gas chromatograph-mass spectrometry without their isolation and characterization. The preparation of sila-functional oligosiloxanes often occurs due to their high reactivity to provide byproducts. This is why sila-functional oligosiloxanes have not been a versatile reagent and why only several difunctional disiloxanes are commercially available so far.

Recently, we have developed a facile synthetic route of sila-functional oligosiloxanes using isocyanatosilanes as already communicated.[14,15] This technique provides the isolation of sila-functional oligosiloxanes on a preparative scale. In this study, we wish to report the selective synthesis of methyl and vinyl substituted oligosiloxanes as isolatable reagents.

Results and Discussion

A serious problem for the oligosiloxanes is the synthetic routes. Certainly there are several procedures to form siloxane bonds: (1) Hydrolysis of sila-functional silanes, (2) condensation reaction between silanes with different sila-functional groups such as chloro, hydroxy, amino and alkoxy groups, and (3) oxidation of silanes with silicon-silicon bond. Route (3) may be preferable when oligosilanes with definite structure and suitable reaction conditions are provided. Route (2) has led to the synthesis of polysiloxanes rather than oligosiloxanes. Of course, siloxanes are conveniently prepared by route (1) using chlorosilanes as the starting material. In the conventional procedure, however, oligosiloxanes are obtained in a very low yield by repeated fractional distillation of a hydrolysis product formed as a mixture. No convenient route has yet been developed to synthesize only the desirable sila-functional oligosiloxane.

The key factor to obtain such sila-functional oligosiloxanes should be the reaction based on the reactivity of the sila-func-



Scheme 1.

tional groups; the organic groups, the procedure and the reaction conditions will also be important. The reactivity of the chloro group is too high to control the hydrolysis and condensation of methyl- and vinyltrichlorosilanes, while the reactivity of the alkoxy group is too low to promote the reactions smoothly. We reported that the isocyanato group attached to silicon is stepwise substituted during the reaction with alcohols to give partially substituted derivatives of alkoxyisocyanatosilanes;[15] moreover, the vapor phase hydrolysis of isocyanatosilanes using the apparatus we designed provides isocyanatodisiloxanes in almost quantitative yields.[14] These results allow us to do further experiments on the synthesis of sila-functional isocyanatooligosiloxanes starting with $RSi(NCO)_3$ **1** (R = Me, Vinyl) which have been commercially available or easily prepared by the reaction of the trichlorosilane with sodium cyanate,[16] as shown in Scheme 1.

Synthesis of 2 by the Vapor or Liquid Phase Hydrolysis of Triisocyanatosilanes. In order to confirm the effectiveness of these methods, the hydrolysis was operated in the liquid phase (process A) or vapor phase (process B), followed by gas chromatography (GC) to determine the relative yield of the products as a volatile component. In process A, water in THF at various molar ratios H_2O/**1** (Me: 0.250–0.875, Vinyl: 0.250–0.625) was added dropwise to the silanes (R = Me, Vinyl) in THF at 0 °C and then the mixtures were stirred for a certain time. Filtration and distillation under reduced pressure gave the isocyanatodisiloxanes **2**. In process B, a mixed vapor of water and 1,4-dioxane was introduced at the rate of 500 mL/min into the silane **1** refluxing under reduced pressure using an apparatus described in a previous paper.[14] Distillation of the product under reduced pressure gave the isocyanatodisiloxanes **2**.

Table 1 summarizes the results and the reaction conditions. In process A, the GC yield of **2** increased to 58% (R = Me) and 41% (R = Vinyl) with the increasing yield of the oligomers other than **2**, when the molar ratio of H_2O/**1** increases up to 0.500. The yield of **2** decreases when the molar ratio was higher than the stoichiometry, accompanied by an increasing amount of residual product as a nonvolatile component. The isolated yield of **2** is higher in the case of No. 1 than that of No. 3, which is correlated to the higher reactivity of the nucleophilic substitution of **1** (R = Me) compared with **1** (R = Vinyl). The lower the reactivity of **1**, the slower the hydrolysis and condensation, which results in an uncontrolled reaction and/or the formation of oligosiloxanes other than **2**.

