



Synthesis and structure of ladder polymethylsilsesquioxanes from sila-functionalized cyclotetrasiloxanes

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ABSTRACT

Highly regulated ladder-structured polymethylsilsesquioxanes soluble in solvents with high molecular weight were synthesized from sila-functionalized tetramethylcyclotetrasiloxanes $[\text{MeSiXO}]_4$ ($X = \text{H}$, OEt , NCO) by the dehydrogenative condensation of $[\text{MeSiHO}]_4$ with water in the presence of *N,N*-diethylhydroxylamine or the hydrolytic polycondensation of $[\text{MeSiXO}]_4$ ($X = \text{OEt}$, NCO). Formation of a siloxane-ladder structure was confirmed based on the appearance of two absorption bands and a signal due to Si–O–Si linkage in the infrared spectra and a silsesquioxane unit in ^{29}Si nuclear magnetic resonance spectra, respectively. The narrow half-peak width of the ^{29}Si nuclear magnetic resonance spectra suggested the formation of a highly regulated ladder structure for polymethylsilsesquioxanes.

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1. Introduction

Recently, much attention has been focused on the synthesis of ladder polysilsesquioxanes due to their excellent chemical, physical and electrical properties derived from the double-chained siloxane structure with formula $(\text{RSiO}_{3/2})_n$. The ladder polyphenylsilsesquioxane (PPSQ) was first reported by Brown et al. by a two-step hydrolysis of trichloro(phenyl)silane followed by an equilibration reaction of the hydrolyzate with potassium hydroxide [1]. The PPSQ, they proposed, possesses a *cis*-syndiotactic ladder structure, as indicated by the powder X-ray diffraction (XRD), infrared (IR) spectra, and calculation of the a value in the Sakurada–Mark–Houwink equation.

Many PPSQs have been synthesized by utilizing the ‘alkali equilibration reaction’ method. However, the method cannot be applied to the synthesis of ladder polymethylsilsesquioxane (PMSQ) because gels are often obtained under these harsh reaction conditions. Thus, a very few papers has been published on the synthesis of PMSQ. PMSQ was synthesized by Suminoe et al. in 1978 by adding water dropwise to a methyl isobutyl ketone/tetrahydrofuran (THF) solution of trichloro(methyl)silane in the presence of triethylamine followed by heating [2]. PMSQ, thus formed, has a number-average molecular weight (M_n) of 9×10^3 and soluble in organic solvents such as THF or toluene, even after

standing for a month, but no other analytical data to discuss the structure were given.

In contrast to PPSQ, only a little information is available on the structure of PMSQ. PMSQs are simply described to have ladder structures based on their IR spectra, ^{29}Si nuclear magnetic resonance (NMR) spectra, and XRD: Maciel et al. studied the ^{29}Si cross polarization/magic angle spinning NMR spectra for solid PMSQ, which were prepared by the hydrolysis of trichloro(methyl)silane with a large excess of water or the hydrolysis of trimethoxy(methyl)silane in ethanol with hydrochloric acid [3]. In the ^{29}Si NMR spectrum, a strong signal at -65 ppm and a weak signal at -55 ppm were assigned to $\text{CH}_3\text{SiO}_{3/2}$ and $\text{CH}_3\text{Si}(\text{OH})\text{O}_{2/2}$ units, respectively. The XRD analysis of PMSQ showed broad reflections corresponding to a plane-to-plane distance of 8.7 Å and a 3.6 Å thickness of the molecular chains [4]. The structure of PMSQ, however, was suggested by Itoh et al. not to have a perfect ladder structure, based on the ^{29}Si NMR, GC-MS analysis of PMSQ, and silylated PMSQ [5]. It is, therefore, difficult to obtain PMSQ with a highly regulated ladder structure by such hydrolysis method of trifunctional silanes.

On the other hand, interest has grown in recent years regarding sila-functional cyclotetrasiloxanes as potential precursors for polysilsesquioxanes. *cis,cis,cis*-2,4,6,8-Tetrahydroxy-2,4,6,8-tetra-phenylcyclotetrasiloxane was synthesized as an intermediate by the hydrolysis of trichloro(phenyl)silane, which undergoes further condensation to give PPSQ [6]. 2,4,6,8-Tetrachloro-2,4,6,8-tetra-R substituted cyclotetrasiloxanes ($R = \text{Me}$ [7], Vi [7], Ph [8]) and 2,4,6,8-tetrahydroxy-2,4,6,8-tetra-R substituted

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cyclotetrasiloxanes (R = Ph [9], ¹Pr [10]) were synthesized. These silanols were confirmed to have a *cis,cis,cis*-configuration by the X-ray crystallography.

