

Synthesis and Polymerization Behavior of Oligosiloxanes Possessing Alkoxy Groups

アルコキシ基を有する
オリゴシロキサンの合成と重合挙動

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Preface

Siloxane-based materials have been developed not only academically but also industrially because of their features. The amounts of main components (silicon and oxygen) are plenty as resources and the functionalization by combining with other materials is feasible. Because the structure of siloxane networks is one of the key factors to govern the properties of siloxane-based materials, the structural control of the network on a molecular level is quite important for preparation of the materials with desired functionality. However, conventional synthetic methods of siloxane-based materials (condensation of monomeric organosilanes as typified by sol-gel process) have a limitation on the construction of controlled siloxane networks because of the difficulty of controlling the siloxane bond formation reaction, the different reactivity among starting materials for the reaction, and so on.

Building block approach is an effective strategy to control siloxane networks on a molecular level because molecules with well-defined siloxane structure are used as starting materials. In this synthetic methodology, the structures and functions of products depend on not only the structure of building blocks but also their bonding states; therefore, the selection of siloxane bond formation reaction is critical for the construction of siloxane networks by connecting them. In particular, siloxane bond formation reactions by using organosilanes with alkoxysilyl groups as precursors are useful to cross-link building blocks because of the controllability of reactions and variety of starting materials; therefore, oligosiloxanes possessing alkoxy groups are valuable compounds as building blocks. However, the synthetic methods of such oligosiloxanes are limited and the variety of composition and structure of oligosiloxanes synthesized by those methods are restricted.

In this thesis, the development of novel synthetic methods for oligosiloxanes

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possessing alkoxy groups and the evaluation of polymerization behaviors of the synthesized oligosiloxanes are described. Novel synthetic methods of oligosiloxanes are developed by introducing knowledge of synthetic organic chemistry into their syntheses. In addition, the investigation on the polymerization behaviors of synthesized compounds shows their usefulness as precursors for siloxane-based materials.

This thesis is composed of six chapters as follows.

Chapter 1 describes the background of this thesis and the general introduction of oligosiloxanes possessing alkoxy groups. First, siloxane-based materials prepared using oligosiloxanes as building blocks are reviewed. Then, siloxane bond formation reactions for synthesis and polymerization of oligosiloxanes are summarized. Next, the synthetic methodologies of oligosiloxanes, in particular oligosiloxanes possessing alkoxy groups, are described.

Chapter 2 describes the synthesis and polymerization by sol–gel reaction of oligosiloxane possessing both several organic functional groups and alkoxy groups. An oligosiloxane was synthesized by stepwise alkoxylation of organosilane possessing two different functional groups, of which the reactivities are different, with two kinds of organoalkoxychlorosilanes. In order to construct the objective siloxane structure with retaining alkoxy groups, non-hydrolytic siloxane bond formation reactions were used for alkoxylation. In addition, the reaction indicating a different selectivity from the first alkoxylation was used for the second alkoxylation to suppress the substitution of alkoxy groups which were introduced to the starting materials in the first step. These considerations for the selection of reactions and their conditions enabled the synthesis of oligosiloxane possessing both several organic functional groups and alkoxy groups while satisfying the two conditions simultaneously as follows: (i) construction of oligosiloxane structure without degradation of alkoxy groups and (ii) introduction of organic functional

groups and alkoxy groups without cleavages of siloxane bonds. The synthesized oligosiloxane can be hydrolyzed and polycondensed with retaining the original siloxane structure, which indicates that the oligosiloxane can be used as a precursor for siloxane-based materials with homogeneous composition.

Chapter 3 describes the development of novel synthetic methodology of oligosiloxanes possessing alkoxy groups by introducing the concept of protecting groups in synthetic organic chemistry into the synthesis of oligosiloxanes. Trimethylsilyl ($-\text{SiMe}_3$, TMS) group are often used as a protecting group for hydroxy groups in synthetic organic chemistry; therefore, TMS group is expected to act as a protecting group for silanol ($-\text{SiOH}$) groups. First, novel substitution reaction of trimethylsilyl groups with alkoxy groups was discovered by the reaction between $\text{Si}(\text{OSiMe}_3)_4$ and $\text{ClSiMe}(\text{OMe})_2$ in the presence of BiCl_3 catalyst. The conversion of TMS groups of $\text{Si}(\text{OSiMe}_3)_4$ was 84% and it was increased to 98% through biasing the equilibrium of the reaction by removing the by-product. Then, the substrate versatility of the substitution reaction was investigated by using trimethylsilylated oligosiloxanes such as disiloxane and polyoctahedraloctasiloxane as starting materials. The conversion of TMS groups linked to such oligosiloxanes was about 30% because of the steric hindrance around TMS groups in oligosiloxanes, which indicates that the substitution reaction substrate tolerance of the substitution reaction of TMS groups is limited. Finally, TMS groups of the organosilane possessing both silanol and TMS groups were substituted with alkoxy groups after the alkoxylation of the silanol groups while the first introduced alkoxy groups to silanol group was retained during the substitution of TMS groups. This result shows both TMS groups can work as a protecting group of silanol groups and the substitution reaction of TMS groups is useful for the synthesis of oligosiloxanes possessing alkoxy silyl groups.

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Chapter 4 describes the synthesis and polymerization behaviors of cyclic oligosiloxane (cyclododecasiloxane) possessing alkoxy groups and the structural analysis of the polymerization products. First, novel cyclododecasiloxane with triethoxysilyl groups was synthesized by alkoxylation of the complex containing cyclododecasiloxane with chlorotriethoxysilane. Next, the synthesized cyclic siloxane was hydrolyzed and polycondensed under acidic conditions. Considering the reaction conditions, the hydrolysis and polycondensation proceeded with retaining the original cyclic structure. Xerogels were prepared from the hydrolyzed solution of the synthesized cyclododecasiloxane and the original cyclic structure was retained when the drying temperature of the gels was lower than 200 °C. To evaluate the gas permeance of the xerogels, the hydrolyzed solution of cyclododecasiloxane was coated onto a porous alumina tube to prepare gas permeable membranes. The gas permeance which is expected from the cyclic structure was not obtained and the permeance was similar to that of the membrane prepared from two kinds of alkoxy silane monomers. This result indicates that when cyclic oligosiloxanes are used as building blocks to utilize their inner spaces, guest species should be used to open the cyclic structure or the kinds of polymerization reactions and their conditions should be considered to suppress the formation of small cyclic structures.

Chapter 5 describes the synthesis and non-hydrolytic polymerization (Piers-Rubinsztajn reaction, P-R reaction) of cyclododecasiloxane possessing alkoxy groups and the structural evaluation of the polymerization products. First, two kinds of cyclododecasiloxanes were synthesized; one possesses $-\text{SiHMe}_2$ groups and the other possesses $-\text{SiMe}_2(\text{OEt})$ groups. The latter one was newly synthesized by ethoxylation of the former. Then, these two oligosiloxanes were polymerized by the P-R reaction in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ catalyst. Using the non-hydrolytic siloxane bond formation reaction

led to the polymerization with retaining their original ring structures. These results show the effectiveness of the P-R reaction for polymerization of two kinds of oligosiloxanes toward the construction of polyorganosiloxanes with well-defined architectures.

Chapter 6 describes the conclusion of this thesis. This thesis shows usefulness of oligosiloxanes possessing alkoxy groups for the preparation of siloxane-based materials by both the development of their novel synthetic methods and the evaluations of their polymerized products. The development of the concept described in this thesis will contribute to the precise design of siloxane-based materials.

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Chapter 1

General Introduction

1.1 Introduction

Materials consisting of silicon and oxygen as main components (hereafter denoted as “siloxane-based materials” in this thesis) are widely used not only commodities but also industrials. The structure of siloxane networks is a key factor to govern the properties; therefore, the structural control of siloxane network is essential for the preparation of siloxane-based materials. To control siloxane networks, the use of oligosiloxanes with well-defined siloxane structure as building blocks is an effective methodology.

Chapter 1 describes the background of this study and the general introduction of oligosiloxanes. The background of this thesis is described in section 1.2. In section 1.3, applications of oligosiloxanes as building blocks for the preparation of siloxane-based materials are overviewed. Siloxane bond formation reactions, which are used to synthesize and polymerize oligosiloxanes, are summarized in section 1.4. Synthetic methods of oligosiloxanes possessing alkoxy groups are described in section 1.5. The motivation and purpose of this thesis are shown in section 1.6.

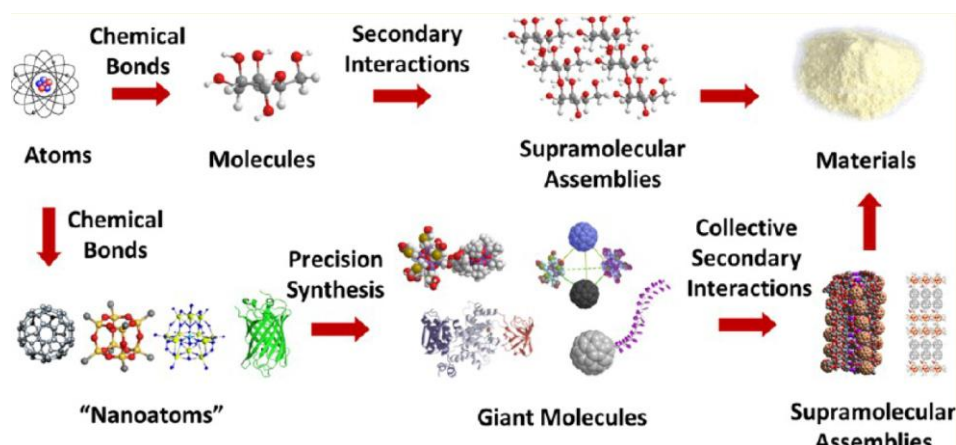
1.2 Background

In this section, brief overview of siloxane-based materials, in particular, relationships between structures and functions are summarized as a background of this thesis.

Siloxane-based materials, such as zeolites, clays, silica, and silicone, are mainly composed oxygen and silicon which are the most abundant elements in earth's crust. Their frameworks are constructed with siloxane bonds (Si–O), and structural control of siloxane networks is a key factor to govern the properties. For example, one-dimensional (1-D) structured materials, such as silicone oil, show flexibility, gas permeability, and so

on. Some minerals of layered silicates and clays, which are typical examples of 2-D structured siloxane-based materials, exhibit intercalation ability. Crystalline 3-D siloxane frameworks like zeolites perform molecular sieving effects. From the viewpoint of functionalization of siloxane-based materials, they are easily hybridized with other materials (organic materials and metal oxides *etc.*) via Si–C or Si–O–M bonds (M: metal). Therefore, the structural design of siloxane networks is also important for functionalization because it leads to distribution control of other components. Although the structural control of siloxane networks is quite important for the development of novel materials and functionalities as mentioned above, conventional synthetic methodologies, such as solid-phase reaction and polymerization of monomeric silicon compounds, can not be fully applied for their structural control.

Recently, bottom-up synthetic methodology (building block approach) has been focused as a structural control method for siloxane-based materials (Scheme 1.1).¹⁻⁵ Molecules with well-defined siloxane structures, that are oligosiloxanes, are used as single precursors for the preparation of desired materials (summarized in details in section 1.3). The structures and functions of final products directly depend on those of building blocks; therefore, the precise structural design of building blocks is essential. The synthesis of well-defined oligosiloxanes has been widely conducted and various oligosiloxanes like linear-, branched-, cyclic-, and cage-type siloxanes have been reported. In addition, hybridization of such oligosiloxanes with organic compounds or metal ions has been also developed for their functionalization.