In process B, the controlled hydrolysis and condensation are realized as exemplified by the almost quantitative yields in Table 1 in addition to absences of starting and residual materials. The key factors in this process are the reaction molar ratio H_2O/**1** and the flow rate of the water–1,4-dioxane mixed vapor. The process is characterized by the controlled vapor phase hydrolytic condensation without solvents where a small amount of 1,4-dioxane acts as a diluent to control the flow rate of the mixed vapor of water–1,4-dioxane. Water and **1** should mix at the molecular level and the intermediate hydrolysis product will immediately condense with **1** between the isocyanato group and silanol group to yield **2**. Since the formed disiloxanes **2** are not vaporized under the experimental conditions be-

Table 1. Results on the Preparation of **2**

No.	R in **1**	Process[a]	Relative yield by gas chromatography/%[b]			Isolated yield of **2**/%
			1	**2**	Oligomers[c]	
1	Me[d]	A	8	58	34	46
2	Me[e]	B	0	88	12	85
3	Vi[f]	A	15	41	44	30
4	Vi[g]	B	0	97	3	92

a) Process A: Liquid phase hydrolysis. Process B: Vapor phase hydrolysis. b) Calculated based on gas chromatography peak area. c) Oligomers except for **2**. d) Scale of **1** (R = Me) in operation: 16.9 g (0.1 mol). Water: 0.9 g (0.05 mol). Solvent: THF (40 mL). Temp: 0 °C. e) Scale of **1** (R = Me) in operation: 169.2 g (1.0 mol). 1,4-Dioxane: 100 mL. Flow rate: 500 mL/min. Pressure: 1.3 kPa. f) Scale of **1** (R = Vi) in operation: 108.7 g (0.6 mol). Water: 5.4 g (0.3 mol). Solvent: THF (200 ml). Temp: 0 °C. g) Scale of **1** (R = Vi) in operation: 108.7 g (0.6 mol). 1,4-Dioxane: 60 mL. Flow rate: 500 mL/min. Pressure: 3.1 kPa

Table 2. Results on the Hydrolysis of **2**

No.	R in **2**	Process[a]	Pressure /kPa	Molar ratio H_2O/**2**	Relative yield/%[b]				Isolated yield/%	
					2	**3**	**4**	Oligomers[c]	**3**	**4**
1	Me[d]	A	101	0.5	13	38	12	37	27	
2	Me[d]	A	101	1.0	0	28	15	73		12
3	Me[e]	B	2.2	0.5	6	75	5	14	71	
4	Vi[f]	A	101	0.5	14	51	12	23	42	
5	Vi[g]	A	101	1.0	0	10	40	50		33
6	Vi[h]	B	2.6	0.5	5	80	5	10	69	

a) Process A: Liquid phase hydrolysis. Process B: Vapor phase hydrolysis. b) Calculated based on gas chromatograph peak area. c) Oligomers except for **2**, **3** and **4**. d) Scale of **2** (R = Me) in operation: 27.0 g (0.1 mol). THF: 40 mL. e) Scale of **2** (R = Me) in operation: 54.0 g (0.2 mol). 1,4-Dioxane: 40mL. Flow rate 500 mL/min. f) Scale of **2** (R = Vi) in operation: 29.4 g (0.1 mol). THF: 40 mL. g) Scale of **2** (R = Vi) in operation: 14.7 g (0.05 mol). THF: 20 ml. h) Scale of **2** (R = Vi) in operation: 88.3 g (0.3 mol). 1,4-Dioxane: 30mL. Flow rate 400 mL/min.

cause their boiling points are higher than those of **1**, no further hydrolysis and condensation take place, and **2** is easily isolated only by distillation of the hydrolysis product.

Synthesis of Linear and Cyclic Isocyanatotetrasiloxanes 3 and 4. The tetrasiloxanes **3** and **4** were synthesized by processes A and B with **2**, which essentially used the procedures for the synthesis of **2** according to Scheme 1. Table 2 summarizes the results and the reaction conditions. For the synthesis of **3** by process A, it is important to establish the reaction conditions to minimize the formation of **4** and/or to prevent an azeotropic distillation and the formation of oligomers other than **3** and **4**. As the molar ratio of water increasesd above 0.05, the relative yield of oligomers increased more than those of **3** and **4**. The reaction conditions of Nos. 1 and 4 were found to be preferable to isolate **3** (R = Me, Vinyl). In the liquid phase, the hydrolysis was uncontrollable, because the starting material and the product coexisted, and subsequently, complicated condensations took place to form polysiloxanes. On the other hand, process B selectively provided the tetrasiloxanes (Nos. 3 and 6) based on the same mechanism as in the vapor phase hydrolysis of **1**. The isolated yield was lower compared with that for the synthesis of **2**, which is due to the difficulty in the flow rate control of the mixed vapor of water–1,4-dioxane. The higher the boiling point, the more difficult the controlled hydrolysis.