Tri- and penta-cyclic ladder oligosilsesquioxanes were synthesized by the heterofunctional condensation of sila-functional cyclotetrasiloxanes which are a precursor for the synthesis of highly regulated polysilsesquioxanes [10–13]. There are few reports on the synthesis of PMSQ using sila-functionalized cyclotetrasiloxanes: Uuno et al. reported on the synthesis of *cis,trans,cis*-2,4,6,8-tetrabromo-2,4,6,8-tetramethylcyclotetrasiloxane by a dearylhalogenation of *cis,trans,cis*-2,4,6,8-tetraphenyl-2,4,6,8-tetramethylcyclotetrasiloxane [14]. Because the methyl group of this compound is not bulky enough to prevent the hydrolysis of bromosilane, gelation easily takes place in air to give a white solid insoluble in organic solvents. The hydrolyzate was expected to be a PMSQ with high thermal stability and stereoregularity.

We have, therefore, selected an isocyanatosilane of pseudohalosilane as a precursor which is less reactive than chlorosilane but more reactive compared to alkoxy silane. *cis,trans,cis*-2,4,6,8-Tetraisocyanato-2,4,6,8-tetramethylcyclotetrasiloxane (**3**) was obtained as a crystal by step-wise hydrolyses of triisocyanato(methyl)silane [15]. In addition, we have reported the synthesis of tricyclic ladder oligomethylsilsesquioxanes by the heterofunctional condensation reaction of **3** with 1,3-di-*tert*-butoxy-1,3-dimethylsiloxane-1,3-diol, which reveals that **3** is a suitable building block for the synthesis of highly regulated PMSQ [16].

In this report, therefore, we will describe the synthesis of PMSQ by the dehydrogenative (X = H **1**) and the hydrolysis (X = OEt **2** and NCO **3**) of sila-functional cyclotetrasiloxanes [MeSiXO]₄, as depicted in Scheme 1. The structure and physical properties are reported based on analyses using Fourier transform infrared (FTIR) spectra, NMR spectra, and size exclusion chromatography (SEC).

2. Results and discussion

2.1. Synthesis of PMSQ-H

The synthesis of polysiloxanes from hydrosilane was performed by a non-hydrolytic condensation process and/or dehydrogenative condensation. Pyridine is reported to be an excellent catalyst for the reaction of silanes with alcohols or silanols. However, it is not suitable for the reaction of cubic silsesquioxane [17] because pyridine catalyzes the degradation reaction of siloxane frames in parallel with the siloxane bond formation. On the other hand, *N,N*-diethylhydroxylamine has been reported to be an effective catalyst for the dehydrogenative condensation reaction of (HSiO_{3/2})₈ with alcohol or silanol, without ring cleavage of cyclic and cubic siloxanes [17,18]. PMSQ-H was synthesized by the dehydrogenative polycondensation reaction of **1** with water in the presence of *N,N*-diethylhydroxylamine at room temperature. In this reaction, silanol is formed by the reaction of **1** with water with

the aid of *N,N*-diethylhydroxylamine. A siloxane bond is then formed by the condensation reactions between silanols and the dehydrogenative reaction of silanol with a hydrosilane.

The results for the synthesis of PMSQ-H are summarized in Table 1. The progress of the reaction was monitored by the evolution of hydrogen gas when *N,N*-diethylhydroxylamine was added to the reaction mixture. After the reaction under room temperature, the residual silanols were capped with chloro(trimethyl)silane to isolate PMSQ-H in a yield of 97% as a white solid. The molecular weights were calculated based on standard polystyrene using a refractive index detector with the weight-averaged molecular weight (*M_w*) = 42,000 and *M_w*/*M_n* = 2.7 (Table 2). The product was obtained in a short time at 50 °C, while a gel was gradually generated when the reaction was allowed to continue for 5 h or more. On the reaction at 66 °C, the gel was obtained in 1 h. Without the trimethylsilylation process, silica gel was formed by the condensation between silanol groups. The product was soluble in many organic solvents except for polar solvents such as methanol and acetonitrile.

In the IR spectrum (Fig. 1a) of the product, no absorption bands due to the Si–OH groups were observed, while those due to the Si–H (2171 cm⁻¹) and Si–O–Si bonds (1129 and 1038 cm⁻¹) were observed. The ¹H NMR spectrum showed signals due to methyl groups (MeSiO_{3/2} and Me₃SiO) and hydrido groups at 0.09 and 4.66 ppm, respectively, while no signal due to silanol group was observed. The ²⁹Si NMR spectrum showed broad signals at 9.0 ppm due to the (CH₃)₃SiO (M) units, at –34.9 ppm due to the CH₃Si(H)O_{2/2} (D²) units, and at –65.1 and –66.5 ppm due to the (CH₃)SiO_{3/2} (T³) units with an integration ratio of M:D²:T³ = 8:14:78 and a degree of condensation of 3.8 (Table 3).

TG-DTA analysis (Fig. 2) showed exothermic peaks at 330 °C and 440 °C due to the oxidation of hydrido groups and elimination of methyl groups. PMSQ-H showed high thermal stability based on a 5% weight loss at 435 °C and a ceramic yield of 86% under an air atmosphere.

