



Hydrolysis and condensation behavior of tetraethoxysilane, hexaethoxydisiloxane, and octaethoxytrisiloxane

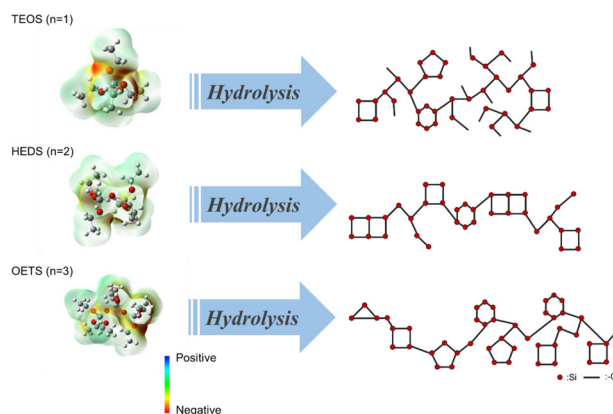
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Abstract

In the initial stage of the hydrolysis–condensation of tetraethoxysilane (TEOS), hexaethoxydisiloxane (HEDS) and octaethoxytrisiloxane (OETS) are formed. However, little is known about the hydrolysis–condensation of HEDS and OETS. In this study, the hydrolysis–condensation of TEOS, HEDS, and OETS was investigated. HEDS and OETS were synthesized from diethoxy(diisocyanato)silane, a raw material with controllable functionality. The hydrolysis of TEOS, HEDS, and OETS was analyzed by mass spectroscopy, gel permeation chromatography, and nuclear magnetic resonance. The hydrolysis–condensation product of TEOS was a three-dimensional network-type polysiloxane. The hydrolysis–condensation product of HEDS consisted mainly of four-membered cyclic siloxane. The hydrolysis–condensation product of OETS consisted mainly of various membered cyclic siloxanes.

Graphical Abstract



Keywords Ethoxysilane · Hydrolysis–condensation reaction · Oligosiloxane · NMR

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Highlights

- Hexaethoxydisiloxane (HEDS) and octaethoxytrisiloxane (OETS) were synthesized from diethoxy(diisocyanato)silane.
- Trimethylsilylates of hydrolyzates in the initial stage of tetraethoxysilane (TEOS), HEDS, and OETS hydrolysis were analyzed by FTIR, MS, and NMR.
- Hydrolysis behaviors of TEOS, HEDS, and OETS were monitored by GPC and NMR.

1 Introduction

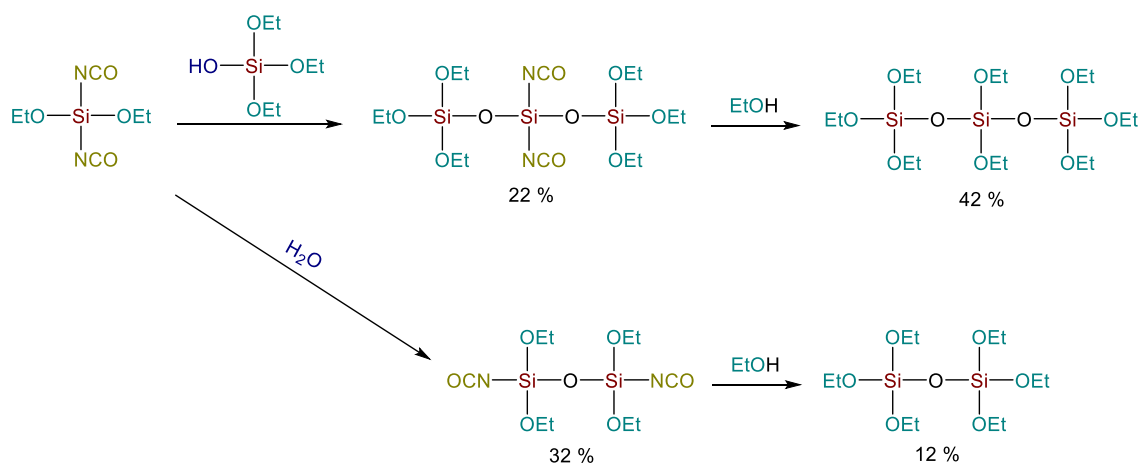
Hydrolysis–condensation of alkoxy silanes is a representative synthesis method for siloxanes [1, 2]. Tetraethoxysilane (TEOS) is the most versatile raw material for preparing silica and silicate glasses. Several studies on TEOS regarding its kinetic rate constant and hydrolysis behavior under various pH, temperature, and catalytic conditions have been conducted [3–9]. Regarding the kinetic rate constant of hydrolysis–condensation reaction of tetraethoxysilane under acidic condition, Kay and Assink reported as follows: 1) hydrolysis reaction is faster than condensation reaction; 2) water producing condensation reaction is faster than methanol producing condensation reaction (hydrolysis reaction: $0.2 \text{ mol}^{-1} \text{ min}^{-1}$, water producing condensation reaction: $0.006 \text{ mol}^{-1} \text{ min}^{-1}$, methanol producing condensation reaction: $0.001 \text{ mol}^{-1} \text{ min}^{-1}$) [10]. This kinetic rate constant is widely accepted. In contrast, we recently reported that ethanol producing condensation reaction is faster than water producing condensation reaction in the condensation reaction between triethoxysilane and triethoxysilanol (ethanol producing condensation reaction: $0.12 \text{ mol}^{-1} \text{ min}^{-1}$, water producing condensation reaction: $0.08 \text{ mol}^{-1} \text{ min}^{-1}$) [11, 12]. These results indicate that steric hindrance dominates the hydrolysis–condensation reaction of alkoxy silane. In the initial hydrolysis–condensation reaction of TEOS, linear oligosiloxanes such as disiloxane and trisiloxane are formed under acidic conditions. Subsequently, long linear components, cyclic components, and randomly condensed structural oligomers and polymers are formed. The properties

of siloxanes also differ according to the molecular weight and the ratio of $\text{Si}(\text{OSi})_n(\text{OR})_{4-n}$ ($n = 1-4$; Q^n) in low-molecular-weight polysiloxanes [13, 14]. Therefore, it is not difficult to imagine that hydrolysis and condensation behaviors depend on the structure of the raw material. Although hydrolyzates of hexaethoxydisiloxane (HEDS) and octaethoxytrisiloxane (OETS) have been identified by ^{29}Si nuclear magnetic resonance (NMR) [15–17], the behavior of hydrolysis–condensation of HEDS and OETS has not been investigated. Therefore, in this work, we report the hydrolysis–condensation behavior of TEOS, HEDS, and OETS in detail based on instrumental analysis. Moreover, the reactivity and the synthesis of an alkoxy-substituted isocyanatosilane from tetraisocyanatosilane is reported using a new synthetic method for alkoxydisiloxanes and trisiloxanes, as shown in Scheme 1.

2 Experimental section

2.1 Measurements

Gas chromatography (GC) was performed using a GC-390 instrument (GL Science, Japan) packed with an SE-30 capillary column (Agilent, USA) and a thermal conductivity detector. Helium was used as the carrier gas. The column temperature was programmed as follows: injection temperature of $250 \text{ }^\circ\text{C}$, isothermal state at $80 \text{ }^\circ\text{C}$ for 2 min, then heating up to $200 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C min}^{-1}$, followed by heating up to $280 \text{ }^\circ\text{C}$ at a rate of $20 \text{ }^\circ\text{C min}^{-1}$, and held at the



Scheme 1 Synthesis of alkoxydisiloxanes and trisiloxanes

final temperature of 280 °C for 2 min. Gas chromatography/mass spectroscopy (GC/MS) was performed using a GCmate™ GC/MS double-focusing mass spectrometer (JEOL, Japan). Helium was used as the carrier gas. The column temperature was programmed as follows: injection temperature of 280 °C, isothermal state at 80 °C for 2 min, then heating up to 200 °C at a rate of 10 °C min⁻¹, followed by heating up to 280 °C at a rate of 20 °C min⁻¹, and held at the final temperature of 280 °C for 20 min. Nuclear magnetic resonance (NMR) spectra were recorded using a JEOL Resonance JNM-ECZ 400 spectrometer (¹H: 400 MHz, ¹³C: 100 MHz, ²⁹Si: 80 MHz). The chemical shifts were reported in ppm relative to the residual chloroform in chloroform-*d* (CDCl₃) (¹H: 7.26 ppm), chloroform (¹³C:77.16 ppm), and tetramethylsilane (²⁹Si{¹H}:0.00 ppm) as internal standards. For the ²⁹Si{¹H} NMR spectra, chromium(III) acetylacetonate was added to the sample as a paramagnetic relaxant. Fourier-transform infrared (FTIR) spectra were recorded on an FT/IR-6100 spectrophotometer (JASCO, Japan) using the neat method, in which the sample was sandwiched between two KBr crystal disks. High-resolution electrospray ionization time-of-flight mass spectrometry (HR-ESI-TOF MS) was performed using JEOL JMS-T100CS AccuTOF CS. The molecular weights of the oligomers and polymers were determined by gel permeation chromatography (GPC) using an LC-20AD HPLC prominent liquid chromatograph (Shimadzu, Japan) attached to a PLgel 5-μm Mixed-D column. Tetrahydrofuran (THF) was used as an eluent (1 mL min⁻¹), and a RID-20A was used as the detector at 40 °C. Molecular simulations of ethoxysilane oligomers were performed using quantum chemical calculations. Optimized structures, electrostatic potential (ESP) maps, dipole moments, and solvation-free energies for TEOS, HEDS, and OETS were determined at the B3LYP/6-31 G(d,p) level of theory using Gaussian 16 software [18].