The synthesis of **4** was performed according to the two routes in process A as shown in the Scheme, i.e. direct hydrolysis of **2** to **4** or the liquid phase hydrolysis of **3** followed by the vapor phase hydrolysis of **2**. For the direct hydrolysis with the molar ratio of H_2O/**3** less than 0.5, **4** was formed in low yield and was unable to be isolated. Compound **4** was provided in yields of 12% (No. 3) and 33% (No. 5) for the hydrolysis in the molar ratio of H_2O/**2** = 1.00, accompanied by the formation of a large amount of oligomers. The vapor phase hydrolysis of **2** provided **3** in yields of 71% (No. 3, R = Me) and 69% (No. 6, R = Vinyl) as is shown in Table 2. The following liquid phase hydrolysis of **3** in the molar ratio of H_2O/**3** = 1.00 gave **4** in yields of 26% (R = Me) and 34% (R = Vinyl). The overall yields of the processes were evaluated to be 18% (R = Me) and 23% (R = Vinyl). Because of the short process and the almost comparable yields in process A, the direct hydrolysis is preferable.

Synthesis of Isopropoxy Substituted Di- and Tetrasiloxanes 5–12. We already reported that triisocyanato(methyl)silane reacts with ethanol to provide ethoxyisocyanato(methyl)silanes with various degrees of substitution in quantitative yields. These facts are due to the moderate reactivity of the isocyanato group under the selected reaction conditions in the

Table 3. Results on the Hydrolysis of **8**[a)]

No.	R in **8**	Solvent (mL)	Molar ratio		Isolated yield/%	
			H_2O/**8**	Et_3N/**8**	**10**	**11**
1	Me[b)]	THF (20)/Diethyl ether (20)	0.5	0.1	50	
2	Me[b),c)]	THF (40)	1.0	1.0		61
3	Vi[d)]	THF (15)/Diethyl ether (15)	0.5	0.5	56	
4	Vi[c),d)]	THF (30)	1.0	1.0		62

a) Temp: 0 °C. Time: 2 h. Reflux time: 2 h. b) Scale of **8** (R = Me) in operation: 15.2 g (0.05 mol). c) Compound **8** was added dropwise to water for hydrolysis. d) Scale of **8** (R = Vi) in operation: 9.58 g (0.03 mol).

presence of triethylamine.[12] In this study, the isopropoxy substituted silanes **5**–**7** and the disiloxanes and tetrasiloxanes **8**–**12** were synthesized according to Scheme 1. The silanes **5**–**7** were provided in quantitative yields by the same procedures in the absence (**5** and **6**) or presence (**7**) of triethylamine, where the reaction with 2-propanol proceeds more slowly than that with ethanol.

Although the reaction of **2** with 2-propanol provides the disiloxanes **8** and **9**, they were synthesized by the hydrolysis of **5** and **6** in this study. Depending on the hydrolyzability of the isocyanato group, the vapor phase hydrolysis of **5** and the liquid phase hydrolysis of **6** were found to be preferable for preparing the disiloxanes **8** and **9**, respectively. The hydrolysis and condensation of **5** in the liquid phase was uncontrollable because of the fast reaction rates. The selective hydrolysis of **6** in the vapor phase was also unexpected, because both the isopropoxy and isocyanato groups were found to be competitively hydrolyzed. In addition, a slight difference in the boiling point between **6** and **9** makes it difficult to separate them by distillation.