Scheme 1.1. Schematic image of material synthesis based on the building block approach. Reprinted with permission from W.-B. Zhang, X. Yu, C.-L. Wang, H.-J. Sun, I.-F. Hsieh, Y. Li, X.-H. Dong, K. Yue, R. V. Horn, S. Z. D. Cheng, “Molecular Nanoparticles Are Unique Elements for Macromolecular Science: From “Nanoatoms” to Giant Molecules”, *Macromolecules* **2014**, *47*, 1221. Copyright 2014 American Chemical Society.

The kind of building blocks and their cross-linking and orientation methods affect both the structures and functions of final. Although organic linkers are often used to connect building blocks, cross-linking by siloxane bonds is more desirable for the preparation of siloxane-based materials with higher stability. For the cross-linking of oligosiloxanes by siloxane bonds, the selection of siloxane bond formation reactions is critical for the construction of siloxane networks. Among various functional groups which can be transformed into siloxane bond, alkoxy groups are useful starting materials for construction of controlled siloxane networks⁶ because of several features as follows: (i) easiness of handling than other silicon compounds, (ii) variety of alkoxy groups (primary, secondary, and tertiary), (iii) versatility of siloxane bond formation reactions using alkoxy groups as precursors (the details are shown in section 1.4), and (iv) relative easy controllability of such reactions. Therefore, oligosiloxanes possessing alkoxy groups are valuable compounds as building blocks for the preparation of siloxane-based

materials. Although the library of building blocks is desirable to be plenty, the synthetic methods of oligosiloxanes having alkoxy groups are limited (summarized in section 1.5). In addition, the variety of composition and structure of oligosiloxanes obtained by those methods are restricted. Therefore, novel synthetic methods must be developed to solve the issue.

1.3 Siloxane-based materials prepared by using oligosiloxanes as building blocks

In this section, applications of oligosiloxanes as building blocks for siloxane-based materials are described. They are classified by focusing on the presence or absence of noncovalent interactions or not in cross-linking process of building blocks. In section 1.3.1, materials prepared without noncovalent interactions (direct polymerization) are summarized. Section 1.3.2 shows the orientation control of building blocks by noncovalent interactions.

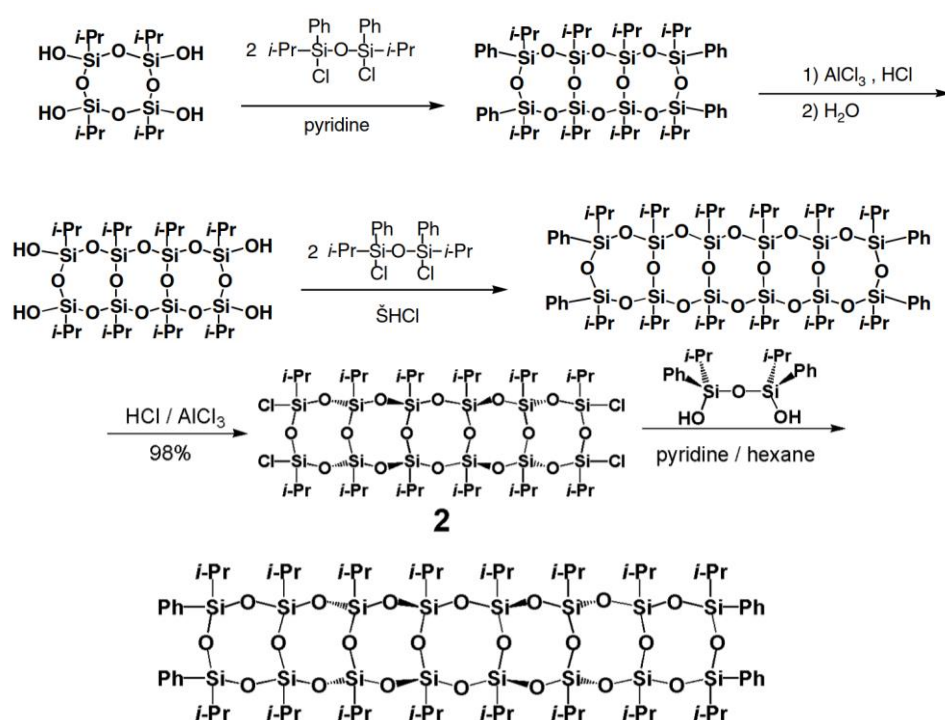
1.3.1 Direct polymerization of oligosiloxanes

Architectures of the siloxane network formed by polymerizing oligosiloxanes are dependent on both the number of reaction sites and structures of oligosiloxanes. In the case of direct polymerization of oligosiloxanes (not using self-assembly), the formed siloxane structures are 1-D and 3-D. Two-dimensional structures are not reported by direct polymerization to the best of my knowledge. 1-D and 3-D structured polymers are summarized in section 1.3.1.1 and 1.3.1.2, respectively.

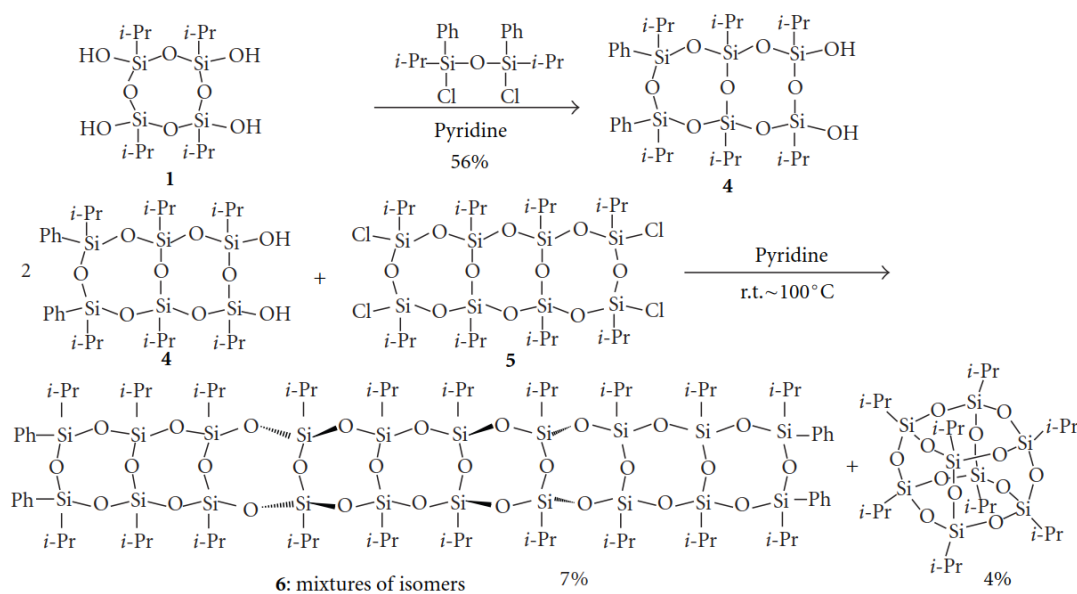
1.3.1.1 1-D structured polymers

1-D structured polymers are synthesized by stepwise elongation of polymer

chains or one-pot polymerization. The previous studies using the former method are few in number. Unno *et al.* reported the synthesis of ladder structured siloxanes via the former method by condensation between cyclotetrasiloxane and disiloxanes. They succeeded in synthesizing tri-,⁷ penta-,⁸ hepta-,⁹ and nonacyclic ladder siloxanes¹⁰ (Schemes 1.2⁹ and 1.3¹⁰). These ladder siloxanes are difficult to be synthesized by polycondensation of trifunctional organosilicon compounds, so that building block approach is useful for the construction of controlled siloxane architectures.



Scheme 1.2. Synthesis of tri-, penta-, and heptacyclic ladder siloxanes. Reprinted with permission from S. Chang, T. Matsumoto, H. Matsumoto, M. Unno, “Synthesis and Characterization of Heptacyclic Laddersiloxanes and Ladder Polysilsesquioxane”, *Appl. Organometal. Chem.* **2010**, 24, 241. Copyright 2010 John Wiley & Sons, Ltd.



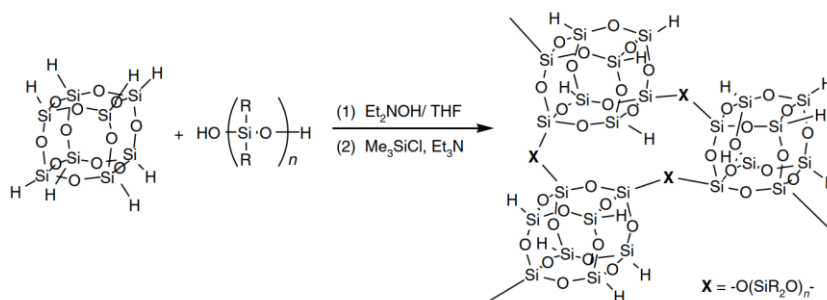
Scheme 1.3. Synthesis of nonacyclic ladder siloxane. Reprinted with permission from M. Unno, T. Matsumoto, H. Matsumoto, “Nonacyclic Ladder Silsesquioxanes and Spectral Features of Ladder Polysilsesquioxanes”, *Int. J. Polym. Sci.*, **2012**, 2012, Article ID 723892. Copyright 2012 Hindawi Publishing Corporation.

One-pot polymerization (the latter method) is the most general way to obtain 1-D structured polymers. Ladder siloxanes mentioned above are also synthesized by polymerization of disiloxanes^{11, 12} or cyclotetrasiloxanes¹³⁻¹⁵ though the products contain disordered cross-linking between ladder chains, judging from their broad ^{29}Si NMR signals. In addition to disiloxanes and cyclic siloxanes, bifunctional cage-type siloxanes, containing double-decker-type siloxane, are often used as monomers for the preparation of 1-D structured polymers.¹⁶⁻¹⁹

1.3.1.2 3-D structured polymers

3-D structured polymers are synthesized by polymerization of oligosiloxanes possessing more than three reactive sites. Cage-type oligosiloxanes are often used as precursors for the preparation of porous materials because of their multifunctionality and

rigid siloxane structure (a typical example is shown in Scheme 1.4). Many researchers reported various polymerization of cage-type oligosiloxanes as follows: (i) cross-linking of a polyhedral octasilicate with dichlorosilane,²⁰ (ii) polymerization of alkoxyated cage-type siloxanes by sol–gel reaction,^{21–23} (iii) oxidation of Si–H groups of a cubic siloxane to form Si–OH groups and the following condensation among them,^{24, 25} (iv) dehydrogenative condensation between a cage-type siloxane having Si–H groups and linear oligosiloxane with Si–OH groups,²⁶ and (v) polymerization by Piers-Rubinsztajn reaction of a cage-type siloxane having Si–H groups and a tetraalkoxysilane or a bridged-organoalkoxysilane.²⁷



Scheme 1.4. A Reprinted with permission from T. Gunji, T. Shioda, K. Tsuchihira, H. Seki, T. Kajiwara, A. Abe, “Preparation and properties of polyhedral oligomeric silsesquioxane–polysiloxane copolymers”, *Appl. Organometal. Chem.* **2010**, *24*, 545. Copyright 2010 John Wiley & Sons, Ltd.

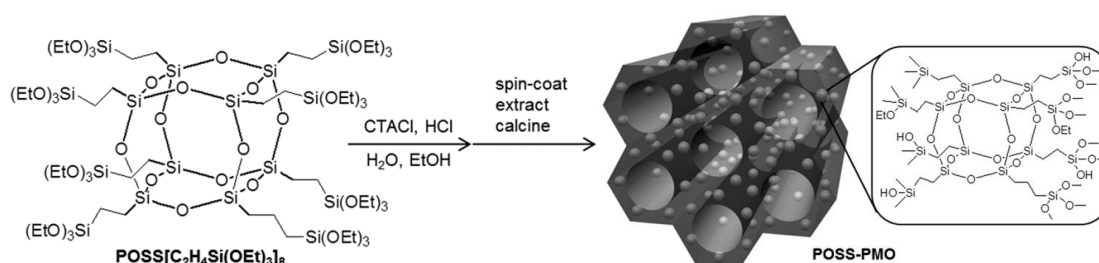
1.3.2 Self-assembly of oligosiloxanes

Utilization of self-assembly based on noncovalent interactions, such as hydrogen bond and hydrophobic interaction, is effective to orientate building blocks. To control assembled structures of oligosiloxanes, three methods are mainly used as follows: (i) self-assembly with surfactants, (ii) template-free self-assembly (self-directed assembly), and (iii) crystallization via hydrogen bond among silanol groups. These three methods are

summarized in section 1.3.2.1, 1.3.2.2, and 1.3.2.3, respectively. These studies can be categorized by the kinds of noncovalent interactions. However, such classification seems not to be appropriate because several kinds of interactions often affect the orientations of building blocks.