2.2 Materials

Ethanol (EtOH), THF, toluene, and diethyl ether were purified using standard processes and stored over activated molecular sieves. Tetraisocyanatosilane was provided by Matsumoto Chemical Industry Co., Ltd. (Japan). Ammonium carbonate ((NH₄)₂CO₃) and molecular sieves were purchased from Kanto Chemical Co., Inc. (Japan). Anhydrous sodium sulfate, *N,N*-dimethylformamide (DMF), and 6 M hydrochloric acid (HCl aq.) were purchased from FUJIFILM Wako Pure Chemical Corporation (Japan). TEOS, thionyl chloride (SOCl₂), chlorodimethylsilane, and chromium(III) acetylacetonate were purchased from Tokyo Chemical Industry Co., Ltd. (Japan). TEOS and tetraisocyanatosilane were purified by distillation (106.5–111.0 °C/160 mmHg and 133.5–136.5 °C/123 mmHg, respectively). Diethoxy(diisocyanato)silane (DEDIS) was prepared by the ethoxylation of tetraisocyanatosilane [19].

Chloro(triethoxy)silane (CTES) was prepared by the chlorination of TEOS, and triethoxysilanol (TESOL) was prepared by the hydrolysis of CTES [20, 21]. The preparation methods and characterization are provided in Supporting Information.

2.3 Synthesis of 1,1,3,3-tetraethoxy-1,3-diisocyanatodisiloxane (TEDIDS)

A solution of water (0.18 g, 0.01 mol) and THF (20 ml) was added dropwise into a solution of DEDIS (4.04 g, 0.02 mol) and THF (20 ml) at 0 °C. The solution was stirred at 0 °C for 2 h followed by stirring at room temperature or 85 °C for the prescribed time. The solution was dried over anhydrous sodium sulfate, filtered, and evaporated. TEDIDS was isolated by distillation.

TEDIDS: colorless liquid; yield 13–32%; b.p. 54.8–58.9 °C/0.25 mmHg; ¹H NMR (400 MHz, CDCl₃/ppm): δ 3.90–3.85 (m, 8H, CH₂), 1.28–1.23 (m, 12H, CH₃); ²⁹Si NMR (80 MHz, CDCl₃/ppm): δ –94.6.

2.4 Synthesis of 1,1,1,5,5,5-hexaethoxy-3,3-diisocyanatotrisiloxane (HEDITS)

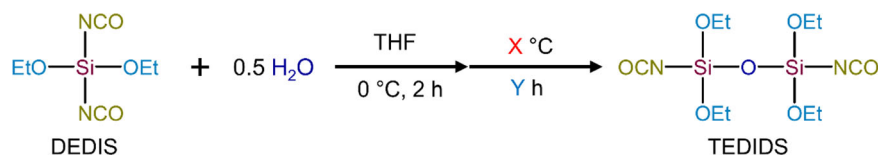
A solution of TESOL and THF (20 ml) was added dropwise to a solution of DEDIS (4.04 g, 0.02 mol) and THF (20 ml) at 0 °C. Then, the solution was stirred at 0 °C for 2 h, followed by stirring at room temperature for the prescribed time. After the completion of this reaction, the solvent was evaporated, and HEDITS was obtained by distillation.

HEDITS: colorless liquid; yield 24–44%; 100.8–104.8 °C/1.3 mmHg; ¹H NMR (400 MHz, CDCl₃ / ppm): δ 3.88–3.77 (m, 12H), 1.23–1.16 (m, 18H); ¹³C NMR (100 MHz, CDCl₃ / ppm): δ 122.5 (NCO), 59.0 (CH₂), 17.6 (CH₃); ²⁹Si NMR (80 MHz, CDCl₃ / ppm): δ –88.8, –89.0; IR (cm⁻¹): 2978, 2929, 2894, 2290, 1169, 1103, 1081; HRMS (HR-ESI-TOF) *m/z*: Calcd. for C₁₄H₃₁N₂O₁₀Si₃: 471.1208 [M + H]⁺, Found: 471.1459.

2.5 Synthesis of hexaethoxydisiloxane (HEDS) and octaethoxytrisiloxane (OETS)

Based on the alcoholysis of isocyanatosilane [22], TEDIDS (2 mmol) or HEDITS (1.5 mmol) were dissolved in THF (1 ml). Subsequently, 20 equiv. EtOH against oligosiloxane was added to the solution and refluxed overnight. After the reaction, the solvents were evaporated and distilled to obtain HEDS or OETS.

HEDS: colorless liquid; yield 12%; b.p. 51.4–54.2 °C/0.5 mmHg; ¹H NMR (400 MHz, CDCl₃ / ppm): δ 3.83 (q, *J* = 6.0 Hz, 12H, CH₂), 1.20 (t, *J* = 6.0 Hz, 18H, CH₃); ¹³C NMR (100 MHz, CDCl₃ / ppm): δ 59.2 (CH₂), 18.1 (CH₃); ²⁹Si NMR (80 MHz, CDCl₃ / ppm): δ –88.8.

Scheme 2 Synthesis of TEDIDS via the hydrolysis of DEDIS**Table 1** Synthetic conditions and yield of TEDIDS

Entry	Temperature ^a (°C)	Time ^b (h)	Yield (%)
1	85	3	12
2	23	3	32
3	23	16	28

^aCorresponding to “X” in Scheme 2^bCorresponding to “Y” in Scheme 2

OETS: colorless liquid; yield 42%; b.p. 90.2–90.5 °C/0.3 mmHg; ¹H NMR (400 MHz, CDCl₃ / ppm): δ 3.79–3.74 (m, 16H), 1.15–1.11 (m, 24H); ¹³C NMR (100 MHz, CDCl₃ / ppm): δ 59.3 (CH₂), 59.2 (CH₂), 18.1 (CH₃), 18.6 (CH₃); ²⁹Si NMR (80 MHz, CDCl₃ / ppm): δ –89.0, –96.2.

2.6 Initial hydrolysis reaction of ethoxysilane monomers

HCl aq. was slowly added to an EtOH solution of the ethoxysilane monomer (TEOS, HEDS, or OETS) in an ice bath, and the molar ratio of HCl:H₂O:EtOH:monomer was 0.1:2:10:1. After stirring the mixture in an ice bath for 10 min, chloro(trimethyl)silane (equal to the mol amount of H₂O) was added to the mixture to stop hydrolysis. The mixture was then poured into a mixture of hexane/THF (1/2 v/v) and washed twice with water and twice with brine. The organic layer was dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was characterized by mass spectroscopy and ²⁹Si{¹H} NMR.

2.7 Polymerization behavior of ethoxysilane monomers

HCl aq. was slowly added to an EtOH solution of the ethoxysilane monomer (TEOS, HEDS, or OETS) in an ice bath, and the molar ratio of HCl:H₂O:EtOH:monomer was 0.1:2:10:1. After stirring in an ice bath for 10 min, the mixture was heated to room temperature. The mixture was then aged for GPC and ²⁹Si{¹H} NMR monitoring.

3 Results and discussion

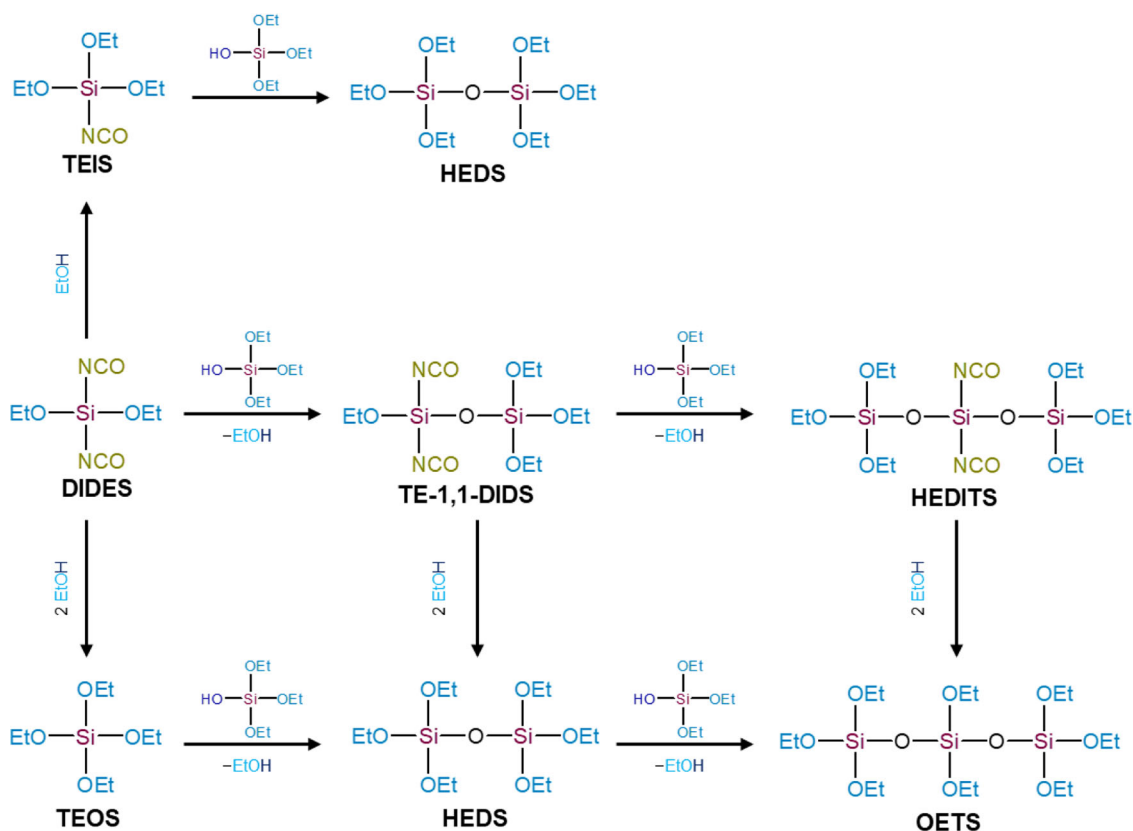
3.1 Reactivity of diethoxy(diisocyanato)silane

Diethoxy (diisocyanato)silane (DEDIS) was used as the raw material for the selective synthesis of HEDS and

OETS. The reactivity of isocyanatosilanes is lower than that of chlorosilanes and higher than that of the corresponding alkoxy-silanes [23–25]. We previously reported the synthesis and isolation of partially alkoxy-substituted isocyanatosilanes by the reaction of tetraisocyanatosilane with alcohol [19], as isocyanatosilanes are easier to handle than chlorosilanes. However, the reactivities of alkoxy-substituted isocyanatosilanes have not yet been investigated. In this section, the reactivity of DEDIS with water and silanol is discussed.