The results for the synthesis of tetrasiloxanes **10** and **11** according to Scheme 1 are summarized in Table 3. Since the vapor phase hydrolysis of **8** did not proceed, the liquid phase hydrolysis was investigated under the various processes (A and C) and reaction conditions: The reaction appreciably proceeded in the presence of triethylamine and subsequently formed the linear siloxane **10** or the cyclic siloxane **11** as the predominant component depending on the molar ratio to **8**. The reaction in THF (Nos. 2 and 4) tends to form **11** rather than **10** in relatively high yields compared with that in the mixed solvent of THF–ether (Nos. 1 and 3). The siloxane **10** was formed by the addition of water to **8** (Process A, Nos. 1 and 3), while the addition of **8** to water (Process C, Nos. 2 and 4) afforded the siloxane **11**. Thus the polarity of the solvent, the catalyst, and the molar ratio of water were found to establish a controlled hydrolysis for the production of silanes **10** and **11** as the major products in good yields.

The cyclic tetrasiloxane **11** was synthesized in yields of 74% (R = Me) and 71% (R = Vinyl) by Process A when started from **10**. The total yield of **11** starting from **8** is 37% (R = Me) or 40% (R = Vinyl), which is lower than that of 61% (R = Me) or 62% (R = Vinyl) by Process C starting from **8**. Therefore, the direct route by Process C is confirmed to be better to obtain **11**. The fully isopropoxy substituted silane **12** (R = Vinyl) was synthesized in the quantitative yield of 94% by the reaction of **10** with 2-propanol using THF as the solvent in the molar ratio of Pr^iOH/**10** = 4 in the presence of triethylamine. Two moles of isopropyl carbamate were filtered out as a precipitate.

Experimental

General Procedure. The gas chromatograms (GC) were recorded by using a GL Science GC-390 Gas Chromatograph equipped with an SE-30 packed column (5 mmϕ × 5 m). Injection temp: 290 °C. Column temp: 80–290 °C. TCD detector temp: 290 °C. Carrier gas and flow rate: helium (65 mL/min).

The ^{1}H, ^{13}C, and ^{29}Si nuclear magnetic resonance (NMR) spectra were measured using JEOL JNM-FX400 or Bruker DPX 300 NMR spectrometers in chloroform-*d*.

The Fourier transformed infrared (FTIR) spectra were recorded on a JASCO FT/IR 410 spectrometer by the carbon tetrachloride solution method or the KBr disk method.

Gas chromatograph-mass spectrometry (GC-MS) results were acquired using a Shimadzu GCMS-QP2000A Gas Chromatograph/Mass Spectrometer equipped with an OV-1 coated capillary column (0.25 mmϕ × 50 m). Injection temp: 290 °C. Column temp: 80–300 °C.

The silicon content was determined by the wet method as follows: a 0.1 g sample was weighed in a flask and heated in the presence of ammonium nitrate (0.8 g), ammonium sulfate (0.8 g), and sulfuric acid (15 mL). The residue was poured into ice (100 g) carefully, followed by filtration. The residue was then subjected to firing in a crucible, followed by weighing and calculated as SiO_2.

Syntheses of Triisocyanato(methyl)silane (1, R = Me) and Triisocyanato(vinyl)silane (1, R = Vi). Triisocyanato(methyl)silane (**1**, R = Me) and triisocyanato(vinyl)silane (**1**, R = Vi) were synthesized according to the literature methods.[16]

Syntheses of 1,1,3,3-Tetraisocyanato-1,3-dimethyldisiloxane (2, R = Me) and 1,1,3,3-Tetraisocyanato-1,3-divinyldisiloxane (2, R = Vi). The synthesis of **2** was examined using Processes A and B.

Process A: A THF solution of water was added dropwise to the THF solution of **1** at 0 °C. **2** was isolated by filtration, followed by distillation under reduced pressure.

Process B[11]: Into refluxing **1** at the pressure of 1.33–3.33 kPa, the mixed vapor of water and 1,4-dioxane was pumped at the rate of 500 ml/min. Compound **2** was isolated by distillation under reduced pressure.

2 (R = Vi) Yield 92% (Process B). Bp 91.8–92.5 (240 Pa). IR 1100, 1450, 1620, 2272, 3000 cm^{-1}; ^{1}H NMR (400 MHz) δ 6.09 (dd, 2H), 6.25 (dd, 2H), 6.42 (dd, 2H); ^{13}C NMR (100.6 MHz) δ 123.2 (s), 127.7 (t), 139.4 (d); ^{29}Si NMR (79.5 MHz) δ −74.8 (s). MS *m*/*z* 267 ($M^+ - 27$). Found: Si, 18.9%. Calcd for $C_8H_6O_5N_4$-

Si_2: Si, 19.1%.