1.3.2.1 Self-assembly with surfactants

When monomeric polymerizable silicon compounds are used as starting materials, the use of surfactants as a structure directing agent or a template is one of the most general ways to prepare the self-assembled structures. However, previous studies have been limited for the cases of oligosiloxanes where they are used as precursors for preparation of mesoporous materials. Hagiwara *et al.*,²¹ Kuge *et al.*,²³ and Ozin *et al.*²⁸ reported mesoporous silica prepared by self-assembly of cubic siloxanes possessing alkoxy groups and surfactants (Scheme 1.5²⁸).

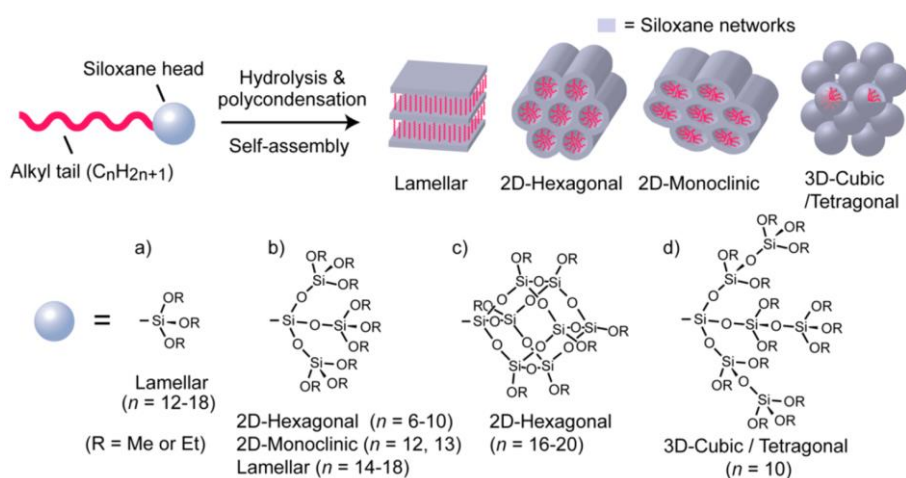


Scheme 1.5. Preparation of mesoporous material by self-assembly of cubic oligosiloxane. Reprinted with permission from M. Seino, W. Wang, J. E. Lofgreen, D. P. Puzzo, T. Manabe, G. A. Ozin, “Low-k Periodic Mesoporous Organosilica with Air Walls: POSS-PMO”, *J. Am. Chem. Soc.* **2011**, *133*, 18082. Copyright 2011 American Chemical Society.

1.3.2.2 Template-free self-assembly (self-directed assembly)

Another method for self-assembly of oligosiloxanes is template-free self-assembly developed by Shimojima *et al.* Oligosiloxanes possessing amphiphilic groups

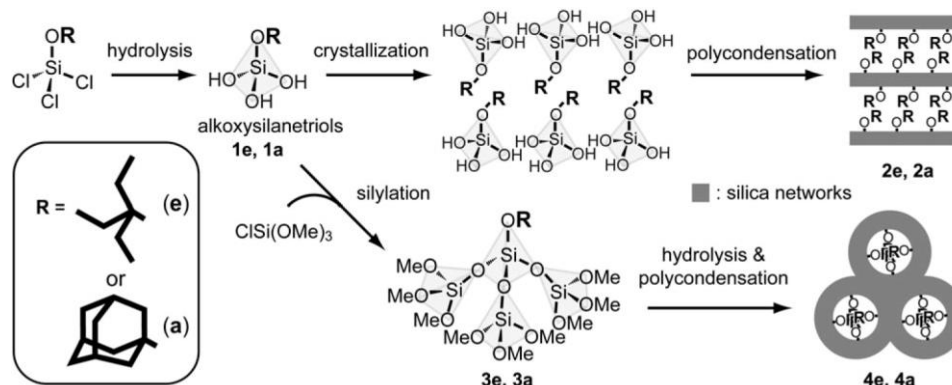
can be used as a single precursor. The formed mesostructures are dependent on the difference in size between hydrophobic alkyl chain and hydrophilic siloxane part (Scheme 1.6).⁶ The mesostructure changes from lamellar^{29, 30} to higher curvature 2D monoclinic,³⁰ 2D hexagonal,²⁹⁻³³ and 3D cubic³⁴ by the increase in the number of SiO₄ units in siloxane moiety of amphiphilic oligosiloxanes.



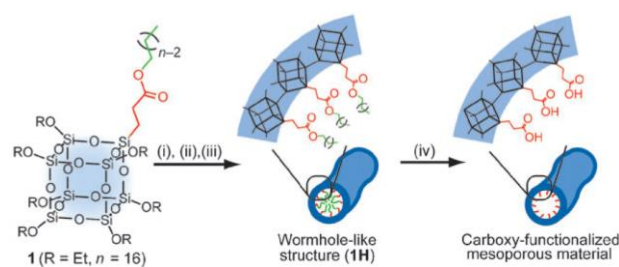
Scheme 1.6. Formation of various mesostructures by self-directed assembly of oligosiloxanes without surfactants. Reprinted with permission from K. Kuroda, A. Shimojima, K. Kawahara, R. Wakabayashi, Y. Tamura, Y. Asakura, M. Kitahara, “Utilization of Alkoxysilyl Groups for the Creation of Structurally Controlled Siloxane-Based Nanomaterials”, *Chem. Mater.* **2014**, *26*, 211. Copyright 2014 American Chemical Society.

When cage-type octa- and decasiloxanes are used as siloxane heads, 2D hexagonal mesostructured compounds are formed through self-assembly with retaining the cage structures (Scheme 1.6c).^{32, 33} The curvature of the formed mesophase is lower than that of the branched heptasiloxane although the number of silicon atoms of cage-siloxane are larger than that of branched heptasiloxane. These results indicate that the mesostructure formed by self-directed assembly of oligosiloxanes is dependent not only on the number of silicon atoms, but also on the rigidity of oligosiloxane structures.

To prepare microporous and mesoporous silicas from mesostructured materials obtained by self-directed assembly, it is necessary to remove alkyl chains by calcination. However, calcination induces thermal deterioration of oligosiloxane structures of building blocks. The use of hydrolysable functional groups instead of alkyl chains is an effective methodology. Suzuki *et al.* used oligosiloxanes possessing a tertiary alkoxy group instead of long alkyl chain (Scheme 1.7).³⁵ Such a sterically hindered functional groups are not hydrolyzed during hydrolysis of primary alkoxy groups like methoxy groups and the remaining bulky alkoxy groups can be removed by acid treatment after self-assembly and condensation. As an alternative approach for removal of alkyl chain under mild condition, Goto *et al.* inserted an ester bond between cage-type oligosiloxane and alkyl chain (Scheme 1.8).³⁶ The alkyl chain can be removed by acid treatment after the formation of mesostructure by self-assembly. The obtained mesoporous material possesses regularly arranged carboxy groups on the pore wall.



Scheme 1.7. Preparation of mesoporous materials self-directed assembled molecules possessing *tert*-alkoxy groups. Reprinted with permission from J. Suzuki, A. Shimojima, Y. Fujimoto, K. Kuroda, “Stable Silanetriols That Contain *tert*-Alkoxy Groups: Versatile Precursors of Siloxane-Based Nanomaterials”, *Chem. Eur. J.* **2008**, *14*, 973. Copyright 2008 John Wiley & Sons, Ltd.



Scheme 1.8. Preparation of mesoporous material possessing carboxy groups on the pore wall by self-assembly and the following hydrolysis of cage-type oligosiloxane with ester bond. Reprinted with permission from R. Goto, A. Shimojima, H. Kuge, K. Kuroda, “A hybrid mesoporous material with uniform distribution of carboxy groups assembled from a cubic siloxane-based precursor”, *Chem. Commun.* **2008**, 6152. Copyright 2008 Royal Chemical Society.

1.3.2.3 Crystallization via hydrogen bond among silanol groups

Silanol groups easily self-condense to form siloxane bond generally. However, several oligosiloxanes possessing stable silanol groups have been reported, and these compounds tend to orientate and crystallize via hydrogen bonds among silanol groups. Such crystals can be transformed other crystalline compounds by solid-phase condensation by heat or acid treatment. Cyclic- and cage-type oligosiloxanes have been reported.

Cyclic tri-,^{37, 38} tetra-,³⁹⁻⁴⁵ hexa-,⁴⁰ and dodecasiloxanes^{40, 46} possessing silanol groups on Si atoms constituting cyclic siloxanes have been reported (Figure 1.1). In particular, Shchegolikhina *et al.* reported solid-phase condensation of a molecular crystal composed of cyclododecasiloxane having silanol groups, and they suggested the formation of a layered compound (Scheme 1.9).^{46, 47}

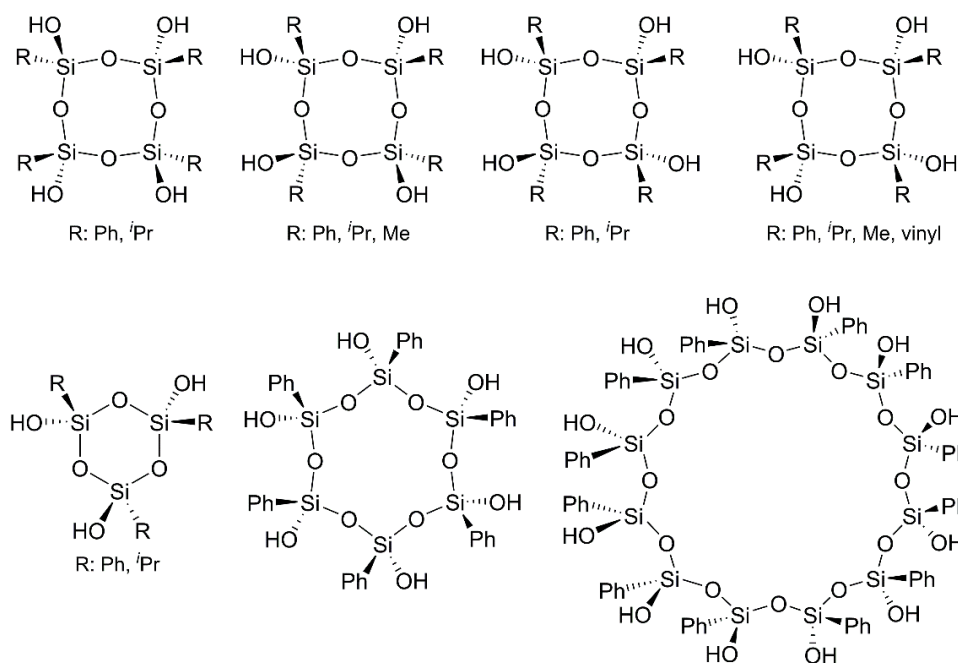
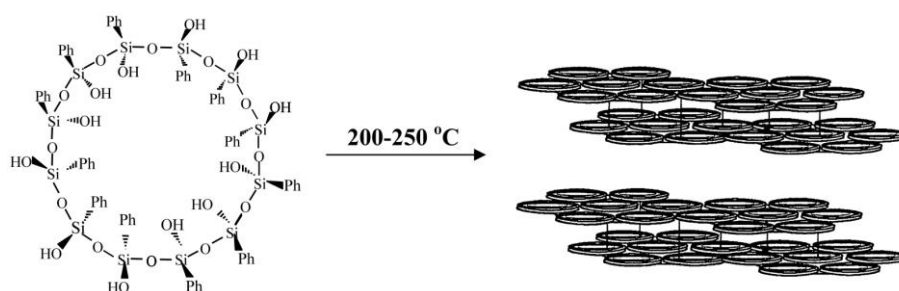


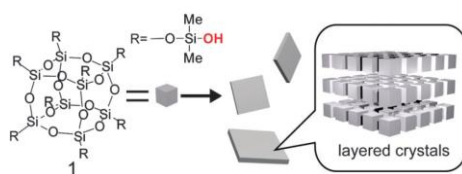
Figure 1.1. Cyclic siloxanes possessing silanol groups.