To synthesize tetraethoxy(diisocyanato)disiloxane (TEDIDS), the hydrolysis–condensation of DEDIS was performed according to Scheme 2; the results are summarized in Table 1. The yield of TEDIDS depended on the temperature and time. When condensation reaction was performed at 85 °C for 3 h (Entry 1), the yield of TEDIDS was 13% because condensation reaction was favored to form oligosiloxanes. When the reaction was performed at room temperature (23 °C) for 3 h (Entry 2), the yield of TEDIDS was maximum at 32%. However, the yield decreased to 28% when the reaction time was 16 h (Entry 3). The yield of TEDIDS via ethanolysis of hexa(isocyanato)disiloxane from tetraisocyanatosilane was 11% [26]; in contrast, the yield of TEDIDS via ethanolysis of DEDIS from tetra(isocyanate)silane was 29%. Hence, this method is useful for synthesizing disiloxanes containing isocyanate and alkoxy groups.

The reaction between DEDIS and TESOL was monitored for 8 h by GC/MS (Supplementary Fig. S1), and a strong signal attributed to ethanol was observed, indicating that the reaction proceeded between Si–OH and Si–OEt rather than between Si–OH and Si–NCO. DEDIS, triethoxy(isocyanato)silane (TEIS), and TEOS were observed, implying the reaction of DEDIS with ethanol. Additionally, 1,3,3,3-Tetraethoxy-1,1-diisocyanatodisiloxane (TE-1,1-DIDS) and hexaethoxydisiloxane (HEDS) were identified, supporting the ethanolysis of TE-1,1-DIDS and/or the condensation reaction between TEOS and TESOL or between TEIS and TESOL. Hexaethoxy(diisocyanato)trisiloxane (HEDITS) and octaethoxytrisiloxane (OETS) were also identified. Moreover, various other signals were observed, but the structures could not be determined because the molecular ion peak could not be identified or because there were many plausible isomers. The reaction between DEDIS and TESOL produced TE-1,1-DIDS and ethanol, whereas the reaction between TE-1,1-DIDS and TESOL produced



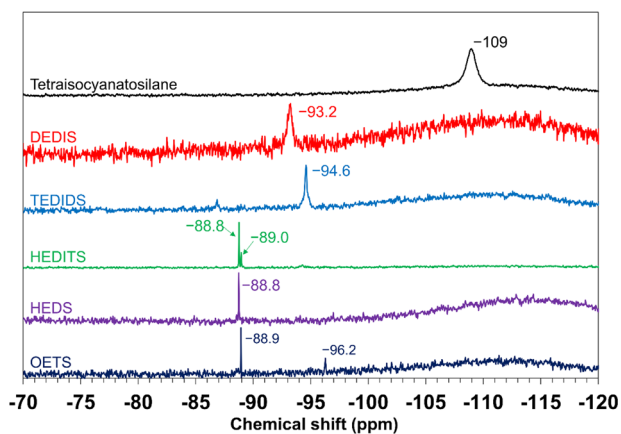
Scheme 3 Reaction between DEDIS and TESOL

Table 2 Isolated yield of HEDITS by the reaction of DEDIS with TESOL

Entry	TESOL (equiv.)	Time (day)	Isolated yield of HEDITS (%)	
			Based on DEDIS	Based on TESOL
1	1	0.67	18	36
2	1	2.00	22	44
3	1	3.00	12	24
4	2	0.67	– ^a	

^aComplicated mixture

HEDITS and ethanol, as shown in Scheme 3. Because the generated ethanol attacks Si–NCO, the reaction mixture was complex because of the formation of various compounds during the ethanolysis reaction. HEDITS in the reaction mixture was isolated by distillation because the reactive isocyanato group was protected by two bulky triethoxysiloxy groups. The isolated yield of HEDITS depended on the reaction time and the additional molar amount of TESOL, as shown in Table 2. The isolated yield of HEDITS first increased (Entries 1 and 2) and then decreased (Entry 3) because of ethanolysis and siloxane bond formation. When the molar ratio was set to 2 (Entry 4), HEDITS could not be isolated by distillation because the distillate contained many byproducts. HEDS and

**Fig. 1** ²⁹Si NMR spectra of tetraisocyanatosilane, DEDIS, TEDIDS, HEDITS, HEDS, and OETS

OETS were yielded in 12 and 42% by the ethanolysis of TEDIDS and HEDITS, respectively.

The ²⁹Si NMR spectra of tetraisocyanatosilane, DEDIS, TEDIDS, HEDITS, HEDS, and OETS are shown in Fig. 1. The chemical shift of Q¹ unit for –OSi(OEt)₃ appeared at –88.8 ppm. In contrast, the chemical shift of the silicon atom bound to the isocyanate group was irregular. In general, the chemical shift is influenced by the shielding effect of *p*(X) $\pi \rightarrow d(\text{Si})\pi$ and *p*(X) $\pi \rightarrow \sigma^*(\text{Si}-\text{Y})$, and bonding angles

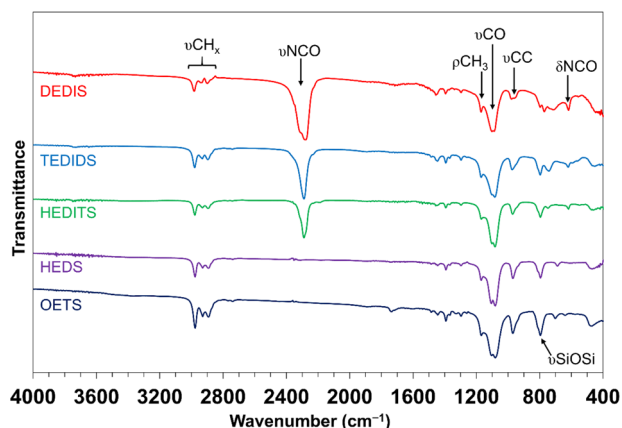


Fig. 2 FTIR spectra of DEDIS, TEDIDS, HEDITS, HEDS, and OETS using neat method

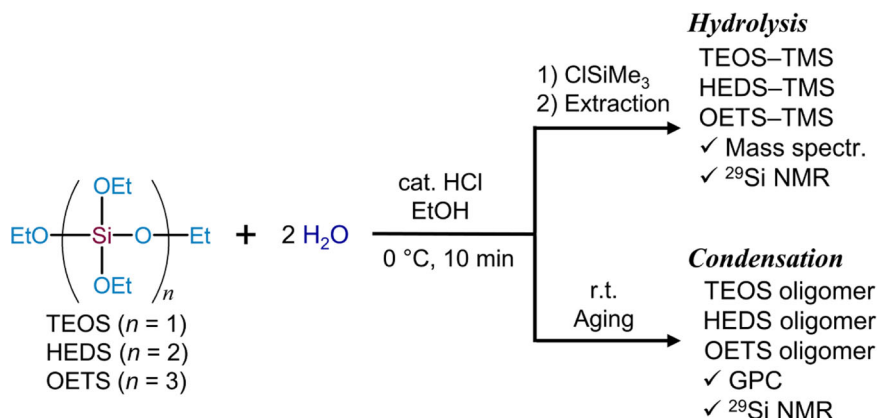
Table 3 FTIR assignment of DEDIS, TEDIDS, HEDITS, HEDS, and OETS

Wavenumber (cm ⁻¹) ^a					Assignment ^b
DEDIS	TEDIDS	HEDITS	HEDS	OETS	
2983m	2980m	2980m	2978m	2977m	$\nu_{as}CH_3$
2940w	2930w	2930w	2930w	2930w	ν_sCH_2
2901w	2897w	2895w	2893w	2893w	ν_sCH_3
2281s	2289s	2291s	–	–	νNCO
1453w	1447w	1449w	1445w	1443w	δCH_3
1394vw	1394vw	1394vw	1394vw	1394vw	δCH_2
1299vw	1297vw	1295vw	1297vw	1297vw	δCH_2
1172m	1171m	1169m	1170m	1169m	ρCH_3
1105s	1104s	1103s	1106s	1105s	νCO
1086s	1081s	1082s	1082s	1080s	νCO
980w	975w	971w	970m	970m	$\nu CC, \rho CH_3$
–	796m	795m	795m	796m	$\nu_s SiOSi$
771m	–	–	–	–	–
–	740w	746vw	–	–	–
–	–	–	688vw	703vw	–
618w	619vw	618vw	–	–	δNCO
–	459w	468w	473w	477w	$\delta SiOSi$
448w	447sh	448sh	447sh	448sh	δCCO

^as strong, m middle, w weak, vw very weak, sh shoulder

^b ν stretching, δ scissoring, ρ rocking, *as* asymmetric, *s* symmetric

Fig. 3 Experimental processes of the hydrolysis and condensation of ethoxyoligosiloxanes



around Si atom [27, 28]. The signal of tetraisocyanatosilane appeared at high magnetic field due to the shielding effect of $p(N)\pi \rightarrow d(Si)\pi$ [19, 29, 30]. The chemical shifts of DEDIS, TEDIDS, and HEDITS were observed at lower magnetic fields than that of tetraisocyanatosilane.