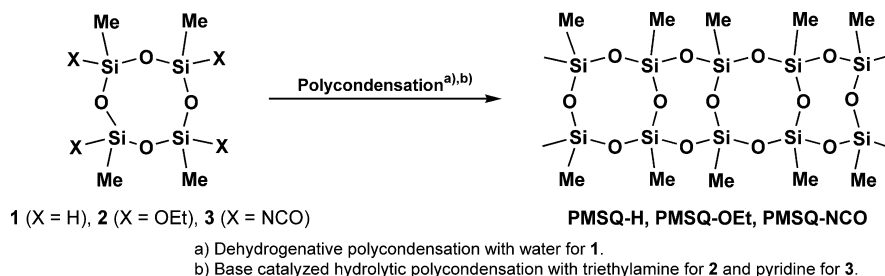
Table 1
Results on the synthesis of PMSQ.

	Monomer	Time (h)	Temperature (°C)	State	Yield (%)
PMSQ-H ^a	1	24	r.t.	white powder	97
PMSQ-OEt ^b	2	20	60	highly viscous liquid	56
PMSQ-NCO ^c	3	14	66	white powder	72

^a Scale in operation: **1** 1.20 g (5.0 mmol), water 0.18 g (10 mmol), *N,N*-diethylhydroxylamine 25 μL (0.25 mmol), THF 30 mL.

^b Scale in operation: **2** 0.83 g (2.0 mmol), water 72 mg (4.0 mmol), triethylamine 40 mg (0.40 mmol), ethanol 0.5 mL.

^c Scale in operation: **3** 0.81 g (2.0 mmol), water 72 mg (4.0 mmol), pyridine 0.32 g (4.0 mmol), THF 6 mL.



Scheme 1.

Table 2
Molecular weight information by SEC analyzed using triplicate detection system.^a

	SEC ^b			SEC-MALS ^c				
	M_w	M_n	M_w/M_n	M_w	M_n	M_w/M_n	R_{gw} (nm)	S–M–H α
PMSQ-H	42 000	16 000	2.7	214 000	71 000	3.0	5.8	0.38
PMSQ-NCO	70 000	33 000	2.1	285 000	110 000	2.7	8.3	0.53

^a M_w = weight-average molecular weight; M_n = number-average molecular weight; R_{gw} = the weight-average radius of gyration; S–M–H α = the Sakurada–Mark–Houwink “ α ” parameter.

^b With polystyrene standards.

^c With triplicate detection.

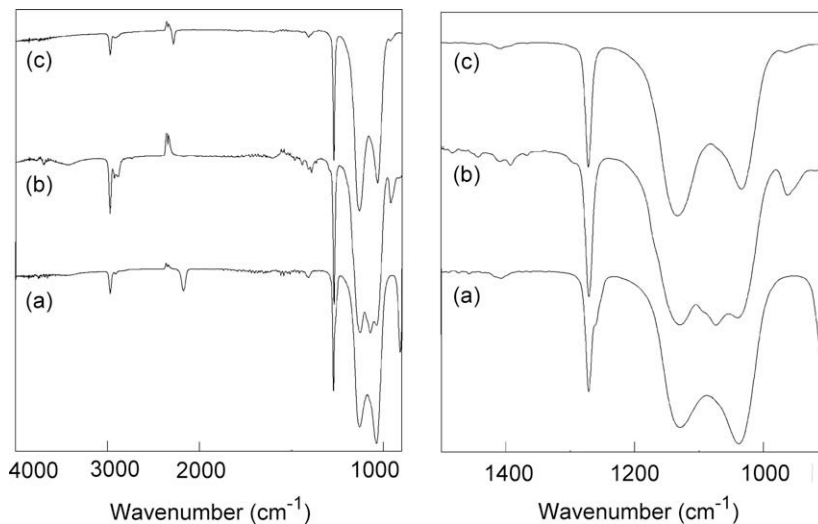


Fig. 1. FTIR spectra of (a) PMSQ-H, (b) PMSQ-OEt, and (c) PMSQ-NCO in CCl_4 (left) and their magnified spectra (right).

Table 3
Half peak width of T^3 units.

	M_w^a	$\Delta_{1/2}$ of T^{3Me} (Hz) ^b	DC ^c
PMSQ-H	42 000	190	3.8 ^d
PMSQ-OEt	55 000	184	1.3
PMSQ-NCO	70 000	118	8.9

^a Measured by SEC based on standard polystyrene.

^b Calculated by ^{29}Si NMR. Observed frequency was 60 MHz.

^c Degree of condensation. Calculated by integral ratio of T^3/T^2 in ^{29}Si NMR.

^d Calculated by integral ratio of $(T^3 - M/T^2)$ in ^{29}Si NMR.