Scheme 1.9. Solid-phase condensation of cyclododecasiloxane with silanol groups and the formed layered compound (proposed structure). Reprinted with permission from S. D. Korkin, M. I. Buzin, E. V. Matukhina, L. N. Zherlitsyna, N. Auner, O. I. Shchegolikhina, “Phenylsilanetriol — synthesis, stability, and reactivity”, *J. Organomet. Chem.*, **2003**, 686, 313-320. Copyright 2003 Elsevier B.V.

In the case of cage-type oligosiloxanes, silanol groups are linked through organic linker or siloxane bond at the cage corners. Kabe *et al.* reported porous crystals composed of cage-type siloxanes with silanol groups which linked through phenylene bridge at the corners.⁴⁸ These cage-type oligosiloxanes cannot be condensed in solid-phase. Kawahara *et al.* synthesized the cage-type oligosiloxane possessing $-\text{OSiPh}_2(\text{OH})$ groups at the

corners.⁴⁹ The obtained crystalline compound can be condensed in solid-phase; however, the obtained polymer was a low crystalline compound. Sato *et al.* reported the crystallization and solid-phase condensation of cage-type siloxanes modified with –OSiMe₂(OH) groups at the corners (Scheme 1.10).⁵⁰ The condensed molecular crystal showed a high crystallinity.



Scheme 1.10. The formation of molecular crystal through hydrogen bonds among cage-type oligosiloxanes possessing silanol groups. Reprinted from N. Sato, Y. Kuroda, T. Abe, H. Wada, A. Shimojima, K. Kuroda, “Regular assembly of cage siloxanes by hydrogen bonding of dimethylsilanol groups”, *Chem. Commun.* **2015**, 11034-11037. Copyright 2015 Royal Chemical Society.

1.3.3 Summary of 1.3

As mentioned in section 1.2, controlled siloxane networks can be constructed by using oligosiloxanes as building blocks, and its effectiveness can be re-realized by previous studies as summarized this section. Oligosiloxanes of which the number of reaction sites and their direction are defined are used to prepare the desired siloxane frameworks. Recently, noncovalent interactions are introduced for their orientation and structural control. These previous studies seem to focus on the structural control of final products rather than their functions. For further development of this area, oligosiloxanes should be used not only structural control but also functional expression based on their molecular structures. For example, inner spaces of cyclic siloxanes are expected to work as host spaces. Based on this idea, the availability of large cyclic siloxanes (cyclododecasiloxanes) as building blocks is investigated in this thesis (chapter 4 and 5).

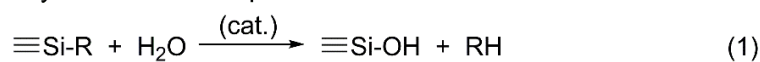
1.4 Siloxane bond formation reactions

This section describes the siloxane bond formation reactions, which are fundamental reactions for the synthesis of oligosiloxanes and their cross-linking. In this thesis, the reactions are classified from the viewpoint of the presence of water in the reaction systems. The reaction systems containing water, which includes the case that water forms as a by-product, are summarized in section 1.4.1. In section 1.4.2, non-hydrolytic siloxane bond formations are described.

1.4.1 Siloxane bond formation reactions in hydrolytic system

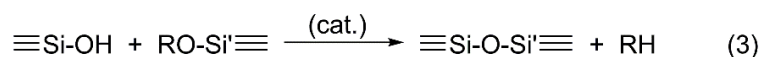
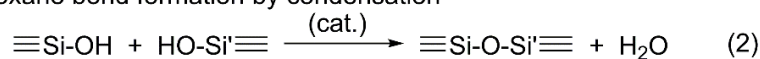
Representative hydrolytic siloxane bond formations are hydrolysis and the following condensation of organosilane compounds, which is known as sol–gel reaction, as shown in Scheme 1.11. Hydrolysis of organosilanes occurs to form silanol groups (Scheme 1.11, eq. 1) and the following dehydration condensation of silanols to form siloxane bond (Scheme 1.11, eq. 2). Depending on the kinds of leaving groups (R), the condensation which is different from dehydration (Scheme 1.11, eq. 3) competes with dehydration condensation. These three fundamental reactions occur continuously and concertedly to form siloxane-based materials.

Hydrolysis of silicon compounds



R: alkoxy, halogen, amino, acetoxy,
isocyanate, allyl, hydride

Siloxane bond formation by condensation



Scheme 1.11. Basic reactions of sol–gel reaction.

Chapter 1

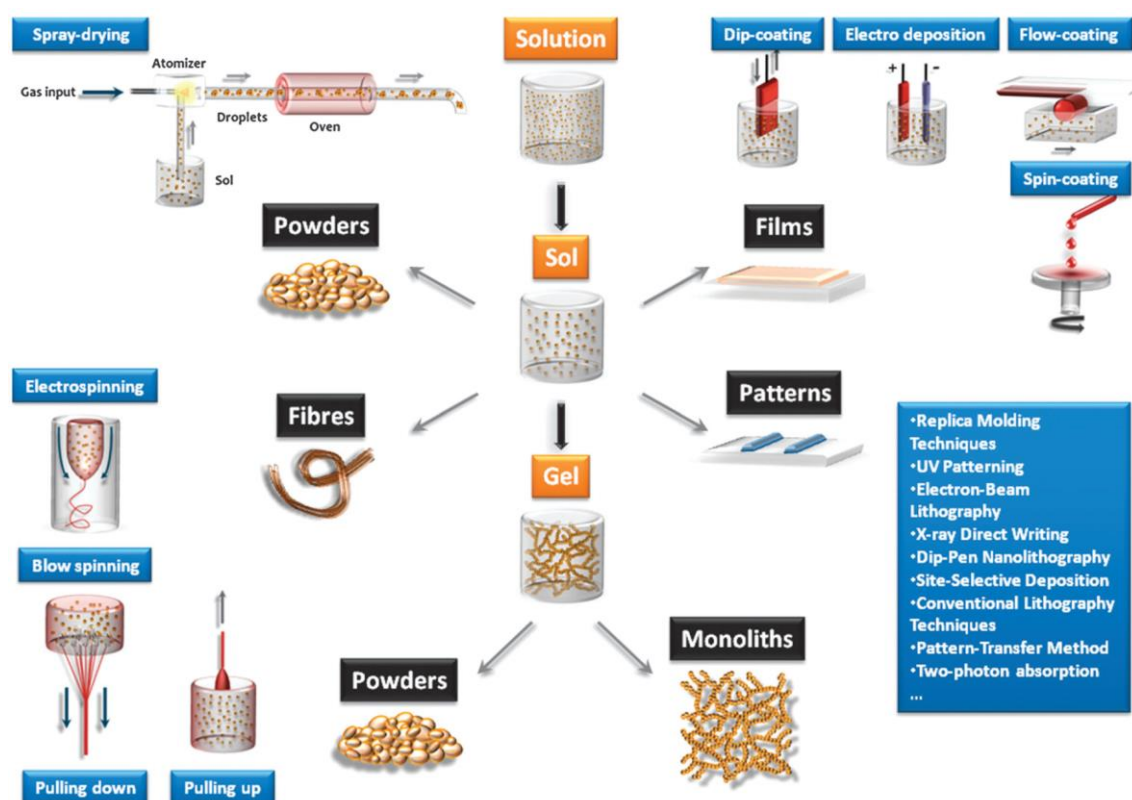
The hydrolysable silicon compounds to form silanol groups are summarized in Table 1.1. Alkoxysilanes are widely used as starting materials for not only sol–gel process but also synthesis of oligosiloxanes because they are handled relatively easily than other organosilane compounds. Chloro-, amino-, acetoxy- and isocyanate silanes show high reactivity with water, so that their sol–gel process are difficult to control and they are not suitable as precursors for construction 3-D siloxane networks. These compounds are used as precursors of oligosiloxanes under strict dry condition to use them in a controlled manner. Allylsilanes are proposed as new class of starting materials for siloxane bond formation because of their stability for hydrolysis at ambient conditions.^{51, 52}

Table 1.1. Hydrolysable silicon compounds to form silanol group

Compounds	Reactions
Alkoxysilane	$\equiv\text{Si-OR} + \text{H}_2\text{O} \rightarrow \equiv\text{Si-OH} + \text{ROH}$
Chlorosilane	$\equiv\text{Si-Cl} + \text{H}_2\text{O} \rightarrow \equiv\text{Si-OH} + \text{HCl}$
Aminosilane	$\equiv\text{Si-NR}_2 + \text{H}_2\text{O} \rightarrow \equiv\text{Si-OH} + \text{R}_2\text{NH}$ (R: H or alkyl)
Acetoxysilane	$\equiv\text{Si-OAc} + \text{H}_2\text{O} \rightarrow \equiv\text{Si-OH} + \text{AcOH}$
Isocyanate silane	$\equiv\text{Si-NCO} + \text{H}_2\text{O} \rightarrow \equiv\text{Si-OH} + \text{HNCO}$ ($\text{CO}_2 + \text{NH}_3$)
Allylsilane	$\equiv\text{Si-CH}_2\text{CH=CH}_2 + \text{H}_2\text{O} \rightarrow \equiv\text{Si-OH} + \text{CH}_3\text{CH=CH}_2$
Hydrosilane	$\equiv\text{Si-H} + \text{H}_2\text{O} \rightarrow \equiv\text{Si-OH} + \text{H}_2$

As mentioned above, because alkoxysilanes are often used as precursors for sol–gel process, the features of sol–gel reaction of alkoxysilanes are described from here. The rates of basic reactions shown in Scheme 1.11 are influenced by various factors, such as reaction temperature, concentration of precursors and catalyst, kinds of catalyst, solvent, and organic substituent of organosilanes (details are well summarized by Brinker and Scherer as a book titled “Sol–Gel Science”⁵³). In addition, because the three reactions

progress concertedly, various chemical species are formed in the reaction systems, for example, ten species are generated for the dimerization of tetraalkoxysilane in principle. In fact, a lot of chemical species are confirmed by ^{29}Si NMR spectroscopy at the initial stage of hydrolysis and condensation of tetraalkoxysilanes and organoalkoxysilanes.⁵⁴⁻⁶⁴ These reactions feature complicated reaction systems; therefore, siloxane bond formation through sol-gel reaction is difficult to control from a viewpoint of reaction chemistry. On the other hand, from a standpoint of material chemistry, sol-gel process is an attractive method for material preparations because of high processability (Scheme 1.12⁶⁵), such as mild reaction conditions, hydrolytic system, and morphological controllability.



Scheme 1.12. Preparation routes of materials by sol-gel process. Reprinted with permission from C. Sanchez, P. Belleville, M. Popall, L. Nicole, “Applications of advanced hybrid organic-inorganic nanomaterials: from laboratory to market”, *Chem. Soc. Rev.* **2011**, *40*, 696. Copyright 2011 Royal Society of Chemistry.