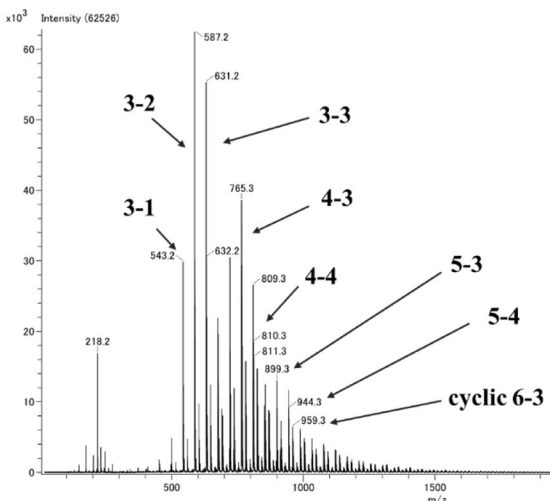
The FTIR spectra of DEDIS, TEDIDS, HEDITS, HEDS, and OETS are shown in Fig. 2, and the assignments are summarized in Table 3. The absorption bands were assigned based on the vibrational frequencies of tetraisocyanatosilane, triethoxysilane, and tetraethoxysilane [31–35]. All siloxanes except for DEDIS exhibited the $\nu SiOSi$ peak at approximately 795 cm⁻¹. DEDIS, TEDIDS, and HEDITS exhibited a band corresponding to νNCO at approximately 2285 cm⁻¹, which was not observed for HEDS or OETS.

3.2 Hydrolysis and condensation of TEOS, HEDS, and OETS

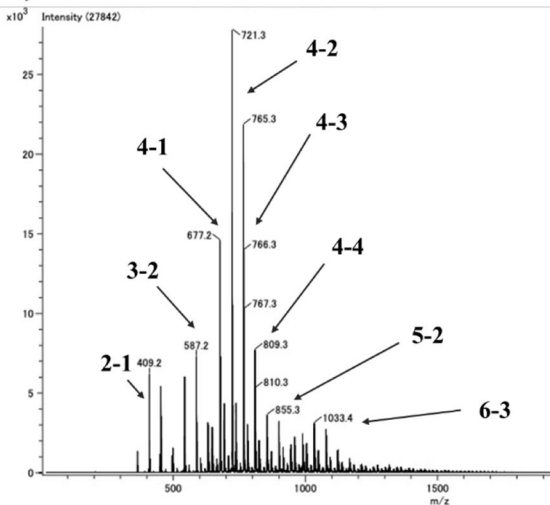
The reaction between alkoxysilanes and water is a well-known competitive reaction involving hydrolysis and condensation. The rate of hydrolysis reaction is faster than that of condensation reaction [10, 36], and condensation reaction can be slowed down at low temperatures (<0 °C) [37]. We performed the hydrolysis reaction of ethoxysilane monomers (TEOS, HEDS, OETS) with the molar ratio of HCl: H₂O: EtOH: monomer = 0.1: 2: 10: 1 at 0 °C for 10 min. To investigate the hydrolysis reaction in the duration of 10 min at 0 °C, the silanol in the hydrolyzed ethoxysilanes was capped using chlorotrimethylsilane [38, 39], and the structures of TEOS–TMS, HEDS–TMS, OETS–TMS were estimated by mass spectroscopy and ²⁹Si{¹H} NMR. In addition, to investigate the progress of condensation reaction, the hydrolysis reaction was performed for ethoxysilane monomers at 0 °C for 10 min followed by aging at room temperature (23 °C). The condensation of the ethoxysilane oligomers was analyzed by ²⁹Si NMR and GPC. These processes are illustrated in Fig. 3.

Fig. 4 ESI-MS of **a** TEOS–TMS, **b** HEDS–TMS, and **c** OETS–TMS detected as $[M + Na]^+$

a) TEOS–TMS



b) HEDS–TMS



c) OETS–TMS

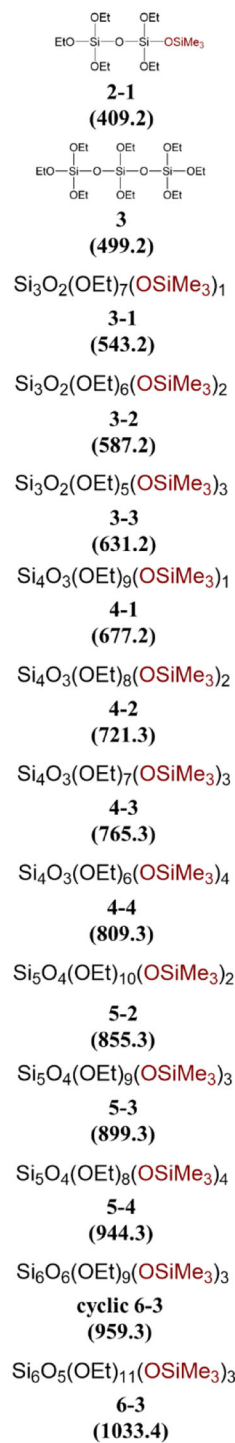
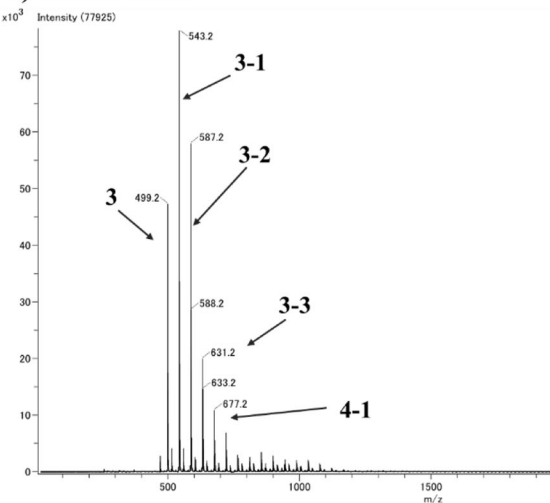
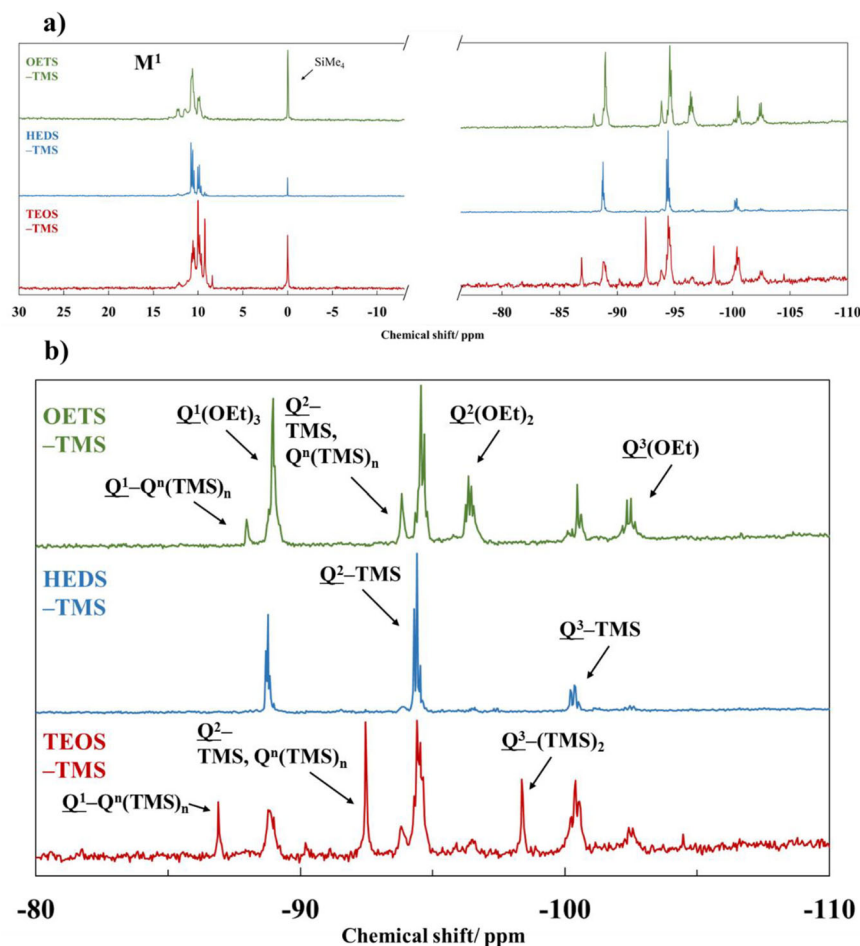


Fig. 5 $^{29}\text{Si}\{^1\text{H}\}$ NMR of TEOS-, HEDS-, and OETS-TMSs **a** 30 to -110 ppm region, and **b** -80 to -110 ppm region



3.2.1 Hydrolysis of TEOS, HEDS, and OETS

Progression of trimethylsilylation was confirmed by FTIR (Supplementary Fig. S2), by the appearance of the adsorption bands corresponding to $\delta\text{Si-Me}$ (approximately 1250 cm^{-1}) and $\rho\text{Si-Me}$ (approximately 840 cm^{-1}), and the no appearance of the band corresponding to $\nu\text{Si-OH}$ (approximately 950 cm^{-1}) [34, 40, 41]. No $\nu\text{Si-O-Si}$ adsorption band was observed at $1200\text{--}1100$ or $1040\text{--}1000\text{ cm}^{-1}$; hence, the main structures of ethoxysilane-TMSs could be attributed to their linear, branched, and cyclic forms [34, 42]. The mass spectra of the ethoxysilane-TMSs are shown in Fig. 4 (results are summarized in Supplementary Table S1). TEOS-TMS was confirmed to be a mixture of linear (trimer to octamer) and cyclic (tetramer to heptamer) oligosiloxanes, with the main components being the trimers, tetramers, and pentamers. This result was similar to that of the general hydrolysis of TOES under acidic conditions [38, 43]. HEDS-TMS was confirmed to be a mixture of linear (dimer to octamer) and cyclic (tetramer to heptamer)

oligosiloxanes, with the main component being the tetramers. The peak intensity of the mass spectrum of the oligosiloxanes with even-numbered silicon atoms in the main structure was higher than that with odd-numbered silicon atoms, indicating that the rearrangement reaction hardly proceeded. The main structure of the OETS-TMS consisted of trimers. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of the ethoxysilane-TMSs are shown in Fig. 5, and the assignments are summarized in Table 4. The M^1/Q ratio was in the order of TEOS-TMS > HEDS-TMS > OETS-TMS, which was consistent with the relationship between the amount of water added and the number of alkoxy groups ($\text{H}_2\text{O}/\text{OEt} = 0.50$ for TEOS, 0.33 for HEDS, and 0.25 for OETS). The degrees of M^1 for TEOS-, HEDS-, and OETS-TMSs were 47.0 , 56.3 , and 72.8% , respectively. The compositions of the siloxane unit structures a, b, c, d, and e (Table 5) were calculated based on the signal area of $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of ethoxysilane-TMSs, as shown in Fig. 6. Unit a was attributed to the end group, whereas Units b, c, and d were attributed to the linear or cyclic structures. Unit e was attributed to the branched structure.