Syntheses of 1,1,3,5,7,7-Hexaisocyanato-1,3,5,7-tetramethyltetrasiloxane (3, R = Me) and 1,1,3,5,7,7-Hexaisocyanato-1,3,5,7-tetravinyltetrasiloxane (3, R = Vi). The synthesis of **3** was examined using Processes A and B.

Process A: A THF solution of water was added dropwise to the THF solution of **2** at 0 °C. **3** was isolated by filtration, followed by distillation under reduced pressure.

Process B: Into refluxing **2** at the pressure of 2.27–2.67 kPa, the mixed vapor of water and 1,4-dioxane was pumped in at the rate of 400–500 ml/min. Compound **3** was isolated by distillation under reduced pressure.

3 (R = Vi) Yield 69% (Process B). Bp 158.2–161.5 (267 Pa). IR 1100, 1404, 1603, 2274, 2962 cm^{-1}; ^1H NMR (400 MHz) δ 5.91–6.29 (br, 12H); ^{13}C NMR (100.6 MHz) δ 123.0 (s), 128.2 (t), 128.3 (t), 139.39 (d), 139.45 (d); ^{29}Si NMR (79.5 MHz) δ −75.3 (s), −76.8 (s). MS *m/z* 494 ($M^+ - 27$). Found: Si, 21.6%. Calcd for $C_{14}H_{12}O_9N_6Si_4$: Si, 21.4%.

Syntheses of 2,4,6,8-Tetraisocyanato-2,4,6,8-tetramethylcyclotetrasiloxane (4, R = Me) and 2,4,6,8-Tetraisocyanato-2,4,6,8-tetravinylcyclotetrasiloxane (4, R = Vi). A THF solution of water was added dropwise to the THF solution of **2** (or **3**) at 0 °C, then stirred for 2 h and refluxed for 2 h. Compound **4** was isolated by filtration, followed by distillation under reduced pressure.

4 (R = Me) Yield 12% (started from **2**), 26% (started from **3**). Bp 133.0–134.2 (400 Pa). IR 1110, 1270, 2290, 2975 cm^{-1}; ^1H NMR (400 MHz) δ 0.36 (br, 12H); ^{13}C NMR (100.6 MHz) δ −2.2 (s), 123.0 (s); ^{29}Si NMR (79.5 MHz) δ −60.4 to −61.1 (br). MS *m/z* 389 ($M^+ - 15$). Found: Si, 27.8%. Calcd for $C_8H_{12}O_8N_4Si_4$: Si, 27.8%.

4 (R = Vi) Yield 33% (started from **2**), 34% (started from **3**). Bp 131.0–132.4 (330 Pa). IR 1112, 1404, 1599, 2288, 2962 cm^{-1}; ^1H NMR (400 MHz) δ 5.95–6.25 (br, 12H); ^{13}C NMR (100.6 MHz) δ 123.0 (s), 128.3 (t), 138.9 (d); ^{29}Si NMR (79.5 MHz) δ −75.72 to −76.14 (br). MS *m/z* 426 ($M^+ - 27$). Found: Si, 24.8%. Calcd for $C_{12}H_{12}O_8N_4Si_4$: Si, 24.9%.

Syntheses of Diisocyanato(isopropoxy)(vinyl)silane (5), Isocyanato(diisopropoxy)(vinyl)silane (6), and Triisopropoxy-(vinyl)silane (7). Into the THF (50 mL) solution of **1** 18.17 g (0.10 mol), isopropyl alcohol 6.00 g (0.10 mol), 12.00 g (0.20 mol), or 18.00 g (0.30 mol) was added dropwise at 0 °C. Upon the synthesis of **7**, triethylamine 5.06 g (0.05 mol) was added. Stirring was continued for 1 h at 0 °C, and then refluxed for 2 h. After removal of the solvents and filtration, **5**, **6**, or **7** was isolated by distillation under reduced pressure.