1.4.2 Siloxane bond formation reactions in non-hydrolytic system

Non-hydrolytic siloxane bond formation is appropriate for the synthesis of oligosiloxanes because the formed siloxane bonds are not hydrolyzed in the reaction

Table 1.2. Non-hydrolytic siloxane bond formation reactions.

Reaction types	Reaction formula	References
Alkoxysilane + Chlorosilane	$\text{Si-OR} + \text{Si-Cl} \rightarrow \text{SiOSi} + \text{RCl}$	66-70
Alkoxysilane + Acetoxysilane	$\text{Si-OR} + \text{Si-OAc} \rightarrow \text{SiOSi} + \text{ROAc}$	71-74
Alkoxysilane + Hydrosilane	$\text{Si-OR} + \text{Si-H} \rightarrow \text{SiOSi} + \text{RH}$	75-77
Alkoxysilane + Alkoxysilane	$\text{Si-OR} + \text{Si-OR} \rightarrow \text{SiOSi} + \text{ROR}$	74, 78, 79
Silanol + Chlorosilane	$\text{Si-OH} + \text{Si-Cl} \rightarrow \text{SiOSi} + \text{HCl}$	80
Silanol + Aminosilane	$\text{Si-OH} + \text{Si-NR}_2 \rightarrow \text{SiOSi} + \text{NHR}_2$	81-84
Silanol + Hydrosilane	$\text{Si-OH} + \text{Si-H} \rightarrow \text{SiOSi} + \text{H}_2$	85
Silanol + Vinylsilane	$\text{Si-OH} + \text{Si-CH=CH}_2$ $\rightarrow \text{SiOSi} + \text{H}_2\text{C=CH}_2$	86
Silanol + 2-Methylallylsilane	$\text{Si-OH} + \text{Si-CH}_2\text{CMe=CH}_2$ $\rightarrow \text{SiOSi} + \text{H}_2\text{C=CMe}_2$	87
Chlorosilane + Silanolate	$\text{Si-Cl} + \text{Si-O}^-\text{M}^+ \rightarrow \text{SiOSi} + \text{MCl}$	88
Hydrosilane + Oxygen donor (Amide etc.)	$\text{Si-H} + \text{HCONR}_2$ $\rightarrow \text{SiOSi} + \text{NMeR}_2$	89
Oxidation of Si-Si bond	$\text{Si-Si} + [\text{O}] \rightarrow \text{SiOSi}$	90, 91
Oxidation of hydrosilane	$\text{Si-H} + \text{O}_2 \text{ or } \text{CO}_2$ $\rightarrow \text{SiOSi} + \text{H}_2 \text{ or } \text{CH}_4$	92-95
Intramolecular rearrangement	$\text{SiOCHCH}_3\text{OSi}^-\text{HR}_2$ $\rightarrow \text{SiOSi}^-\text{R}_2(\text{OCHCH}_3)$	96

systems. Such reactions have been reported by many researchers. The reported reactions as long as the author knows are shown in Table 1.2. Although non-hydrolytic siloxane formations are rich in diversity, the reactions which are developed systematically like sol-gel reaction are limited. Almost all of the reactions have remained in the stage of basic investigation, such as substrate tolerance and reaction mechanism. Among them, non-hydrolytic sol-gel reaction and the Piers-Rubinsztajn reaction have been developed systematically, so that these reactions are summarized in the section 1.4.2.1 and 1.4.2.2, respectively.

1.4.2.1 Non-hydrolytic sol-gel reaction

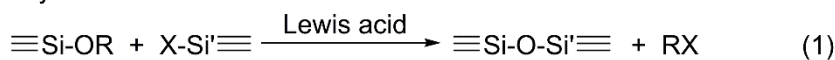
Non-hydrolytic sol-gel reaction is M-O-M (M: Si or transition metal) bond formation reaction proposed by Corriu and co-workers at 1992 (hereafter, silicon is used as a typical instance).⁶⁶⁻⁶⁸ This reaction is not the name for the specific reaction, but it involves various reactions to form M-O-M bond by using molecularly precursors (alkoxides, halides, and so on).

The basic reactions are shown in Scheme 1.13. Lewis acids are needed as catalysts in many cases to progress these reactions. Alkyl halide elimination (Scheme 1.13, eq. 1) and ether elimination (Scheme 1.13, eq. 2) are used for the formation of siloxane bond (There are other routes for the preparation of transition metal oxides. Details are shown in some reviews^{74, 97-99}). Organosilicon compounds containing oxygen (alkoxy- and acetoxysilanes) or organic compounds having oxygen (ethers and sulfoxides *etc.*) are used as oxygen donors for the formation of Si-O-Si bond. In the case of organic compounds as oxygen donors, Si-OR groups are formed *in situ* (Scheme 1.13, eq. 3 to 5) and they are transformed to Si-O-Si bond continuously. The selectivity between alkyl halide- and ether elimination depends on the kinds of Lewis acid catalysts.¹⁰⁰

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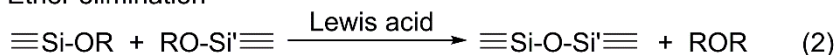
Siloxane reactions

i. Alkyl halide elimination



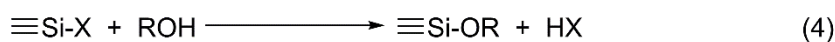
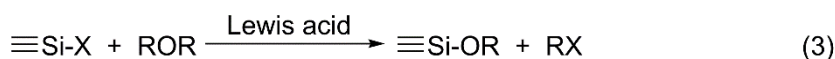
R: alkyl, X: halogen

ii. Ether elimination

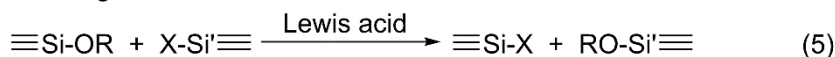


In situ Si-OR formations

i. Alkoxylation of Si-X with organic compounds



ii. Exchange reaction



Scheme 1.13. Basic reactions of non-hydrolytic sol–gel reaction.

Non-hydrolytic sol–gel reactions show potentials to control composition, homogeneity, and morphology easier than conventional hydrolytic sol–gel reaction. In the case of conventional one, it is difficult because of both the stepwise siloxane bond formation (hydrolysis and condensation) and the difference of reaction rates among precursors and chemical species in the reaction systems. On the other hand, siloxane bonds are formed via one-step reaction (alkyl halide or ether elimination). In addition, uncondensed silanol groups are not formed in non-hydrolytic systems; therefore, structural collapses by shrinking due to condensations of silanol groups can be suppressed.

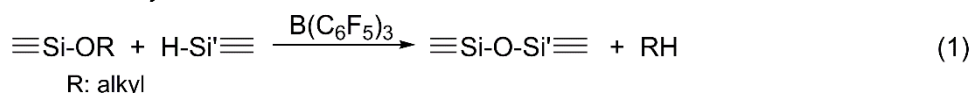
Non-hydrolytic sol–gel reactions have been developed as the preparative method of oxides containing siloxane-based materials with three-dimensional M–O–M network. Recently, Wakabayashi *et al.* succeeded to apply this reaction to synthesize oligosiloxanes possessing alkoxy groups.⁶⁹ They focused on the difference of reactivity among alkoxy silanes for the reaction and succeeded to transform the alkoxy groups which can

release the stable carbocations ($t\text{Bu}^+$ and Ph_2hC^+) into siloxane bonds with retaining primary alkoxy groups (methoxy and ethoxy groups).

1.4.2.2 Piers-Rubinsztajn reaction

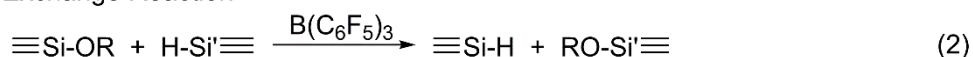
The Piers-Rubinsztajn reaction (hereafter, referred to as P-R reaction) is dehydrocarbon condensation to form siloxane bond between alkoxy silanes and hydrosilanes in the presence of tris(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$) catalyst (Scheme 1.14, eq. 1).

Piers-Rubinsztajn Reaction

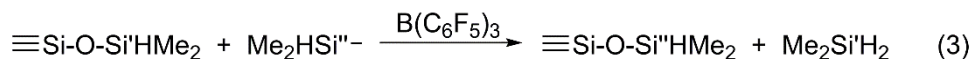


Side Reactions

i. Exchange Reaction



ii. De-dimethylsilane condensation

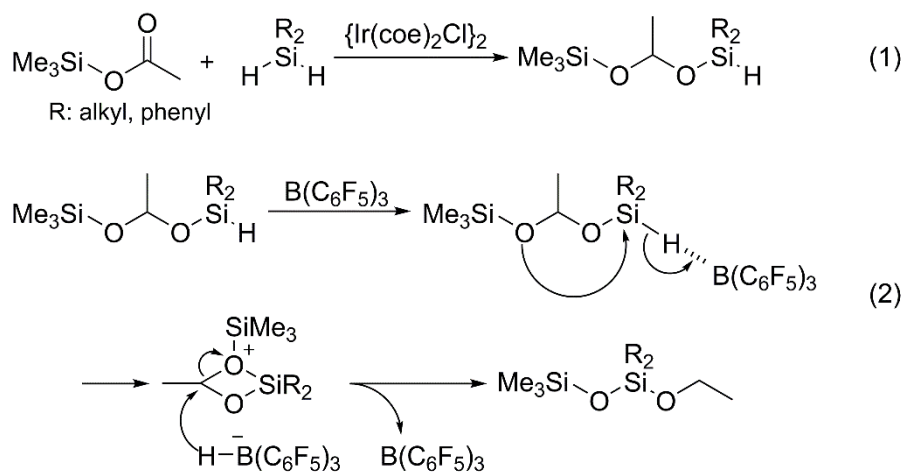


Scheme 1.14. Piers-Rubinsztajn reaction and its side reactions.

Piers *et al.* firstly discovered this reaction as the side reaction when they reduction of carbonyl compounds by hydrosilanes in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$.⁷⁵ Rubinsztajn and co-workers focused on this result from the standpoint of silicone chemistry and investigated the characteristic features of the reaction, such as reaction mechanism, kinetics, and side-reaction (exchange reaction and de-dimethylsilane condensation shown in Scheme 1.14, eq. 2 and 3, respectively).^{76, 77, 101-104} From its discovery, P-R reaction has been developed as the preparative method of silicones oils, resins, and gums because of several features as follows:¹⁰⁵ (i) the reaction proceeds quickly, (ii) byproducts are easily removed because gaseous hydrocarbons are formed, and (iii) the catalyst is not deactivated by

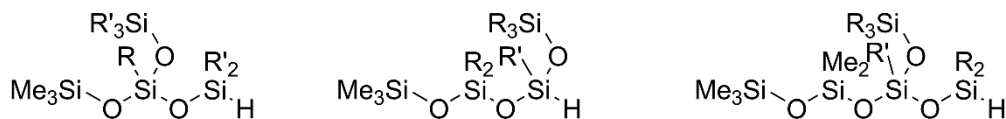
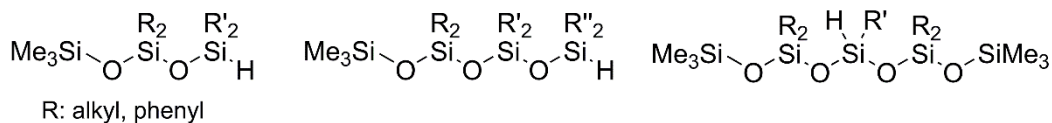
contaminating water. Recently, the P-R reaction is also used for the synthesis of oligosiloxanes. Brook *et al.* reported various branched oligosiloxanes containing dendrimers.¹⁰⁶⁻¹¹¹

Matsumoto *et al.* developed a rearrangement reaction to form siloxane bond, which is inspired by the P-R reaction (Scheme 1.15).⁹⁶ From the viewpoint of reaction chemistry, most of the reactions shown in Table 1.2 are categorized into substitution reaction except for oxidation of Si-Si bond. This is the first siloxane bond formation by rearrangement reaction to the best of my knowledge. This reaction can be considered as an intramolecular P-R reaction. The different point from conventional intermolecular P-R reaction is that by-product is not formed. The alkoxy groups, which are eliminated as alkanes in the case of P-R reaction, retain in the reaction products (Figure 1.2). Therefore, this reaction is siloxane bond formation reaction as well as synthetic way of oligosiloxanes possessing alkoxy groups.