From these results, ethoxysilane–TMSs were confirmed to be mainly consisting of unit a, as shown in Fig. 5 (TEOS–TMS: 58.1%, HEDS–TMS: 70.6%, OETS–TMS: 56.7%) without Q⁴ signal.

Table 4 Assignments for ²⁹Si{¹H} NMR spectra of ethoxysilane–TMSs

Q ⁿ unit	Chemical shift of Q ⁿ unit prepared from linear-oligoethoxysiloxanes/ppm		
	TEOS–TMS	HEDS–TMS	OETS–TMS
monomer	–81.9	–88.8	–88.9, –96.2
M ¹	10.7 to 8.4	11.1 to 10.0	13.3 to 9.9
Q ¹ (OEt) ₃	–88.8	–88.7 to 88.9	–88.9
Q ¹ –Q ⁿ (TMS) _n	–86.9	–88.0	
Q ² (OEt) ₂	–95.9 to –96.5	–96.6 to –97.5	–96.2 to –96.5
Q ² –TMS	–94.3 to –94.6, –93.8, –92.5	–94.3 to –94.5, –93.9	–94.6 to –94.7, 93.8
Q ³ (OEt)	–102.4 to –102.6	–101.2 to –102.5	–102.3 to –102.5
Q ³ –(TMS)	–100.2 to –100.6	–100.2 to –100.5	–100.1 to –100.5
Q ³ –(TMS) ₂	–98.4		

Table 5 Relative ratios of siloxane unit structures for ethoxysilanes–TMS

ethoxysilanes–TMS	M ¹ /M ¹ Q ^a ratio (%)	Ratio of structure units ^b (%)				
		a	b	c	d	e
TEOS–TMS	47.0	58.1	9.1	9.0	16.4	7.5
HEDS–TMS	56.3	70.6	5.5	0	15.7	8.2
OETS–TMS	72.8	56.7	19.3	0	11.0	13.0

^aCalculated based on ²⁹Si{¹H} NMR spectra^b Calculated based on the signal area of ²⁹Si{¹H} NMR spectra

^bCalculated based on the signal area of ²⁹Si{¹H} NMR spectra

3.2.2 ²⁹Si{¹H} NMR spectra of ethoxysiloxane oligomers

GPC traces of the hydrolyzates after 1 h since reaction started are shown in Supplementary Fig. S3. The traces differed for each monomer. The ²⁹Si{¹H} NMR spectra of ethoxysiloxane oligomers are shown in Fig. 5. The structures of the oligomers were estimated based on the hydrolysis–condensation of ethoxysilane and isolated specific structural monomer [7, 9, 17, 34, 44–48]. The hydrolyzate of TEOS after 1 h showed main signals attributed to Q¹(OEt)₂(OH) (–86.2 ppm), 4-membered cyclic Q²(OEt)(OH) (–92.7 ppm), 4-membered cyclic Q²(OEt)₂ (–95.1 ppm), and 5- or 6-membered cyclic Q²(OEt)₂ (–95.4 ppm), and minor signals attributed to linear Q² (–96 ppm) and silanol-terminated species (–85.5 ppm). The Q¹ unit disappeared after 24 h. After 7 days, the intensity of 4-membered cyclic Q² signals decreased, and the signals appeared from –99 to –105 ppm in the Q³ unit region corresponding to cyclic Q³–OH (–99.7 ppm), Q³–OH (–100.5 ppm), cyclic Q³ (–101.5 ppm), cage-type Q³ such as open cage and complete cage (–102.3 ppm), and Q³–OEt (–103.2 ppm). After 14 days, the intensities of the signals decreased and unclear broad signals were observed in the Q² (–92 to –97 ppm), Q³ (–99 to –105 ppm), and Q⁴ (–110 ppm) regions. The molecular weight of the TEOS oligomer increased over time (from 1600 to 2400 Da), and after 14 days, the TEOS oligomer was mainly composed of Q³ structures.

The hydrolyzate of HEDS after 1 h showed the signals attributed to Q¹(OEt)(OH)₂ (–84.0 ppm), Q¹(OEt)₂(OH) (–86.1, –86.2 ppm), Q¹(OEt)₃ (–88.7 ppm), cyclic Q²(OEt)(OH) (–92.7 ppm), 4-membered cyclic Q²(OEt)₂ (–95.1 ppm), 5- or 6-membered cyclic Q²(OEt)₂ (–95.4 ppm), and linear Q² (–96.3 ppm), confirming that the HEDS oligomer after 1 h was mainly composed of 4-membered cyclic Q² and end-terminated Q¹. After 24 h, the signals corresponding to Q¹ units disappeared, and the 4-membered cyclic Q² signal was strong. The small signals due to cyclic Q³ (–101.2, –101.5 ppm) were observed. After seven days, the signal intensity of the 4-membered cyclic Q² decreased, and Q³ unit was grown.

Fig. 6 Structure of ethoxysilane–TMSs

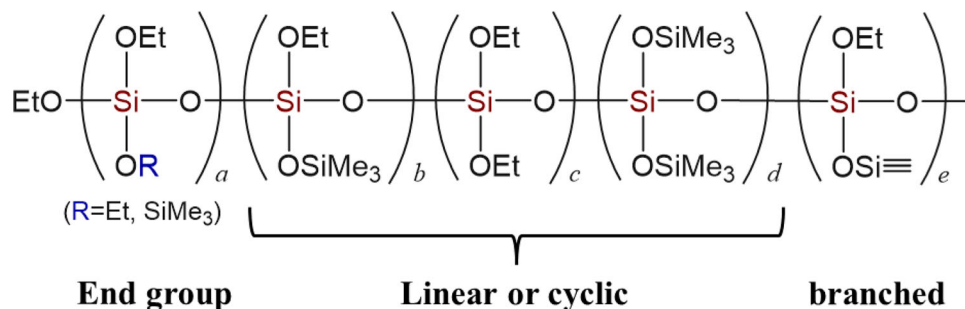
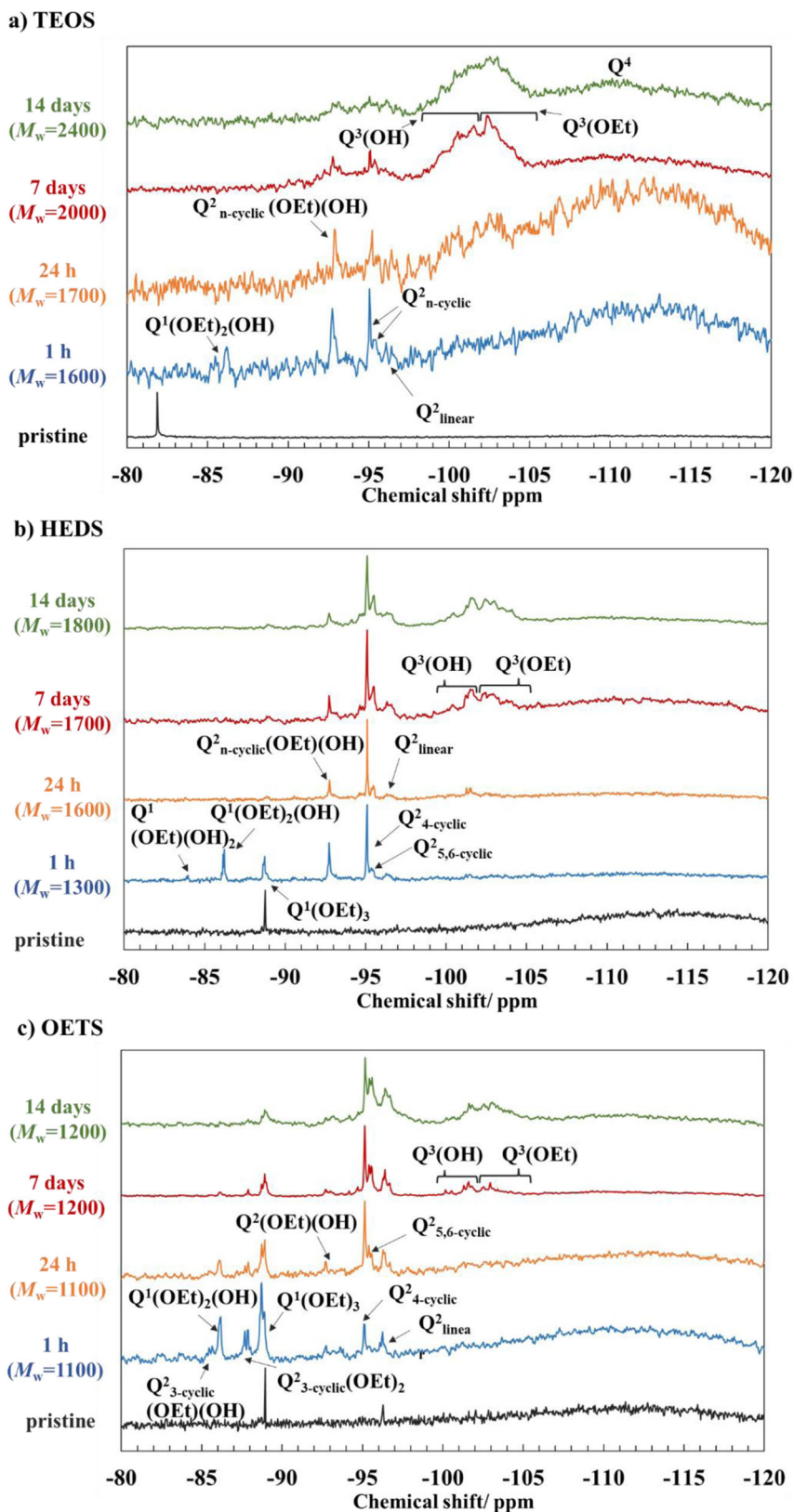