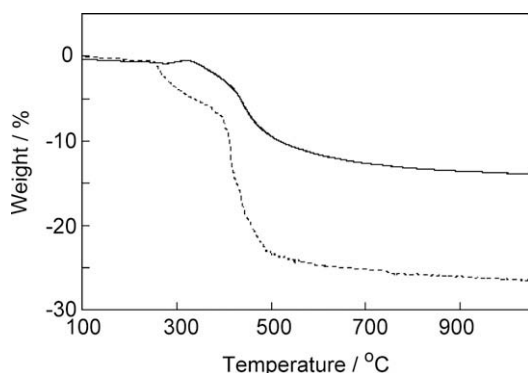


Fig. 2. TG traces of PMSQ-H (solid line) and PMSQ-NCO (dash line) with air atmosphere.

2.2. Synthesis of PMSQ-OEt

The hydrolytic polycondensation of alkoxy silanes is often carried out by using acid or base catalyst. Acid catalyst is preferable because both the molecular weight and the branching of polysiloxanes are easily controlled compared with the base-catalyzed hydrolytic polycondensation. In the hydrolytic polycondensation of **2** in the presence of a strong protic acid such as hydrochloric acid, the ring-degradation polymerization takes place in parallel to the polycondensation of ring systems. Cyclosiloxane ring is cleaved by strong protic acids such as sulfuric and trifluoromethanesulfonic acid [19,20]. In this work, therefore, the hydrolytic polycondensation of **2** was carried out under basic conditions.

The hydrolytic polycondensation reaction of **2** was carried out in the presence of triethylamine at 60 °C to provide PMSQ-OEt in 56% yield as a colorless viscous liquid. When pyridine was used as a basic catalyst, the condensation reaction hardly proceeded and only low-molecular-weight PMSQ-OEt was obtained. The product was soluble in many organic solvents, but less soluble in hexane and methanol, probably resulted from the remaining of many ethoxy groups. The molecular weights were calculated to be $M_w = 55,000$ and $M_w/M_n = 5.8$ based on standard polystyrene using a refractive index detector. High polydispersity indicated that the reaction did not selectively provide a fused-ring or ladder structure but a random structure. In this reaction, an appreciable amount of **2** was recovered, as is usual for the base-catalyzed hydrolytic polycondensation of alkoxy silanes.

The IR spectrum (Fig. 1b), showed the absorption bands at 1129 and 1033 cm^{-1} due to the Si–O–Si bond were observed in addition

to the broad and weak absorption band at 3433 cm^{-1} due to the Si–OH group. In the ^1H NMR spectrum, the signals due to the methyl group and ethoxy group were observed at 0.15 ppm and at 1.21 and 3.79 ppm, respectively, while the signal due to the silanol group was unclear. The ^{29}Si NMR spectrum showed the broad signals at -57 ppm due to the $\text{CH}_3\text{Si}(\text{OEt})\text{O}_{2/2}$ (T^2) units and at -64.6 and -66.1 ppm due to $\text{CH}_3\text{SiO}_{3/2}$ (T^3) units with an integration ratio of $T^3/T^2 = 1.3$. Because the absorption bands and signals due to the cleavage of cyclic siloxane were not observed in IR and NMR spectra, respectively, the base-catalyzed hydrolytic polycondensation reaction seems to progress while maintaining the framework of cyclic siloxane.

2.3. Synthesis of PMSQ-NCO

Isocyanatosilanes are known to be a pseudohalosilane which is hydrolyzed like halosilanes conveniently with a base-catalyst to form siloxanes [16]. PMSQ-NCO was, therefore, synthesized by the hydrolytic polycondensation of **3** in the presence of pyridine.

The hydrolytic polycondensation of **3** followed by the reaction with ethanol to give PMSQ-NCO in 72% yield as a white solid. The molecular weights were calculated to be $M_w = 70,000$ and $M_w/M_n = 2.1$ based on standard polystyrene using a refractive index detector. On the reaction for 37 h, M_w was increased to 230,000 ($M_w/M_n = 5.0$). The product was soluble in many organic solvents except for polar solvents such as methanol and acetonitrile.

In the IR spectrum (Fig. 1c), the absorption bands at 1132 and 1033 cm^{-1} due to the Si–O–Si bond were observed, while a weak absorption band at 2288 cm^{-1} due to the isocyanato group was observed. The remaining isocyanato group suggests that the isocyanato group is not completely substituted by ethoxy group due to the steric hindrance of the polymer framework. In the ^1H NMR spectrum, the signals due to the methyl and ethoxy group appeared at 0.13 ppm and at 1.21 and 3.81 ppm, respectively, while a signal due to silanol was not observed. The ^{29}Si NMR spectrum showed broad signals at -58.2 and -64.8 ppm due to the T^2 units and T^3 units, respectively, with an integration ratio of $T^3/T^2 = 8.9$.