Scheme 1.15. (a) The formation of disilyl acetal by reduction of silyl ester and (b) the following siloxane bond formation by rearrangement reaction.

Oligosiloxanes possessing -SiH groups



Oligosiloxanes possessing alkoxy groups

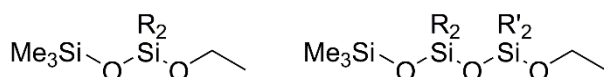


Figure 1.2. Oligosiloxanes synthesized by the rearrangement reaction.

1.4.3 Summary of 1.4

Until now, hydrolytic siloxane bond formation reactions have been well investigated on the viewpoint of reaction chemistry and well used for material preparations. On the other hand, non-hydrolytic siloxane formation reactions are developed individually rather than systematically in comparison with hydrolytic ones. Seeing and organizing non-hydrolytic reactions reported until now at the bird's-eye point of view will contribute to generation of novel reaction and their systematic development.

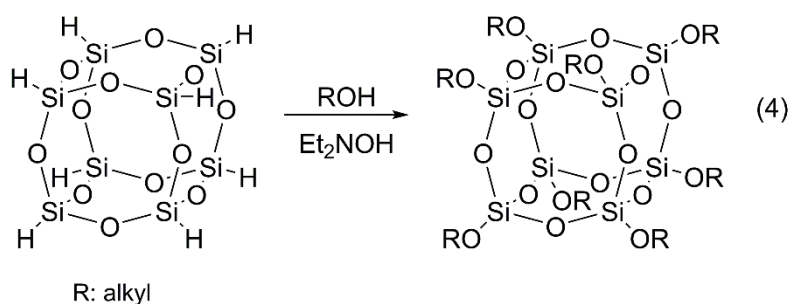
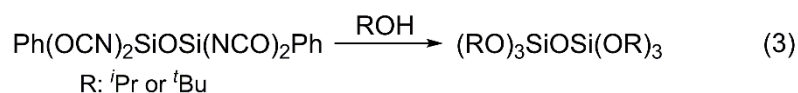
Non-hydrolytic siloxane bond formation reactions often compete with functional group exchange reaction. Because this side reaction induces inhomogeneous reaction, it must be inhibited depending on the purpose of studies. However, such inhibitions are difficult at the present stage because dominant factors of selectivity between siloxane formation and exchange reactions are unknown. The studies on reaction mechanisms and control of selectivity by catalyst design may be necessary to solve the issue.

1.5 Synthetic methods of oligosiloxanes possessing alkoxy groups

In this section, the synthetic methods of oligosiloxanes possessing alkoxy groups are summarized. Please note that oligosiloxanes, which have a certain molecular weight distribution, synthesized by random oligomerization of organosilane compounds^{112, 113} are excluded here because this thesis focuses the oligosiloxanes with a defined structure as building blocks. The synthetic methods of oligosiloxanes possessing alkoxy groups are classified from the point of view that the siloxane bonds are simultaneously formed or not with the introduction of alkoxy groups. Alkoxylation of oligosiloxanes, that is new siloxane bonds are not formed together with the introduction of alkoxy groups, are summarized in section 1.5.1. In section 1.5.2, alkoxylation of monomeric organosilanes and oligosiloxanes, which means siloxane bond formations occur with introduction of alkoxy groups, are described.

1.5.1 Alkoxylation of oligosiloxanes

The simplest way to synthesize oligosiloxanes possessing alkoxy groups is alkoxylation of oligosiloxanes which are prepared before the alkoxylation as shown in Scheme 1.16. The advantage of this method is that the reactions, which decompose alkoxy groups like hydrolysis, can be used for the preparation of oligosiloxanes. Although this method is simple to obtain oligosiloxanes having alkoxy groups, the variety of oligosiloxane structures are poor. The reported oligosiloxanes are limited to linear siloxanes containing T or Q silicon (disiloxane)¹¹⁴⁻¹¹⁶ and cage-type siloxanes containing Q silicon^{32, 33, 36, 85, 117-119} (Scheme 1.16, eq. 1 to 3 and eq. 4, respectively). Regarding the kind of alkoxy groups, it has been limited to the steric hindered ones, such as $-O^iPr$ and $-O^tBu$ groups, for the alkoxylation of $-SiCl$ ^{114, 115} and $-SiNCO$ groups¹¹⁶. In the case of $-SiH$ groups, the sterically less hindered groups can be adoptable.^{32, 33, 36, 85, 117-119}

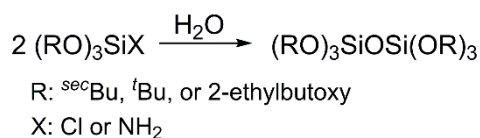


Scheme 1.16. The alkoxylation of oligosiloxanes.

1.5.2 Alkoxysilylation of monomeric organosilanes and oligosiloxanes

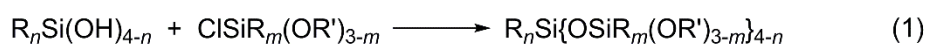
To achieve at the same time both the siloxane bond formation and the introducing alkoxy groups is more difficult than to conduct them separately because of the limitations on the reaction as shown below. Both the kinds of reaction and their conditions for siloxane bond formation and alkoxylation must satisfy that both siloxane bonds and alkoxy groups are not decomposed during the reactions. In particular, the presence of water is the most important factor. The amount of water in the reaction systems must be controlled strictly or excluded. In the case of the presence of water is permitted, the chemical equivalent water is used as a reagent for the dimerization between organosilanes which possess both alkoxy and other functional groups which are more reactive with water than alkoxy groups such as $-\text{SiCl}$ and $-\text{SiNH}_2$ (Scheme 1.17).^{114, 115} The kind of alkoxy groups has been limited to the steric hindered ones because of their relative high hydrolysis resistance.

Chapter 1

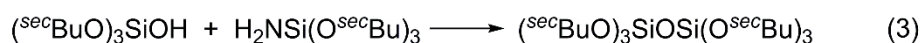
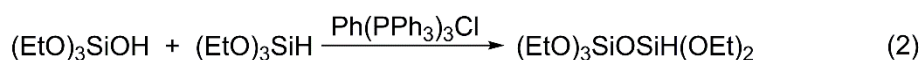


Scheme 1.17. The synthesis of oligosioxanes possessing alkoxy groups by using chemical equivalent water.

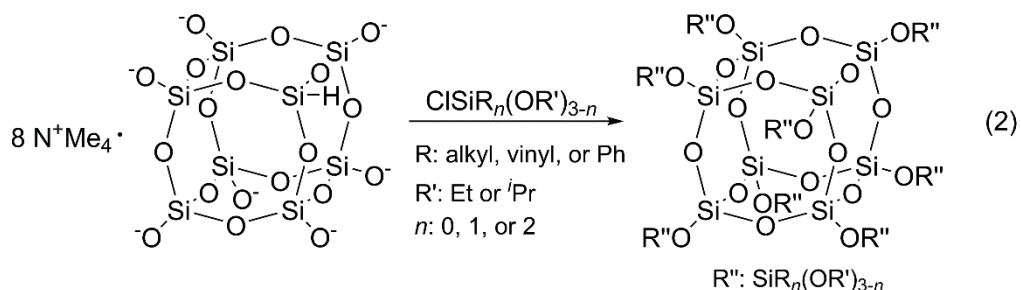
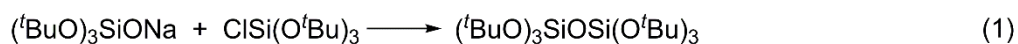
Except for the synthetic methods of oligosiloxanes by alkoxylation as shown in Scheme 1.17, the others are conducted in the non-hydrolytic condition. The conventional one is alkoxylation of monomeric or oligomeric silicon compounds having relative stable silanol^{29-31, 34, 35, 80, 85, 114, 115, 120, 121} or silanolate groups^{21, 23, 49, 88, 122-124} with organosilanes (Scheme 1.18 and 1.19). Because the reactivity of –SiX groups (X: Cl, H, or NH₂) with silanol or silanolate groups is higher than that of –SiOR groups with them, the alkoxy groups can be retained after siloxane bond formations. Regarding oligosiloxane structures, linear siloxanes containing D or T silicons, branched siloxanes containing T or Q silicons, and cage-type siloxanes containing Q silicons are reported.



R: alkyl, vinyl, or Ph R': alkyl
n: 1, 2, or 3 m: 1 or 2

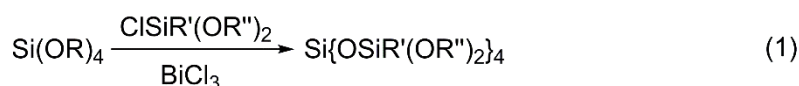


Scheme 1.18. The alkoxylation of organosilanol.



Scheme 1.19. The alkoxysilylation of organosilanolates.

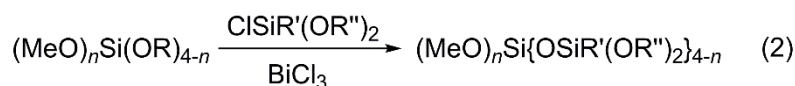
The conventional synthetic methods in non-hydrolytic systems (Scheme 1.18 and 1.19) used silanols and silanolates as precursors, and most of them are unstable and self-condensable so that their variety is limited. To synthesize various oligosiloxanes having alkoxy groups, more stable silicon compounds should be used as precursors. As mentioned in section 1.4.2.1, Wakabayashi *et al.* developed the alkoxysilylation of the alkoxysilanes which can release the stable carbocations (${}^t\text{Bu}^+$ and Ph_2hC^+).^{69, 125} Primary alkoxy groups are not alkoxysilylated by this reaction so that they succeeded to synthesize linear and branched oligosiloxanes containing T and Q silicons and possessing methoxy or ethoxy groups (Scheme 1.20). Likewise, Matsumoto *et al.* developed the rearrangement reaction to form siloxane bond⁹⁶ as mentioned in section 1.4.2.1 (Scheme 1.15). Various linear oligosiloxanes containing D silicons and having alkoxy groups can be synthesized by using this reaction (Figure 1.2).



R: ^tBu or CHPh₂

R': H, Me, Ph, vinyl,
-(CH₂)₃Cl, or ⁿBu

R'': Me or Et



n: 2 or 3

Scheme 1.20. The synthesis of oligosiloxanes possessing alkoxy groups by non-hydrolytic sol–gel reaction.

1.5.3 Summary of 1.5

Oligosiloxanes possessing alkoxy groups have been synthesized by alkoxylation of oligosiloxanes or alkoxysilylation of organosilicon compounds. The former method is relative easy to suppression of both siloxane bonds and alkoxy groups because formation of oligosiloxane structures and introduction of alkoxy groups are separated. The latter method is desirable regarding economical synthesis because those two steps are summarized in one-pot. However, methods for alkoxysilylation reaction of monomeric and oligomeric silicon compounds are limited. Consideration of non-hydrolytic siloxane bond formation reactions from the standpoint of view of reaction chemistry will contribute to development of novel synthetic methods. In chapter 2 and 3 of this thesis, novel synthetic methods are produced.