Fig. 7 $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of the hydrolyzates of **a** TEOS, **b** HEDS, and **c** OETS



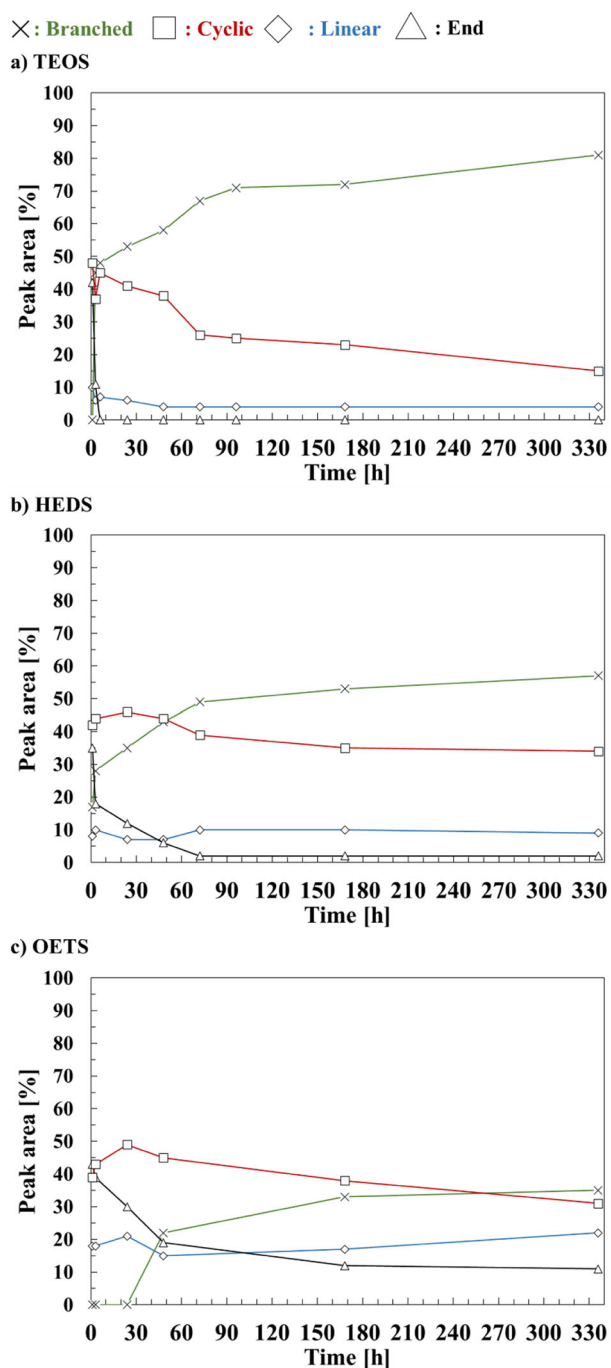


Fig. 8 Variation of the peak area ratio of structures with time on the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of the hydrolyzates of **a** TEOS, **b** HEDS, and **c** OETS (\triangle : End group, \diamond : Linear structure, \square : Cyclic structure, \times : Branch structure)

The spectrum of the HEDS oligomer after 14 days was similar to that after 7 days, and the Q^4 unit was barely formed. The molecular weight of the HEDS oligomer from 1 h to 14 days changed from 1300 to 1800 Da, and the HEDS oligomer after 14 days was composed of

mainly 4-membered cyclic Q^2 , cyclic Q^3 , and Q^3 structures; linear Q^2 and 6-membered cyclic Q^2 was also incorporated in the oligomer.

The hydrolysis–condensation behavior of OETS differed from that of TEOS and HEDS. The hydrolyzate of OETS after 1 h showed the signals corresponding to 3-membered cyclic $\text{Q}^2(\text{OEt})(\text{OH})$ (–85.5, –85.7 ppm), $\text{Q}^1(\text{OEt})_2(\text{OH})$ (–86.2 ppm), 3-membered cyclic $\text{Q}^2(\text{OEt})_2$ (–87.7, –87.9 ppm), $\text{Q}^1(\text{OEt})_3$ (–88.7, –88.9 ppm), cyclic $\text{Q}^2(\text{OEt})(\text{OH})$ (–92.7 ppm), $\text{Q}^2(\text{OEt})(\text{OH})$ (–93.6 ppm), 4-membered cyclic $\text{Q}^2(\text{OEt})_2$ (–95.1 ppm), and linear Q^2 (–96.2 ppm). After 24 h, the intensity of 4-, 5-, or 6-membered cyclic $\text{Q}^2(\text{OEt})_2$ (–95.1, –95.4, –95.6 ppm) increased, and intensity of Q^1 and 3-membered cyclic Q^2 decreased. After seven days, cyclic $\text{Q}^3\text{–OH}$ (–100.5 ppm), $\text{Q}^3\text{–OH}$ (–101.5 ppm), cage-type Q^3 such as open cage and complete cage (–102.3 ppm), cyclic $\text{Q}^3\text{–OEt}$ (–103.2 ppm), and $\text{Q}^3\text{–OEt}$ (–104.5 ppm) were formed, and the content of $\text{Q}^1\text{–OH}$ and 3-membered cyclic Q^2 decreased. After 14 days, $\text{Q}^1\text{–OH}$ and 3-membered cyclic Q^2 disappeared, Q^3 structures grew, and the content of 4-membered cyclic Q^2 decreased. Moreover, end-terminated $\text{Q}^1(\text{OEt})_3$ was observed. After 14 days, the OETS oligomer was mainly composed of 4-, 5-, or 6-membered cyclic Q^2 , linear Q^2 , various Q^3 , and end-terminated $\text{Q}^1(\text{OEt})_3$. These assignments are summarized in Table 6.

Figure 7 shows the changes in the area ratios of the structures in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of the TEOS, HEDS, and OETS oligomers over time. The contents of cyclic and linear structures reached up to approximately 50 and 20%, respectively Fig. 8. The area ratios of these structures decreased with an increasing area ratio of the branched structure. Schematics of the estimated structures generated by the linear ethoxysilane oligomers are shown in Fig. 9.

3.2.3 Computational study of ethoxysiloxane monomers

The optimized structures with their ESP maps and dipole moments were calculated using DFT to supplement the reactivity of the ethoxysilane monomers (Fig. 10). When siloxane bonding was extended, the dipole moment of optimized structure increased (TEOS: 0.11 debye, HEDS: 1.07 debye, OETS: 3.86 debye). The optimized HEDS and OETS structures showed that the electron density was high for the oxygen atoms of the siloxane bond and alkoxy group. In particular, OETS had high electron density on the oxygen atom of the alkoxy group arranged on one side of the molecule. These electron densities may affect the reactivity of the monomers [49–52].

Fig. 9 Schematics of estimated oligomer structures using **a** TEOS, **b** HEDS, and **c** OETS

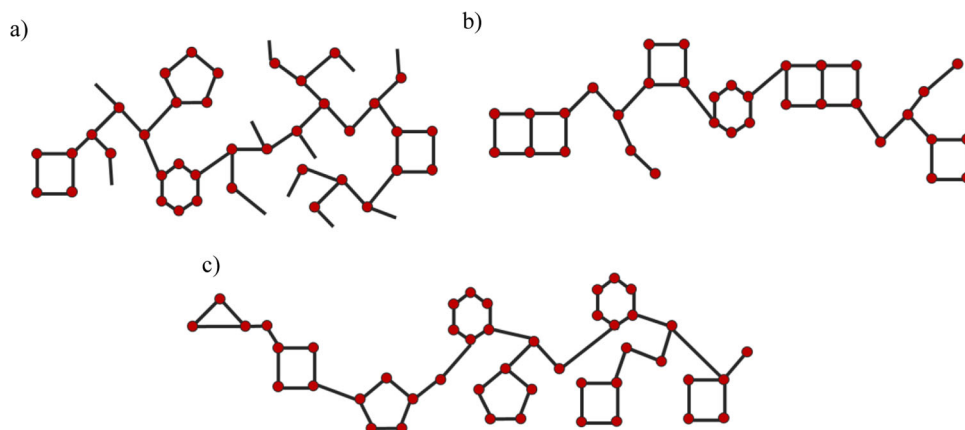
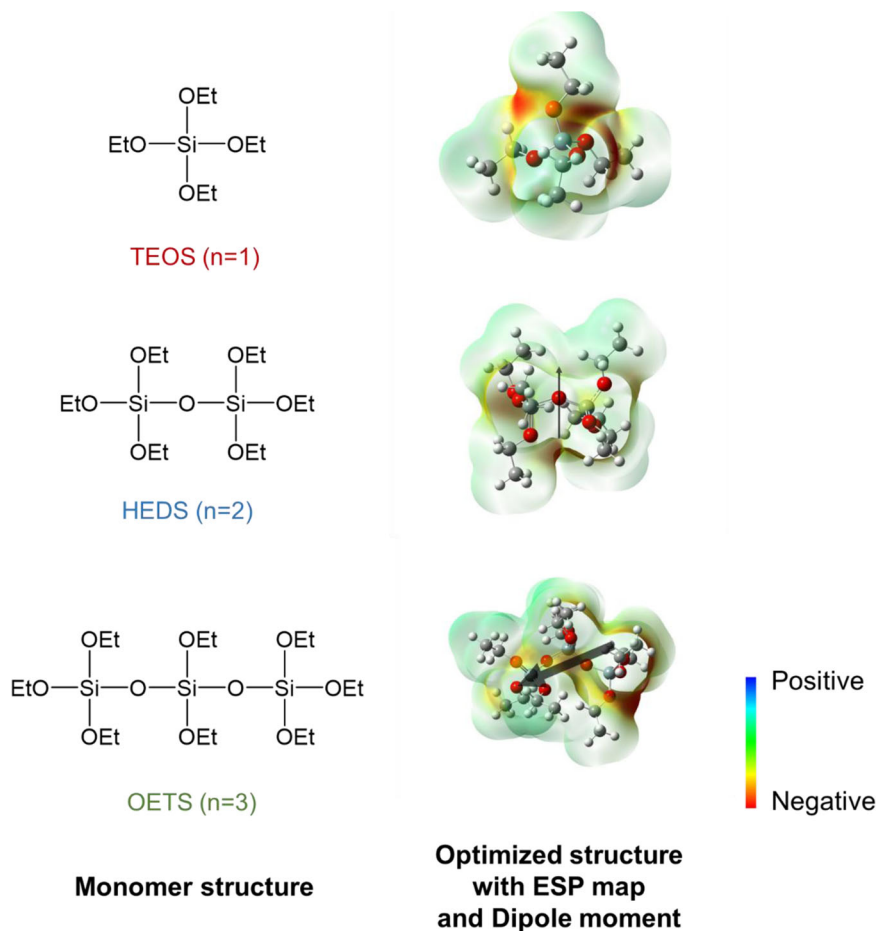