5 Yield 95%. Bp 46.0 (240 Pa). IR 1060, 1410, 1620, 2267, 2980 cm^{-1}; ^1H NMR (400 MHz) δ 1.24 (d, 18H), 4.30 (sep, 3H), 5.93–6.16 (br, 3H); ^{13}C NMR (100.6 MHz) δ 25.6 (q), 65.0 (d), 132.3 (t), 135.8 (d); ^{29}Si NMR (79.5 MHz) δ −62.5 (s). MS *m/z* 183 ($M^+ - 15$). Found: Si, 11.9%. Calcd for $C_7H_{10}O_3N_2Si$: Si, 12.1%.

6 Yield 83%. Bp 86.8 (4.60 kPa). IR 1060, 1420, 1605, 2280, 2980 cm^{-1}; ^1H NMR (400 MHz) δ 0.80 (d, 12H), 3.84 (sep, 2H), 5.54–5.60 (br, 3H); ^{13}C NMR (100.6 MHz) δ 25.6 (q), 65.5 (d), 123.0 (s), 132.3 (t), 135.8 (d); ^{29}Si NMR (79.5 MHz) δ −65.3 (s). MS *m/z* 215 (M^+). Found: Si, 13.4%. Calcd for $C_9H_{17}O_3NSi$: Si, 13.1%.

7 Yield 94%. Bp 89.2 (5.27 kPa). IR 1040, 1420, 1600, 3000 cm^{-1}; ^1H NMR (400 MHz) δ 2.75 (d, 6H), 5.78 (sep, 1H), 7.48–7.56 (br, 3H); ^{13}C NMR (100.6 MHz) δ 25.2 (q), 68.0 (d), 123.5 (s), 129.1 (t), 138.6 (d); ^{29}Si NMR (79.5 MHz) δ −69.7 (s). MS *m/z* 232 (M^+). Found: Si, 14.0%. Calcd for $C_{11}H_{24}O_3Si$: Si, 14.2%.

Synthesis of 1,3-Diisocyanato-1,3-diisopropoxy-1,3-divinyldisiloxane (8, R = Vi). Into a refluxing **5** (R = Vi) at the pressure of 3.73 kPa, a mixed vapor of water and 1,4-dioxane was pumped in at the rate of 500 mL/min. Compound **8** (R = Vi) was isolated by distillation under reduced pressure.

8 (R = Vi) Yield 77%. Bp 83.0–83.8 (240 Pa). IR 1045, 1100, 1420, 1600, 2280, 3000 cm^{-1}; ^1H NMR (400 MHz) δ 1.22 (d, 12H), 4.34 (sep, 2H), 5.89–6.18 (br, 6H); ^{13}C NMR (100.6 MHz) δ 25.4 (q), 67.0 (d), 123.5 (s), 129.7 (t) 139.4 (d); ^{29}Si NMR (79.5 MHz) δ −70.0 (s). MS *m/z* 313 ($M^+ - 59$). Found: Si, 17.0%. Calcd for $C_{12}H_{20}O_5N_2Si_2$: Si, 17.1%.

Synthesis of 1,1,3,3-Tetraisopropoxy-1,3-divinyldisiloxane (9). Into the THF solution of **6** 10.76 g (0.050 mol) and triethylamine 1.01 g (0.01 mol), a THF solution of water was added dropwise at 0 °C. Stirring was continued for 1.5 h at 0 °C, and then the mixture was refluxed for 2 h. After filtration of the precipitate, **9** was isolated by distillation under reduced pressure.

9 Yield 55%. Bp 90.0–91.0 (267–333 Pa). IR 1045, 1150, 1400, 1600, 2980 cm^{-1}; ^1H NMR (400 MHz) δ 1.2 (d, 24H), 4.3 (sep, 4H), 6.0 (br, 6H); ^{13}C NMR (100.6 MHz) δ 25.6 (q), 65.2 (d), 131.8 (t), 135.6 (d); ^{29}Si NMR (79.5 MHz) δ −68.9 (s). MS *m/z* 335 ($M^+ - 27$). Found: Si, 15.6%. Calcd for $C_{16}H_{34}O_5Si_2$: Si, 15.4%.