TG-DTA analysis (Fig. 2) showed the exothermic peaks at $260\text{ }^\circ\text{C}$ and $465\text{ }^\circ\text{C}$ due to the elimination of ethoxy groups and methyl groups with a 5% weight loss ($340\text{ }^\circ\text{C}$) and ceramic yield of 77% under an air atmosphere.

2.4. FTIR spectra

IR spectroscopy has been used as a powerful technique to analyze the ladder structure of siloxane materials. The characteristic asymmetric absorption band of the Si–O–Si bond at 1030 – 1150 cm^{-1} region was found to shift dependent on the structures such as length of the repeating Si–O–Si units, size of the siloxane rings, and symmetry of the molecules [21]. Brown reported that the interconversion between cubes and PPSQs can be monitored by using IR spectroscopy: the cube structure shows one strong absorption band at 1120 – 1130 cm^{-1} , while two absorptions are found at 1150 – 1135 and 1045 cm^{-1} for ladder polymers, regardless of the side group [22].

FTIR spectra of PMSQ-H, PMSQ-OEt, and PMSQ-NCO are shown in Fig. 1. Strong absorption bands attributed to asymmetric Si–O–Si stretching were observed at 1130 and 1030 cm^{-1} . Unno et al. also reported two sharp Si–O–Si stretching absorption bands at 1128 and 1032 cm^{-1} for PMSQ synthesized by the hydrolysis of *cis,trans*-2,4,6,8-tetrabromo-2,4,6,8-tetramethylcyclotetrasiloxane [14]. When the side group was changed from hydrido group in PMSQ-H to an isocyanato group in PMSQ-NCO, the intensity at 1130 cm^{-1} was increased while that at 1030 cm^{-1} was decreased. The absorption band due to Si–O–Si vibration is reported to shift to

a higher frequency up to 1120 cm^{-1} when the siloxane framework becomes rigid in the order of polydimethylsiloxane (1090 , 1020 cm^{-1}), octamethyltetraacyclosiloxane (1080 cm^{-1}), and cage silsesquioxane (1120 cm^{-1}). Because PMSQ-NCO shows a strong absorption band at higher frequency, PMSQ-NCO is composed of rigid siloxane frameworks compared with PMSQ-H and PMSQ-OEt.

2.5. SEC analysis

The absolute molecular weight, intrinsic viscosity, and molecular radius of gyration were analyzed and calculated by the integration of a triplicate detection SEC system (3D SEC: on-line light scattering, viscometry, and refractive index detectors). The absolute molecular weights and other important size and conformational information are summarized in Table 2 and Fig. 3. Unfortunately, PMSQ-OEt could not be analyzed because of the rapid self-condensation to form gels within several days. The M_w s of PMSQ-H and PMSQ-NCO were 214 000 and 285 000, respectively, which are greater than the calculated data based on the standard polystyrene.

The intrinsic viscosity and weight-averaged molecular weight are correlated by the Sakurada–Mark–Houwink equation as $[\eta] = KM_w^a$: $[\eta]$ is an intrinsic viscosity, M_w is the weight-averaged molecular weight, and K and a are the constants that are characteristic of polymers. The value of a is believed to reflect the rigidity and branching of polymer chain as follows: $0.3 < a < 0.5$ for branched chains, $0.5 < a < 0.8$ for flexible chains, $0.8 < a < 1.0$ for inherently stiff molecules, and $1.0 < a < 1.7$ for highly extended chains. The a values for PPSQs are reported to be $0.54 < a < 1.10$, which is dependent on the synthetic conditions and the molecular weights of PPSQs. For example, Brown et al. reported $a = 0.92$ for PPSQ with a linear and almost rigid-rod like double-chain structure [1]. On the other hand, the lower a values in some high-molecular-weight polymers are attributed to the branching of the polymers such as a worm-like chain model for phenylsiloxane resins. In addition, the a value for PMSQ is suggested to be 0.3, which indicates that the siloxane framework is sphere-like but not a stiff structure [23].

In this work, we have proposed a fused-ring structure for PMSQ-H, PMSQ-OEt, and PMSQ-NCO, which shows flexibility to allow the formation of random-coil conformations at high molecular weight. The a value in the Sakurada–Mark–Houwink equation was evaluated for PMSQ-H and PMSQ-NCO to show almost linear correlations between $\log[\eta]$ and $\log[M_w]$ (Fig. 4). The a value was 0.38 for PMSQ-H, which indicates a compact hyper-branched structure. On the other hand, the a value was 0.53 for PMSQ-NCO, which may suggest a flexible ladder structure for PMSQ-NCO. The structure of PMSQ-H and PMSQ-NCO will be discussed in the next section in relation to the ^{29}Si NMR spectra.