Fig. 10 ESP maps and dipole moments for TEOS, HEDS, and OETS calculated using the DFT method (B3LYP/6-31G(d,p))



4 Conclusion

HEDS and OETS were synthesized in 3.5 and 8.4% of the total yield, respectively, from DEDIS by controlling the functionality. The hydrolysates of TEOS, HEDS, and OETS were trimethylsilylated and analyzed by MS, GPC, and NMR. Linear and cyclic oligosiloxanes were generated during the initial stage. The structure was estimated to be a network-type polymer containing a cyclic siloxane

for TEOS. The polymers mainly consisted of four-membered cyclic siloxanes for HEDS. The polymers consisted mainly of cyclic siloxanes for OETS. In addition, the electron densities of the ethoxysilane oligomers calculated using DFT were investigated. The optimized HEDS and OETS structures showed a high electron density on the oxygen atoms in the siloxane bond and alkoxy group. These results suggest that electron density may affect the reactivities of TEOS, HEDS, and OETS.

Table 6 Assignments for the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of ethoxysiloxane oligomers

Q^n unit	Chemical shift of Q^n unit / ppm		
	TEOS oligomer	HEDS oligomer	OETS oligomer
monomer	–81.9	–88.8	–88.9, –96.2
$Q_1(\text{OEt})_3$		–88.7	–88.7, –88.9
$Q_1(\text{OEt})_2(\text{OH})$	–85.5, –86.2	–86.1, –86.2	–86.2
$Q_1(\text{OEt})(\text{OH})_2$		–84.0	
Q^2_{linear}	–96.1, –96.4	–96.3	–96.2
$Q^2_{5,6\text{-cyclic}}$	–95.4	–95.4	–95.4, –95.6
$Q^2_{4\text{-cyclic}}$	–95.1	–95.1	–95.1
$Q^2_{\text{linear}}(\text{OEt})(\text{OH})$			–93.6
$Q^2_{n\text{-cyclic}}(\text{OEt})(\text{OH})$	–92.7	–92.7	–92.7
$Q^2_{3\text{-cyclic}}(\text{OEt})_2$			–87.7, –87.9
$Q^2_{3\text{-cyclic}}(\text{OEt})(\text{OH})$			–85.7, –85.5
$Q^3(\text{OEt})$	–101.5 to –103.8	–102.4 to –103.8	–102.5 to –103.4
$Q^3(\text{OH})$	–99.4 to –101.5	–100.4 to –101.5	–100.2 to –101.6
Q^4	–110.7		

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Author contributions CRediT authorship contribution statement: YS: Investigation, conceptualization, visualization, methodology, writing—original draft. AS: Investigation. TI: Investigation. RH: Writing—review and editing, investigation, visualization. KY: Supervision. TG: Writing—review and editing, conceptualization, and supervision.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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References

- Dislich H (1971) New routes to multicomponent oxide glasses. *Angew Chem Int Ed Engl* 10:363–370. <https://doi.org/10.1002/ange.197103631>
- Abe Y, Gunji T (2004) Oligo- and polysiloxanes. *Prog Polym Sci* 29:149–182. <https://doi.org/10.1016/j.progpolymsci.2003.08.003>
- Cihlář J (1993) Hydrolysis and polycondensation of ethyl silicates. 1. Effect of pH and catalyst on the hydrolysis and polycondensation of tetraethoxysilane (TEOS). *Colloids Surf A* 70:239–251. [https://doi.org/10.1016/0927-7757\(93\)80298-S](https://doi.org/10.1016/0927-7757(93)80298-S)
- Harris MT, Brunson RR, Byers CH (1990) The base-catalyzed hydrolysis and condensation reactions of dilute and concentrated TEOS solutions. *J Non Cryst Solids* 121:397–403. [https://doi.org/10.1016/0022-3093\(90\)90165-I](https://doi.org/10.1016/0022-3093(90)90165-I)
- Tejedor-Tejedor MI, Paredes L, Anderson MA (1998) Evaluation of ATR–FTIR spectroscopy as an “in situ” tool for following the hydrolysis and condensation of alkoxy silanes under rich H_2O conditions. *Chem Mater* 10:3410–3421. <https://doi.org/10.1021/cm980146l>
- Echeverría JC, Moriones P, Arzamendi G, Garrido JJ, Gil MJ, Cornejo A, Martínez-Merino V (2018) Kinetics of the acid-catalyzed hydrolysis of tetraethoxysilane (TEOS) by ^{29}Si NMR spectroscopy and mathematical modeling. *J Sol Gel Sci Technol* 86:316–328. <https://doi.org/10.1007/s10971-018-4637-7>
- Mazúr M, Mlynárik V, Valko M, Pelikán P (2000) The time evolution of the sol-gel process: ^{29}Si NMR study of the hydrolysis and condensation reactions of tetraethoxysilane. *Appl Magn Reson* 18:187–197. <https://doi.org/10.1007/BF03162110>
- Brinker CJ (1988) Hydrolysis and condensation of silicates: Effects on structure. *J Non Cryst Solids* 100:31–50. [https://doi.org/10.1016/0022-3093\(88\)90005-1](https://doi.org/10.1016/0022-3093(88)90005-1)
- Depla A, Lesthaeghe D, Van Erp TS, Aerts A, Houthoofd K, Fan F, Li C, Speybroeck VVAN, Waroquier M, Kirschhock CEA, Martens JA (2011) ^{29}Si NMR and UV–Raman investigation of initial oligomerization reaction pathways in acid-catalyzed silica sol–gel chemistry. *J Phys Chem C* 115:3562–3571. <https://doi.org/10.1021/jp109901v>
- Assink RA, Kay BD (1988) Sol-gel kinetics I. Functional group kinetics. *J Non Cryst Solids* 99:359–370. [https://doi.org/10.1016/0022-3093\(88\)90441-3](https://doi.org/10.1016/0022-3093(88)90441-3)
- Ueda N, Gunji T, Abe Y (2008) Syntheses of linear ethoxysiloxanes by the oxidative condensation of triethoxysilane. *J Sol Gel Sci Technol* 48:163–167. <https://doi.org/10.1007/s10971-008-1808-y>
- Abe I, Sato Y, Hayami R, Yamamoto K, Tsukada S, Gunji T (2023) Oxidation of triethoxysilane by Wilkinson's catalyst and its kinetic constants. *Mater Technol in press*.
- Abe Y, Shimano R, Arimitsu K, Gunji T (2003) Preparation and properties of high molecular weight polyethoxysiloxanes stable to self-condensation by acid-catalyzed hydrolytic polycondensation of tetraethoxysilane. *J Polym Sci A Polym Chem* 41:2250–2255. <https://doi.org/10.1002/pola.10739>
- Gunji T, Hayashi Y, Komatsubara A, Arimitsu K, Abe Y (2012) Preparation and properties of flexible free-standing films via polyalkoxysiloxanes by acid-catalyzed controlled hydrolytic