1.6 Motivation and purpose of this study

The oligosiloxanes possessing alkoxy groups have been synthesized and used as building blocks for siloxane-based materials as mentioned above. However, their synthetic routes and structural variety are limited. The purpose of this PhD study is the development of their novel synthetic routes and the establishment of the usefulness of the

synthesized oligosiloxanes as building blocks. The synthetic methods developed in this thesis are inspired by some concepts of synthetic organic chemistry such as the selective transformation among the same kind of functional groups and the protecting groups. The synthetic methodologies enable to synthesize alkoxyated oligosiloxanes that cannot be synthesized by conventional ways. The synthesized oligosiloxanes can be polymerized without cleaving the original siloxane bonds, which indicates that these compounds are useful to control siloxane networks. In the case of cyclic oligosiloxane, it is clarified that not only retention of the original structure but also control of the conformation of cyclic structure are important to use them as building blocks. This finding is important when such oligosiloxanes are used as precursors of the material synthesis. Therefore, this thesis contributes to synthetic chemistry of siloxane-based compounds and materials.

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Chapter 2

Synthesis of an Alkoxylated Oligosiloxane Possessing Three Different Organic Functional Groups

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2.1 Introduction

Silica-based inorganic-organic hybrid materials have been studied for applications in many fields.¹ Their properties are affected by functional group diversity, distribution, and the separation or distance between individual functional groups. For example, bifunctional catalysts like acid-base catalysts, show higher catalytic activity than monofunctional catalysts because of cooperativity between acidic and basic sites.² In addition, the catalytic activity is generally affected by the change in the distribution and separation between two kinds of functional groups.³⁻⁶ However, it is difficult to control the distribution and/or separation between different kinds of functional groups by conventional methods for preparing hybrids, such as post-grafting^{7,8} and co-condensation using sol-gel methods.^{9,10} Inhomogeneous distributions of functional groups may be induced by post-grafting. Such heterogeneity also results from different rates of reaction between precursors (mainly mixtures of organoalkoxysilanes and tetraalkoxysilanes) by co-condensation methods.

To overcome this problem, it is reasonable to use a well-designed oligomer as hybrid precursors because the separation and number of functional groups can be fixed at the molecular level for such oligomers. Therefore, one expects to control the distribution and/or separation between functional groups in hybrids by using oligomers as single precursors.^{11,12} Alkoxysiloxane oligomers are suitable as building blocks of silica-based inorganic-organic hybrids materials because they have hydrolyzable alkoxy groups. However, examples of alkoxysiloxane oligomers with defined structures are quite limited.¹¹⁻¹⁹ Furthermore, there are few examples that demonstrate the successful synthesis of compounds possessing both plural functional groups and alkoxysilyl groups.²⁰ In fact, a previous report²⁰ used the following two methods. One method uses stepwise synthesis of those compounds and the other does silylation of silanol-containing

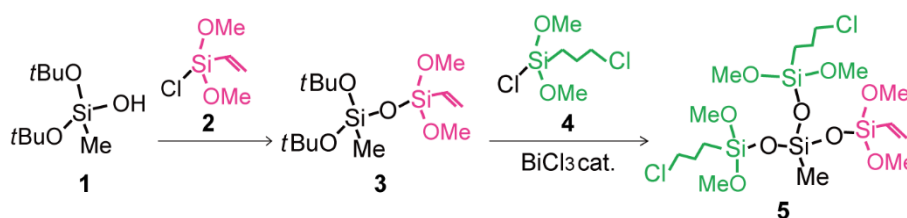
Chapter 2

compounds with chlorosilanes possessing two kinds of functional groups. The former consists of hydrolysis of alkoxy groups and silylation of silanol groups. In this method, it is necessary to use a precursor that is resistant to hydrolysis, such as polyhedral silsesquioxanes (POSSs), to introduce plural functional groups in regioselective ways while retaining the oligosiloxane structure of the precursor. Thus, this approach is not versatile because of the limitation of available precursors. The latter uses chlorosilanes possessing two kinds of functional groups for silylation of silanols allowing the synthesis of an alkoxy siloxane oligomer with different functional groups. However, the ratio and separation of the different functional groups is fixed, and it is difficult to control these factors by this method. Different from those reports, the present study shows stepwise introduction of plural different functional groups under non-hydrolytic conditions, and this method can control the ratio and distance of functional groups. Even though different functional groups can be bonded to POSSs,²¹ such modified POSSs are not normally constructed with alkoxy silyl functional groups.

Recently, Wakabayashi *et al.* reported a non-hydrolytic synthesis of branched alkoxy siloxane oligomers.^{22, 23} Siloxane bonds can form by this method from alkoxy silyl groups which release stable carbocations, such as $t\text{Bu}^+$ and Ph_2HC^+ . Therefore, this approach offers the potential to control the structure and functional groups on the alkoxy siloxane oligomers by designing a precursor and selecting silylating agents. However, the synthesis of an oligomer with several kinds of functional groups has not yet been achieved.

This chapter shows the synthesis of a typical oligomer having different functional groups (Scheme 2.1). In this work, the author succeeded in designing and thereafter constructing an oligosiloxane structure with selected placement of functional groups. Chloropropyl and vinyl groups were chosen as functional groups because these

groups can be converted to catalytically active groups, including amino, thiol, and carboxy groups. In addition, the hydrolysis and condensation process was investigated by liquid state NMR to confirm the absence of siloxane bond cleavage of the oligomer. Because compound **5** (Scheme 2.1) retains the original oligosiloxane structure after condensation, the distribution and separation of functional groups in the resulting hybrids can be controlled by using **5** as a precursor.



Scheme 2.1 Synthesis of alkoxy-siloxane oligomers.

2.2 Experimental and Characterization of starting materials

2.2.1 Materials

Acetonitrile (MeCN, dehydrated, > 99.0%), hexane (> 99.8%), hydrochloric acid (0.01 mol/L), methanol (dehydrated, > 99.8%), pyridine (dehydrated, > 99.5%), sodium sulfate (dehydrated, > 99.0%), and tetrahydrofran (THF, dehydrated, > 99.5%, stabilizer free) were purchased from Wako Pure Chemical Industries, Ltd. (3-Chloropropyl)trichlorosilane (> 97.0%), potassium *tert*-butoxide (*t*BuOK, > 97.0%), trichloromethylsilane (Cl₃SiMe, > 98.0%), and trichlorovinylsilane (Cl₃Si(CH=CH₂), > 98.0%) were purchased from Tokyo Chemical Industry Co., Ltd. All reagents were used as received.

2.2.2 Synthesis of $(t\text{BuO})_2\text{MeSiOH}$ (**1**)

Compound **1** was synthesized from trichloromethylsilane (detail procedures are shown in next paragraph). At first, trichloromethylsilane was alkoxyated with potassium *tert*-butoxide, and $(t\text{BuO})_2\text{MeSiCl}$ was formed. The remaining Cl did not react with the butoxide because of the steric hindrance of two *t*BuO groups. Next, $(t\text{BuO})_2\text{MeSiCl}$ was hydrolyzed with H_2O to synthesize **1**.

Potassium *tert*-butoxide (*t*BuOK, 25 g, 0.22 mol) was dried *in vacuo* in a three-neck flask (500 mL). After hexane (150 mL) was added into the flask under N_2 atmosphere, trichloromethylsilane (MeSiCl_3 , 11.8 mL, 0.10 mol) was dropped into the flask and the mixture was stirred at 0 °C for 1 h and then stirred at room temperature for 4 h. The molar ratio of *t*BuOK/ MeSiCl_3 was 1/2.2. KCl and excess *t*BuOK were removed by filtration under N_2 atmosphere. Then, yellow clear liquid, $(t\text{BuO})_2\text{MeSiCl}$, was obtained after evaporation of the solvent. The ^1H , ^{13}C , and ^{29}Si NMR spectra of $(t\text{BuO})_2\text{MeSiCl}$ are shown in Figures 2.1 to 2.3. The possibility of the formation of $(t\text{BuO})\text{MeSiCl}_2$ and its hydrolysed/polymerized byproducts was excluded on the basis of the ^{29}Si NMR spectrum of the product (Figure 2.3), because no signals due to those species were observed. The formation of $(t\text{BuO})_2\text{MeSiCl}$ was confirmed by NMR spectroscopies. Excess of pyridine and water were added to $(t\text{BuO})_2\text{MeSiCl}$ and stirred for 0.5 h at room temperature. After separating the water layer from the organic layer, the water layer was extracted with hexane. The extracted organic species in hexane were added into the separated organic layer, and the mixture was dehydrated with anhydrous Na_2SO_4 . The possibility of the formation of disiloxane species during the treatment with water was excluded because no signals due to the species were observed. A colorless clear liquid (**1**, 11.0 g, yield 52.7 %) was obtained by evaporation of the solvent after the solid residue was removed by filtration. The ^1H , ^{13}C , and ^{29}Si NMR spectra of **1** are shown in

Figures 2.4 to 2.6.

(*t*BuO)₂MeSiCl. ¹H NMR (500 MHz; CDCl₃; 25 °C; TMS) δ = 1.36 (s, 18H; C(CH₃)₃), 0.41 ppm (s, 3H; SiCH₃); ¹³C NMR (126 MHz; CDCl₃; 25 °C; TMS) δ = 75.0 (CMe₃), 31.5 (CMe₃), 3.9 ppm (SiMe); ²⁹Si (99 MHz; CDCl₃; 25 °C; TMS) δ = -43.3 ppm (1Si, D⁰; O₂SiMeCl). A small amount of hexane remained.

Compound 1. ¹H NMR (500 MHz; CDCl₃; 25 °C; TMS) δ = 1.33 (s, 18H; C(CH₃)₃), 0.16 ppm (s, 3H; SiCH₃); ¹³C NMR (126 MHz; CDCl₃; 25 °C; TMS) δ = 72.5 (CMe₃), 31.7 (CMe₃), -0.6 ppm (SiMe); ²⁹Si (99 MHz; CDCl₃; 25 °C; TMS) δ = -50.8 ppm (1Si, T⁰; O₃SiMe); HRMS (ESI, 1.5 kV) calcd. for C₉H₂₂O₃SiNa⁺ [M+Na]⁺: 229.1230; found: 229.1232. A small amount of pyridine remained.

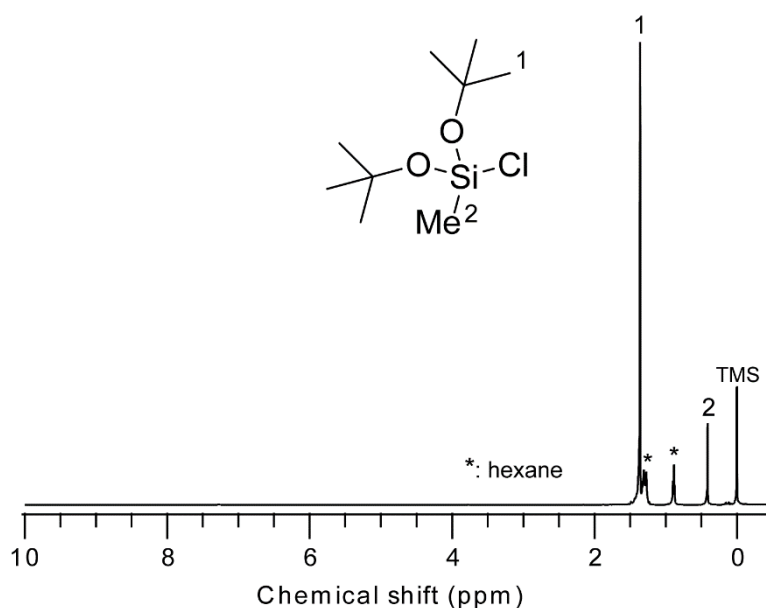


Figure 2.1. ¹H NMR spectrum of (*t*BuO)₂MeSiCl.