2.6. ^{29}Si NMR spectra

The structural regularity of ladder polysilsesquioxanes is actively discussed in ^{29}Si NMR analysis. Because of the difficulty in obtaining structural information of PMSQ, spectral data of various ladder oligosilsesquioxanes were reported. The ^{29}Si NMR spectrum showed the signals at -64 to -66 ppm for pentacyclic ladder oligosilsesquioxanes with isopropyl groups [24] and at -64 to -65 ppm for tricyclic ladder oligosilsesquioxanes with methyl groups [16]. On the other hand, polymethylsilsesquioxane which is composed of three dimensional siloxane structure and synthesized by the acid-catalyzed hydrolytic polycondensation reaction of trimethoxy(methyl)silane, showed a main signal at -67 ppm and a minor signal at -63 ppm [25]. As shown in Fig. 5, the ^{29}Si NMR spectra showed a signal at around -65.0 ppm due to highly regulated ladder structure and a shoulder peak at -66.5 ppm due

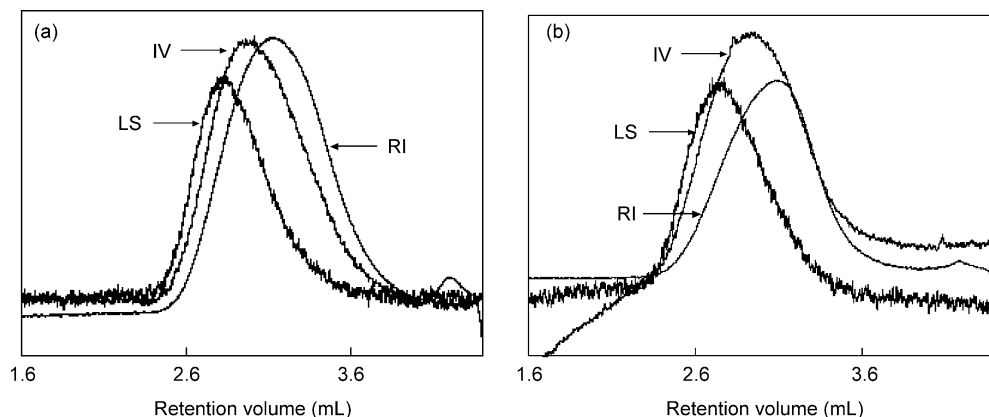


Fig. 3. Overlay of detector signals for SEC; (a) PMSQ-H, (b) PMSQ-NCO in THF (LS; light scattering, IV; viscosity, RI; refractive index).

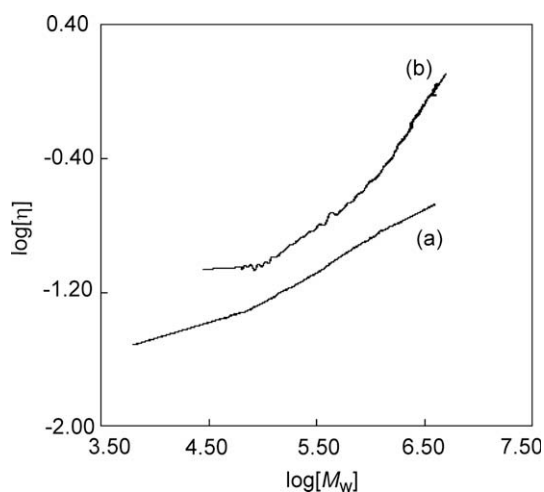


Fig. 4. Plots of $\log[\eta]$ versus $\log[M_w]$; (a) PMSQ-H, (b) PMSQ-NCO.

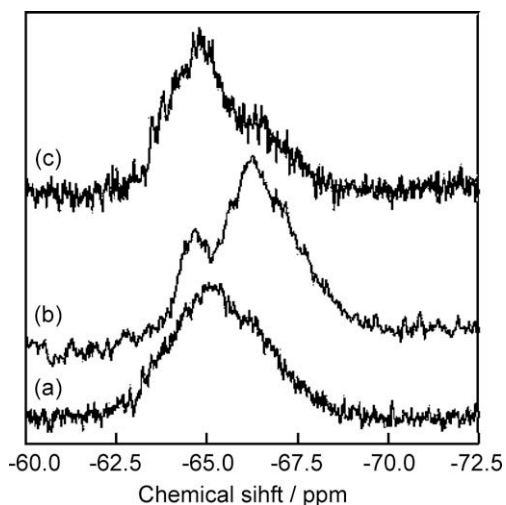


Fig. 5. ^{29}Si NMR spectra of (a) PMSQ-H, (b) PMSQ-OEt, and (c) PMSQ-NCO in CDCl_3 .

to structural defects for PMSQ-H and PMSQ-NCO, respectively. PMSQ-OEt showed a main signal at -66.5 ppm and a minor signal at -65.0 ppm. These results support the presence of an irregular structure for PMSQ-OEt compared with those of PMSQ-H and PMSQ-NCO.