- polycondensation of tetraethoxysilane and tetramethoxysilane. *Appl Organomet Chem* 26:32–36. <https://doi.org/10.1002/aoc.1861>
15. Sanchez J, McCormick A (1992) Kinetic and thermodynamic study of the hydrolysis of silicon alkoxides in acidic alcohol solutions. *J Phys Chem* 96:8973–8979. <https://doi.org/10.1021/j100201a051>
 16. Sanchez J, McCormick AV (1994) Intramolecular vs. intermolecular condensation rates in the acidic polymerization of octaethoxytrisiloxane. *J Non Cryst Solids* 167:289–294. [https://doi.org/10.1016/0022-3093\(94\)90251-8](https://doi.org/10.1016/0022-3093(94)90251-8)
 17. Lin CC, Basil JD (1986) ²⁹Si NMR, sec and ftir studies of the hydrolysis and condensation of Si(OC₂H₅)₄ and Si₂O(OC₂H₅)₆. *Mater Res Soc Symp Proc* 73:585–590. <https://doi.org/10.1557/PROC-73-585>
 18. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Petersson GA, Nakatsuji H, Li X, Caricato M, Marenich AV, Bloino J, Janesko BG, Gomperts R, Mennucci B, Hratchian HP, Ortiz JV, Izmaylov AF, Sonnenberg JL, Williams-Young D, Ding F, Lipparini F, Egidi F, Goings J, Peng B, Petrone A, Henderson T, Ranasinghe D, Zakrzewski VG, Gao J, Rega N, Zheng G, Liang W, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Throssell K, Montgomery JA Jr, Peralta JE, Ogliaro F, Bearpark MJ, Heyd JJ, Brothers EN, Kudin KN, Staroverov VN, Keith TA, Kobayashi R, Normand J, Raghavachari K, Rendell AP, Burant JC, Iyengar SS, Tomasi J, Cossi M, Millam JM, Klene M, Adamo C, Cammi R, Ochterski JW, Martin RL, Morokuma K, Farkas O, Foresman JB, Fox DJ (2016) Gaussian¹⁶ Revision C.01
 19. Abe Y, Motoyama K, Kobayashi T, Iwasaki S, Gunji T (1996) Syntheses of Alkoxyisocyanatosilanes from Tri- and Tetra-isocyanatosilane. *Nippon Kagaku Kaishi* 1996:969–974. <https://doi.org/10.1246/nikkashi.1996.969>
 20. Kazakova VV, Gorbatshevich OB, Skvortsova SA, Demchenko NV, Muzafarov AM (2005) Synthesis of triethoxysilanol. *Russ Chem Bull* 54:1350–1351. <https://doi.org/10.1007/s11172-005-0409-y>
 21. Yamamoto K, Shimoda T, Sato Y, Nakaya T, Ohshita J, Gunji T (2022) Preparation and film properties of polysiloxanes consisting of di- and quadra-functional hybrid units. *J Sol Gel Sci Technol* 104:724–734. <https://doi.org/10.1007/s10971-022-05806-z>
 22. Abe Y, Kanemaru T, Yamazaki T, Nagao Y, Misono T (1991) The reaction of isocyanatosilanes with ethanol and synthesis of their derivatives. *Nippon Kagaku Kaishi* 1991:1094–1101. <https://doi.org/10.1246/nikkashi.1991.1094>
 23. Kondo Y, Miyao K, Aya Y, Yoshino (2004) N synthesis of and glass surface modification with fluorinated silane coupling agents with a benzene ring as a spacer. *J Oleo Sci* 53:143–151. <https://doi.org/10.5650/jos.53.143>
 24. Sakurai H, Nozaki H, Yamamoto S, Tsuji J, Noyori R (1985) Application of organosilicon compounds to organic synthesis, 105. *Kagaku Dojin* (Japan), pp. 33–40
 25. Corriu RJP, Guerin C (1982) Nucleophilic displacement at silicon: recent developments and mechanistic implications. *Adv Organomet Chem* 265–312. [https://doi.org/10.1016/S0065-3055\(08\)60523-7](https://doi.org/10.1016/S0065-3055(08)60523-7)
 26. Gunji T, Setogawa A, Asakura K, Abe Y (1998) Syntheses and properties of isocyanatodisiloxanes and their alkoxy-substituted derivatives. *Bull Chem Soc Jpn* 71:2967–2972. <https://doi.org/10.1246/bcsj.71.2967>
 27. Oberhammer H, Boggs JE (1980) Importance of (p-d).pi. bonding in the siloxane bond. *J Am Chem Soc* 102:7241–7244. <https://doi.org/10.1021/ja00544a011>
 28. Dankert F, Hänisch C (2021) Siloxane coordination revisited: Si–O bond character, reactivity and magnificent molecular shapes. *Eur J Inorg Chem* 2021:2907–2927. <https://doi.org/10.1002/ejic.202100275>
 29. Abe Y, Ito A, Hisano Y, Nagao Y, Misono T (1992) Synthesis and Properties of Polysilazanes from Phenyltriisocyanatosilane. *NIPPON KAGAKU KAISHI* 1992:649–656. <https://doi.org/10.1246/nikkashi.1992.649>
 30. Kozyukov VP, Sheludyakov VD, Mironov VF (1973) *Russian Chem. Rev* 42:662–677. <https://doi.org/10.1070/RC1973v042n08ABEH002704>
 31. Jensen JO (2003) Vibrational frequencies and structural determinations of tetraisocyanatosilane. *Spectrochim Acta Part A* 59:937–947. [https://doi.org/10.1016/S1386-1425\(02\)00280-9](https://doi.org/10.1016/S1386-1425(02)00280-9)
 32. Miller FA, Carlson GL (1961) The vibrational spectra and structure of Si(NCO)₄ and Ge(NCO)₄. *Spectrochim Acta* 17:977–989. [https://doi.org/10.1016/0371-1951\(61\)80033-7](https://doi.org/10.1016/0371-1951(61)80033-7)
 33. Newton WE, Rochow EG (1970) Vibrational spectra of some trialkoxysilanes. *J Chem Soc A* 1970:2664–2668. <https://doi.org/10.1039/J19700002664>
 34. Sato Y, Hayami R, Gunji T (2022) Characterization of NMR, IR, and Raman spectra for siloxanes and silsesquioxanes: a mini review. *J Sol Gel Sci Technol* 104:36–52. <https://doi.org/10.1007/s10971-022-05920-y>
 35. Rubio F, Rubio J, Oteo JL (1998) A FT-IR study of the hydrolysis of tetraethylorthosilicate (TEOS). *Spectrosc Lett* 31:199–219. <https://doi.org/10.1080/00387019808006772>
 36. Kay BD, Assink RA (1988) Sol-gel kinetics: II. Chemical speciation modeling. *J Non Cryst Solids* 104:112–122. [https://doi.org/10.1016/0022-3093\(88\)90189-5](https://doi.org/10.1016/0022-3093(88)90189-5)
 37. Gunji T (1992) Tokyo University of Science, Doctoral dissertations "Studies of the synthesis of metalloxanes and their characterization as ceramic precursors", p110. <https://doi.org/10.11501/3071196>
 38. Gunji T, Sopyan I, Abe Y (1994) Synthesis of polytitanosiloxanes and their transformation to SiO₂-TiO₂ ceramic fibers. *J Polym Sci A Polym Chem* 32:3133–3139. <https://doi.org/10.1002/pola.1994.080321613>
 39. Lentz CW (1964) Silicate minerals as sources of trimethylsilyl silicates and silicate structure analysis of sodium silicate solutions. *Inorg Chem* 3:574–579. <https://doi.org/10.1021/ic50014a029>
 40. Flagg DH, McCarthy TJ (2016) Rediscovering silicones: MQ copolymers. *Macromolecules* 49:8581–8592. <https://doi.org/10.1021/acs.macromol.6b01852>
 41. Liang W, Ge X, Ge J, Li T, Zhao T, Chen X, Song Y, Cui Y, Khan M, Ji J, Pang X, Liu R (2018) Reduced graphene oxide embedded with MQ silicone resin nano-aggregates for silicone rubber composites with enhanced thermal conductivity and mechanical performance. *Polymers* 10:1254. <https://doi.org/10.3390/polym10111254>
 42. Cruz-Quesada G, Espinal-Viguri M, López-Ramón M, Garrido J (2022) Novel silica hybrid xerogels prepared by co-condensation of TEOS and ClPhTEOS: a chemical and morphological study. *Gels* 8:677. <https://doi.org/10.3390/gels8100677>
 43. Klemperer WG, Mainz VV, Ramamurthi SD, Rosenberg FS (1988) Structural characterization of polysilicate intermediates formed during sol-gel polymerization. *Mater Res Soc Symp Proc* 121:15–24. <https://doi.org/10.1557/PROC-121-15>
 44. Brus J, Karhan J, Kotlík P (1996) ²⁹Si NMR study of distribution of oligomers in polycondensation of tetraethoxysilane. *Collect Czech Chem Commun* 61:691–703. <https://doi.org/10.1135/cccc19960691>
 45. Hook RJ (1996) A ²⁹Si NMR study of the sol-gel polymerisation rates of substituted ethoxysilanes. *J Non Cryst Solids* 195:1–15. [https://doi.org/10.1016/0022-3093\(95\)00508-0](https://doi.org/10.1016/0022-3093(95)00508-0)
 46. Ueda N, Gunji T, Abe Y (2008) Synthesis of alkoxy octa-silsesquioxanes by a convenient one-pot reaction. *Mater Technol* 26:162–169
 47. Hayami R, Wada K, Nishikawa I, Sagawa T, Yamamoto K, Tsukada S, Gunji T (2017) Preparation and properties of

- organic–inorganic hybrid materials using titanium phosphonate cluster. *Polym J* 49:665–669. <https://doi.org/10.1038/pj.2017.34>
48. Kelts LW, Armstrong NJ (1989) A silicon-29 NMR study of the structural intermediates in low pH sol-gel reactions. *J Mater Res* 4:423–433. <https://doi.org/10.1557/JMR.1989.0423>
49. Myers SA, Assink RA, Loy DA, Shea KJ (2000) Investigation of the transmission of substituent effects by ^{29}Si NMR. *J Chem Soc Perkin Trans 2*:545–549. <https://doi.org/10.1039/A906569E>
50. Saito H, Nishio Y, Kobayashi M, Sugahara Y (2011) Hydrolysis behavior of a precursor for bridged polysilsesquioxane 1,4-bis (triethoxysilyl) benzene: a ^{29}Si NMR study. *J Sol Gel Sci Technol* 57:51–56. <https://doi.org/10.1007/s10971-010-2323-5>
51. Yamamoto K, Saito I, Amaike Y, Nakaya T, Oshita J, Gunji T (2023) Gel structure and water desalination properties of divinylpyrazine-bridged polysilsesquioxanes. *J Sol Gel Sci Technol*, <https://doi.org/10.1007/s10971-022-06017-2>
52. McIntosh GJ (2013) Theoretical investigations into the nucleation of silica growth in basic solution part I—*ab Initio* studies of the formation of trimers and tetramers. *Phys Chem Chem Phys* 15:3155–3172. <https://doi.org/10.1039/C3CP43399D>
53. Gunji T, Nagao Y, Misono T, Abe Y (1992) Condensation and structure of silicic acid in tetrahydrofuran. *J Polym Sci A Polym Chem* 30:1779–1787. <https://doi.org/10.1002/pola.1992.080300901>