Syntheses of 1,7-Diisocyanato-1,3,5,7-tetraisopropoxy-1,3,5,7-tetramethyltetrasiloxane (10, R = Me) and 1,7-Diisocyanato-1,3,5,7-tetraisopropoxy-1,3,5,7-tetravinyltetrasiloxane (10, R = Vi). Into a THF or a THF/diethyl ether (v/v = 1) mixed-solvent solution of **8** and triethylamine, a THF or a THF/diethyl ether (v/v = 1) mixed-solvent solution of water was added dropwise at 0 °C, and then the mixture was refluxed for 2 h. Compound **10** was isolated by filtration followed by distillation under reduced pressure.

10 (R = Me) Yield 50%. Bp 123.5–125.5 (293 Pa). IR 1040, 1420, 1600, 3000 cm^{-1}; ^1H NMR (400 MHz) δ 0.10 (s, 6H) 0.20 (s, 6H) 1.14 (t, 24H) 4.19 (q, 4H); ^{13}C NMR (100.6 MHz) δ −3.7 (s), −2.2 (s), 25.5 (q), 25.8 (q), 65.4 (d), 66.2 (d), 122.9 (s); ^{29}Si NMR (79.5 MHz) δ −57.6 (s), −60.3 (s). MS *m/z* 481 ($M^+ - 59$). Found: Si, 20.6%. Calcd for $C_{18}H_{40}O_9N_2Si_4$: Si, 20.8%.

10 (R = Vi) Yield 56%. Bp 153.0–155.5 (400 Pa). IR 1045, 1100, 1420, 1600, 2280, 3000 cm^{-1}; ^1H NMR (400 MHz) δ 1.22 (br, 24H), 4.29 (br, 4H), 5.93–6.13 (br, 12H); ^{13}C NMR (100.6 MHz) δ 25.4 (q), 25.5 (q), 65.7 (d), 66.6 (d), 123.3 (s), 130.3 (q), 130.9 (q), 136.2 (d), 137.0 (d); ^{29}Si NMR (79.5 MHz) δ −72.3 (s), −75.2 (s). MS *m/z* 530 ($M^+ - 59$). Found: Si, 19.1%. Calcd for $C_{22}H_{40}O_9N_2Si_4$: Si, 19.1%.

Syntheses of 2,4,6,8-Tetraisopropoxy-2,4,6,8-tetramethylcyclotetrasiloxane (11, R = Me) and 2,4,6,8-Tetraisopropoxy-2,4,6,8-tetravinylcyclotetrasiloxane (11, R = Vi). A THF solution of water was added dropwise to the THF solution of **8** (or **10**) and triethylamine at 0 °C, then the mixture was stirred for 2 h and refluxed for 2 h. Compound **11** was isolated by filtration, followed by distillation under reduced pressure.

11 (R = Me) Yield 61% (started from **8**), 74% (started from **10**). Bp 102.0–103.4 (400 Pa). IR 1060, 1410, 1620, 2267, 2980 cm^{-1}; ^1H NMR (400 MHz) δ 0.86 (br, 12H), 1.91 (br, 24H), 4.95 (br, 4H); ^{13}C NMR (100.6 MHz) δ 3.7 (s), 25.4 (q), 64.8 (d); ^{29}Si NMR (79.5 MHz) δ −59.3 to −59.8 (br). MS *m/z* 457 ($M^+ - 15$). Found: Si, 23.7%. Calcd for $C_{16}H_{40}O_8Si_4$: Si, 23.8%.

11 (R = Vi) Yield 62% (started from **8**), 71% (started from **10**). Bp 127.8–131.0 (307 Pa). IR 1060, 1420, 1605, 2280, 2980 cm^{-1};

^{1}H NMR (400 MHz) δ 1.15–1.24 (br, 24H), 4.24–4.30 (br, 4H), 5.92–6.07 (br, 12H); ^{13}C NMR (100.6 MHz) δ 26.2 (q), 66.2 (d), 131.7 (t), 136.6 (d); ^{29}Si NMR (79.5 MHz) δ −74.17 to −74.22 (br). MS *m*/*z* 505 (M^+ − 15). Found: Si, 21.3%. Calcd for $C_{20}H_{40}O_8Si_4$: Si, 21.5%.