It is well known that the half-peak width ($\Delta_{1/2}$) due to T^3 unit decreases with increases in the regularity of polymer skeleton. As such, polysilsesquioxanes must have a sharp signal due to the high degree of regularity of the polymer structure. Yamamoto et al. have reported the value $\Delta_{1/2} = 240\text{--}300$ Hz for a low-molecular-weight PPSQ [6]. In addition, Zhang et al. have reported the value $\Delta_{1/2} = 149$ Hz for a high-molecular-weight ($M_w = 7690$) PPSQ prepared by the polycondensation of self-organized monomer with a bulky side chain induced by the lyophilization on the surface of flask [26].

As shown in Table 3 and Fig. 5, the ^{29}Si NMR spectra of PMSQ-H and PMSQ-OEt showed the signals at around -65 ppm with $\Delta_{1/2}$ of 190 and 184 Hz, respectively, indicating the presence of many structural defects in the polymer backbone, which corresponds to the low values for the degree of condensation. On the other hand, PMSQ-NCO showed a very small value $\Delta_{1/2} = 118$ Hz and a high degree of condensation resulting from the highly regulated ladder structure and less defects in the siloxane framework, nevertheless PMSQ-NCO has a less bulky side chain of methyl group.

The molecular weights of PMSQ-NCO were confirmed to be $M_w = 70\,000$ (calculated based on standard polystyrene) and $M_w = 285\,000$ (calculated by light scattering as an absolute molecular weight) in THF. The difference between these M_w s was due to the lower solubility and/or swelling of PMSQ-NCO compared with that of polystyrene: a rigid framework of polymer chain causes a low swelling in solvent, which results in a lower molecular weight than the corresponding polystyrene. The rigidity of the polymer framework in PMSQ-NCO is further evidenced by the relatively high glass-transition temperature, 120°C . As a result, PMSQ-NCO is a highly regulated ladder silsesquioxane with appreciably less defects in the siloxane framework, which has a random-coil conformation composed of highly regulated ladder silsesquioxanes.

The experimental results obtained in this work clearly indicate that the structural regularity of PMSQ formed is closely related to the stereostructure of precursor $[\text{MeSiXO}]_4$ ($X = \text{H}, \text{OEt}, \text{NCO}$) and the reactivity of sila-functional group; in the precursor **2**, the stereostructure is not regulated (a mixture of four stereoisomers determined by ^1H and ^{29}Si NMR spectrum) and also the reactivity of ethoxy group is lower than that of hydrido and isocyanato group. Thus the hydrolytic polycondensation has to be carried out with a base, which results in the formation of PMSQ with a high polydispersity in a relatively low yield. The precursor **1** is also a mixture of four stereoisomers. In addition, PMSQ is formed by the two step reaction of hydrolysis followed by condensation, which make it difficult to control the reaction and/or to regulate preferable structure of PMSQ. On the other hand, the stereostructure of **3**

is regulated in *cis,trans,cis*-configuration and the reactivity of isocyanato group is high enough to conduct a controlled hydrolytic polycondensation to afford a desirable silsesquioxane frame with retaining the structure of precursor. This is a first PMSQ with a regulated structure which has never been obtained.

3. Conclusions

Ladder polymethylsilsesquioxanes (PMSQ) were synthesized from sila-functionalized tetramethylcyclotetrasiloxanes [MeSiXO]₄ (X = H, OEt, NCO) by the dehydrogenative condensation of [MeSi(OH)₂]₄ with water in the presence of *N,N*-diethylhydroxylamine or the hydrolytic polycondensation of [MeSi(OEt)O]₄ or *cis,trans,cis*-[MeSi(NCO)O]₄. The formation of the siloxane-ladder structure was estimated by the two bands appeared at low and high wavenumber of due to the Si–O–Si linkage in the infrared spectra and also the signal due to the silsesquioxane unit in the ²⁹Si nuclear magnetic resonance. A narrow half-peak width of the ²⁹Si nuclear magnetic resonance suggested the formation of a highly regulated ladder structure for PMSQs. The size exclusion chromatography with triplicate detection supports the presence of an irregular structure for PMSQ-H and PMSQ-OEt; on the other hand, PMSQ-NCO has a highly regulated ladder structure, or a random-coil conformation, with less defects in the siloxane framework.