Syntheses of 1,1,3,5,7,7-Hexaisopropoxy-1,3,5,7-tetravinyltetrasiloxane (12). Into a THF solution of **10** (R = Vi) 6.57 g (0.02 mol) and triethylamine 1.01 g (0.01 mol), a THF solution of 2-propanol was added dropwise at 0 °C. Stirring was continued for 1 h at 0 °C, and then the mixture was refluxed for 1 h. After filtration of the precipitate, **12** was isolated by distillation under reduced pressure.

12 Yield 94%. Bp 158.5–160.0 (267 Pa). IR 1045, 1150, 1400, 1600, 2980 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.18 (br, 36H), 4.33 (br, 6H), 5.93–6.11 (br, 12H); ^{13}C NMR (100.6 MHz) δ 26.2 (q), 66.2 (q), 131.9 (t), 132.0 (t), 135.2 (d), 135.4 (d); ^{29}Si NMR (79.5 MHz) δ −69.1 (s), −75.9 (s). MS *m*/*z* 563 (M^+ − 59). Found: Si, 18.3%. Calcd for $C_{26}H_{54}O_9Si_4$: Si, 18.1%.

Conclusion

1,1,3,3-Tetraisocyanato-1,3-dimethyldisiloxane (**2**, R = Me) and 1,1,3,3-tetraisocyanato-1,3-divinyldisiloxane (**2**, R = Vi), 1,1,3,5,7,7-hexaisocyanato-1,3,5,7-tetramethyltetrasiloxane, and 1,1,3,5,7,7-hexaisocyanato-1,3,5,7-tetravinyltetrasiloxane were synthesized by pumping a mixed vapor of water and 1,4-dioxane under refluxing triisocyanato(methyl)silane, triisocyanato(vinyl)silane, **2** (R = Me), and **2** (R = Vi), respectively. The mono-, di-, and triisopropoxysilanes were selectively synthesized by the reaction of triisocyanato(vinyl)silane with isopropyl alcohol by selecting the molar ratios of alcohol and triethylamine. Isopropoxy or isocyanato substituted cyclotetrasiloxanes were synthesized by the hydrolysis of the corresponding disiloxanes in good yield.

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References

1 J. Goubeau and D. Paulin, *Chem. Ber.*, **93**, 1111 (1960).
2 Y. Abe, H. Tanaka, N. Shikano, and T. Gunji, *Nippon Kagaku Kaishi*, **2001**, 157.
3 R. M. Pike and E. B. Moynaham, *Inorg. Chem.*, **6**, 168 (1967).
4 J. Goubeau and E. Heubach, *Chem. Ber.*, **93**, 1117 (1960).
5 C. Eaborn, *Nature*, **165**, 685 (1950).
6 C. Eaborn, *J. Chem. Soc.*, **1950**, 3077.
7 H. Muller and J. R. Van Wazer, *J. Organomet. Chem.*, **23**, 395 (1970).
8 Y. Abe, T. Kanemaru, T. Yamazaki, Y. Nagao, and T. Misono, *Nippon Kagaku Kaishi*, **1991**, 1094.
9 Y. Abe, A. Ito, Y. Kuno, Y. Nagao, and T. Misono, *Nippon Kagaku Kaishi*, **1992**, 649.
10 T. Gunji, S. Iwasaki, and Y. Abe, Abstracts of The Sendai International Symposium on the Frontiers of Organosilicon Chemistry, Sendai, 232 (1994).
11 H. Quellhorst, W. Andreas, N. Soger, and M. Binnewies, *Z. Naturforsch., B: Chem. Sci.*, **54**, 577 (1999).
12 S. V. Basenko, I. A. Gebel, M. G. Voronkov, L. V. Klyba, and R. G. Mirskov, Russ. *J. Gener. Chem.*, **68**, 314 (1998).
13 S. V. Basenko, M. G. Voronkov, and I. A. Gebel, *Russ. Chem. Bull.*, **49**, 363 (2000).
14 Y. Abe, K. Abe, M. Watanabe, and T. Gunji, *Chem. Lett.*, **1999**, 259.
15 T. Gunji, A. Setogawa, K. Asakura, and Y. Abe, *Bull. Chem. Soc., Jpn.*, **71**, 2967 (1998).
16 I. Kijima and Y. Mori, Japanese Patent JP 81-26895.