4. Experimental section

4.1. General experimental procedures

All reagents were obtained from commercial sources and used without additional purification. Sila-functional cyclotetrasiloxanes [MeSiXO]₄ (X = H **1**, OEt **2**) was purchased from Shin-Etsu Chemical, and *cis,trans,cis*-[MeSi(NCO)O]₄ (**3**) was prepared according to the literature [15]. Triethylamine, chloro(trimethyl)silane, and tetrahydrofuran were purified by distillation. Fourier transform NMR spectra were obtained by JEOL ECP-300 (¹H at 300 MHz, ¹³C at 75 MHz, and ²⁹Si at 60 MHz). Chemical shifts were reported as δ units (ppm) relative to SiMe₄, and/or the residual solvent peaks used as a standard. ²⁹Si NMR spectra were obtained on samples with chromium(III) acetylacetonate as a relaxation agent. FTIR spectra were measured using a JASCO FT-IR-6100 IR spectrophotometer by means of a carbon tetrachloride solution method. Size exclusion chromatography (SEC) was carried out by Shimadzu LD-10AD with two Polymer Laboratory Mixed-D 250 mm × 20 mm columns and a refractive index detector. THF was used as an eluent (1 mL/min). SEC using triplicate detection was performed on a TOSOH HLC-8220 GPC using two TSK#gel SuperMultiHZ-M × 2 (150 × 4.6 mm, 4 μm). The columns were thermostated at 40 °C. The detection system consisted of a Viscotek TDA302 multiple detectors (viscosity and right angle laser light scattering). Tetrahydrofuran was used as an eluent (0.35 mL/min). Differential thermogravimetric analysis (TG-DTA) was performed using a MAC Science TG-DTA2020S at a heating rate of 10.0 °C/min under an air atmosphere. Differential scanning calorimetric (DSC) analysis was performed using a Shimadzu DSC-60 at a heating rate of 10.0 °C/min under a nitrogen atmosphere.

4.2. Synthesis of PMSQ-H by dehydrogenative hydrolytic polycondensation of **1**

A two-necked flask equipped with a reflux condenser was charged with **1** 1.20 g (5.0 mmol), water 0.18 g (10 mmol), and THF 30 mL, while *N,N*-diethylhydroxylamine 25 μL (0.25 mmol) was added to the flask and subjected to stirring at room temperature for 24 h. Chloro(trimethyl)silane 1.00 g (10.0 mmol) and

triethylamine 0.80 g (8.0 mmol) were added to the mixture. The reaction mixture was refluxed for 2 h, and the triethylamine hydrochloride was then filtered out. The solution was evaporated and poured into methanol with vigorous stirring. The precipitate was filtrated and dried under reduced pressure to give a white powder.

¹H NMR (CDCl₃) δ 0.09 (br, 20H), 4.66 (br, 1H). ¹³C NMR (CDCl₃) δ -3.1, 0.62, 1.53. ²⁹Si NMR (CDCl₃) δ 9.0, -34.9, -65.1, -66.5. IR (CCl₄) 2969, 2171, 1129, 1038, 909 cm⁻¹.

4.3. Synthesis of PMSQ-OEt by hydrolytic polycondensation of **2**

A two-necked flask equipped with a reflux condenser was charged with **2** 0.83 g (2.0 mmol), water 72 mg (4.0 mmol), triethylamine 40 mg (0.40 mmol), and ethanol 0.5 mL, and then the solution was stirred at 60 °C for 20 h. Diethyl ether was added to the solution and washed with dilute hydrochloric acid, followed by washing three times with water. The organic phase was dried over magnesium sulfate. After filtration and evaporation, methanol was added to the resulting highly viscous liquid and kept at -60 °C for 2 h. The supernatant liquid was decanted off, and the resulting product was washed with cooled methanol. The final product was then dried under reduced pressure to give a colorless viscous liquid.

¹H NMR (CDCl₃) δ 0.15 (br, 17H), 1.21 (br, 6H), 3.79 (br, 4H). ¹³C NMR (CDCl₃) δ -4.7, -3.5, 18.1, 58.1. ²⁹Si NMR (CDCl₃) δ -57.2, -57.4, -57.5, -57.6, -57.9, -58.1, -64.6, -66.1. IR (CCl₄) 3433, 2975, 2927, 1270, 1129, 1073, 1033, 961 cm⁻¹.

4.4. Synthesis of PMSQ-NCO by hydrolytic polycondensation of **3**

A two-necked flask equipped with a reflux condenser was charged with **3** 0.81 g (2.0 mmol) and THF 4 mL, while a solution of water 72 mg (4.0 mmol), pyridine 0.32 g (4.0 mmol) in THF 2 mL was added to the flask and subjected to reflux for 14 h. Ethanol (5 mL) was added to the mixture and refluxed for 2 h. After filtering the cyanuric acid, diethyl ether was added to the solution and washed with dilute hydrochloric acid, followed by washing three times with water. The organic phase was dried over magnesium sulfate and evaporated. The solution was poured into methanol with vigorous stirring. The precipitate was filtrated and dried under reduced pressure to give a white powder.

¹H NMR (CDCl₃) δ 0.13 (br, 30H), 1.21 (br, 3H), 3.81 (br, 2H). ¹³C NMR (CDCl₃) δ -4.0, 18.1, 58.0. ²⁹Si NMR (CDCl₃) δ -58.2, -64.8, -66.5. IR (CCl₄) 2972, 2288, 1270, 1132, 1033 cm⁻¹.

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