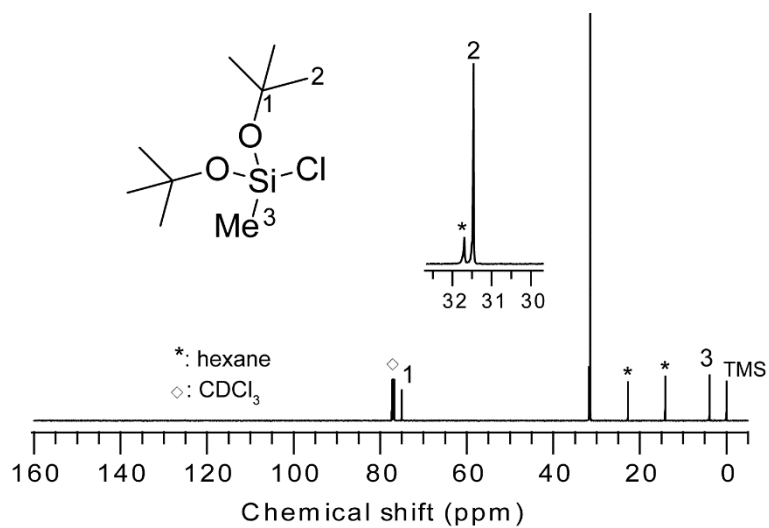


Figure 2.2. ^{13}C NMR spectrum of $(t\text{BuO})_2\text{MeSiCl}$.

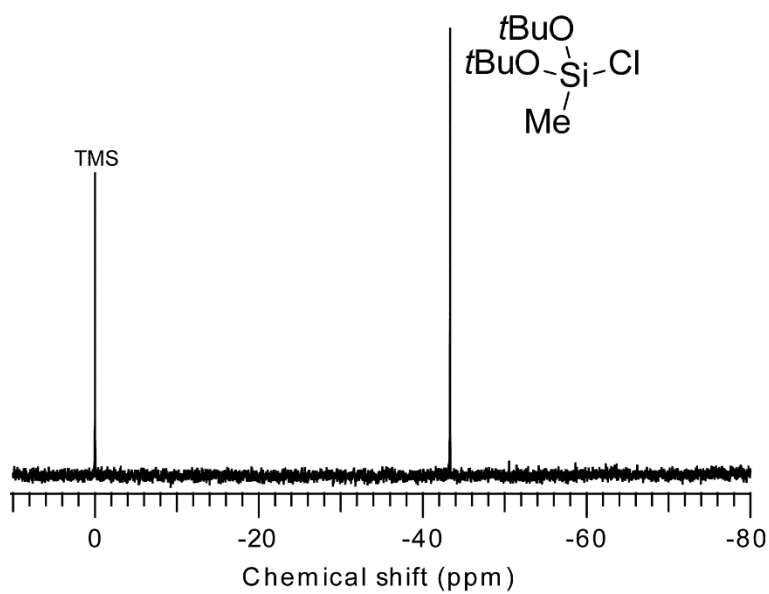


Figure 2.3. ^{29}Si NMR spectrum of $(t\text{BuO})_2\text{MeSiCl}$.

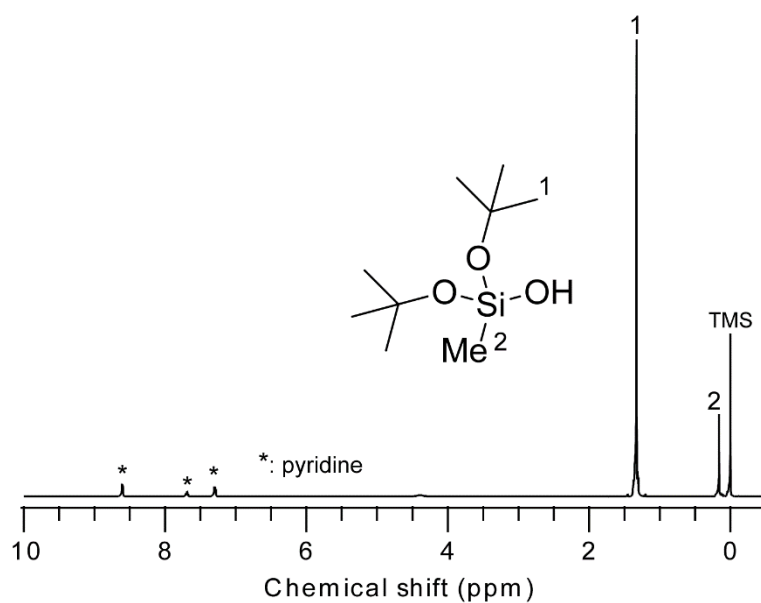


Figure 2.4. ^1H NMR spectrum of compound 1.

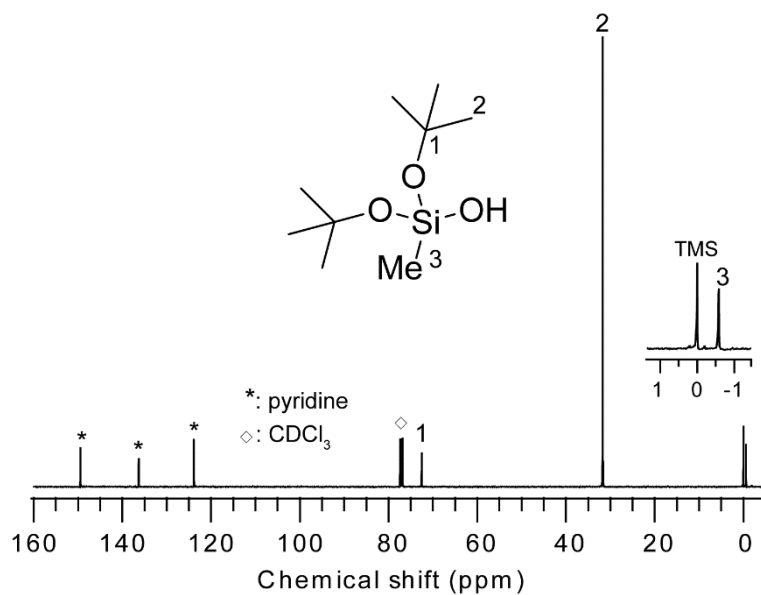


Figure 2.5. ^{13}C NMR spectrum of compound 1.

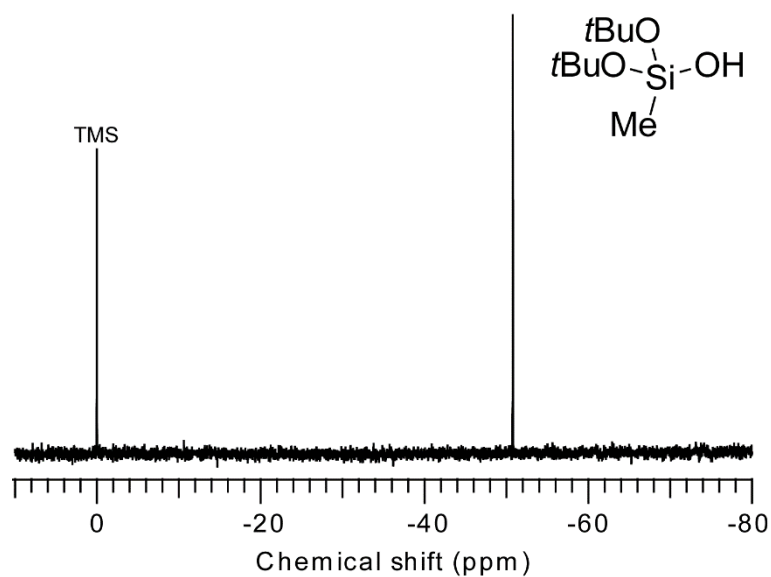


Figure 2.6. ^{29}Si NMR spectrum of compound **1**.

2.2.3 Synthesis of $(\text{MeO})_2(\text{CH}_2=\text{CH})\text{SiCl}$ (**2**)

Compound **2** was synthesized by the alkoxylation of trichlorovinylsilane with *tert*-butyl methyl ether as previously reported²⁴. BiCl_3 (0.2697 g, 0.86 mmol) was dried *in vacuo* in a Schlenk flask (200 mL). MeCN (10 mL) was added into the flask under N_2 atmosphere and the mixture was stirred until BiCl_3 was dissolved. Trichlorovinylsilane ($(\text{CH}_2=\text{CH})\text{SiCl}_3$, 10.7 mL, 0.084 mol) was added into the mixture at 0 °C, and then *tert*-butyl methyl ether (22.9 mL, 0.193 mol) was dropped into the mixture. The mixture was stirred for 6 h at room temperature to form yellow clear liquid. The molar ratio of $(\text{CH}_2=\text{CH})\text{SiCl}_3$ /*tert*-butyl methyl ether/ BiCl_3 was 1/2.3/0.01. Although $(\text{CH}_2=\text{CH})\text{Si}(\text{OMe})_3$ was also present in the solution, proved by NMR data, the solution was used for alkoxylation of **1** without further purification because $(\text{CH}_2=\text{CH})\text{Si}(\text{OMe})_3$ does not possess SiCl groups, therefore it does not affect the reaction. The formation of *tert*-butyl chloride was confirmed, which also indicates the proceeding of methoxylation. Because the presence of this compound does not affect the following reaction, the solution obtained in this stage was directly used for the next step of silylation

of **1**. The ^1H , ^{13}C , and ^{29}Si NMR spectra of **2** are shown in Figures 2.7 to 2.9.

Compound 2. ^1H NMR (500 MHz; CDCl_3 ; 25 °C; TMS) $\delta = 6.21$ (dd, $J = 2.8$, 12.2 Hz, 1H; $\text{SiCH}=\text{CH}_2$ (*trans* position to Si)), 6.10 (dd, $J = 2.8$, 17.0 Hz, 1H; $\text{SiCH}=\text{CH}_2$ (*cis* position to Si)), 5.94 (dd, $J = 12.2$, 17.0 Hz, 1H; $\text{SiCH}=\text{CH}_2$), 3.61 ppm (s, 9H; SiOCH_3); ^{13}C NMR (126 MHz; CDCl_3 ; 25 °C; TMS) $\delta = 138.6$ ($\text{SiCH}=\text{CH}_2$), 128.8 ($\text{SiCH}=\text{CH}_2$), 51.2 ppm (SiOMe); ^{29}Si (99 MHz; CDCl_3 ; 25 °C; TMS) $\delta = -40.1$ ppm (1Si, D^0 ; $\text{O}_2\text{SiCl}(\text{CH}=\text{CH}_2)$).

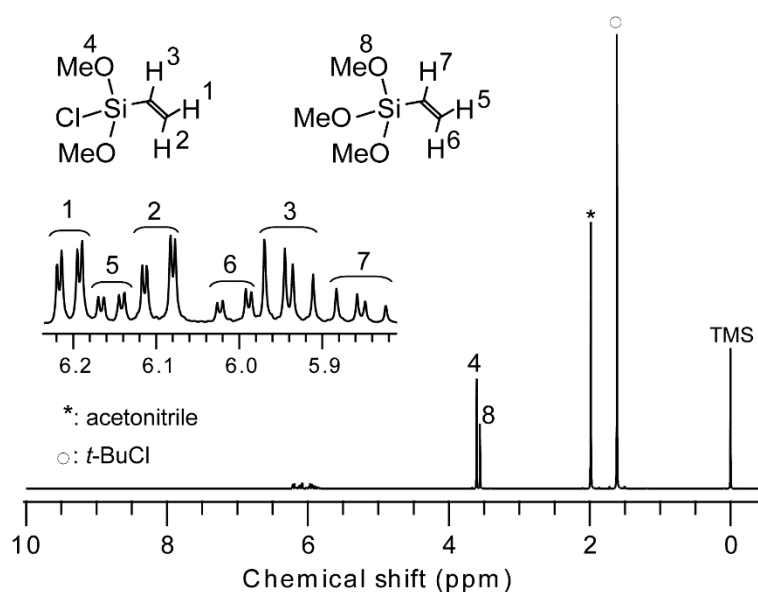


Figure 2.7. ^1H NMR spectrum of compound **2**.

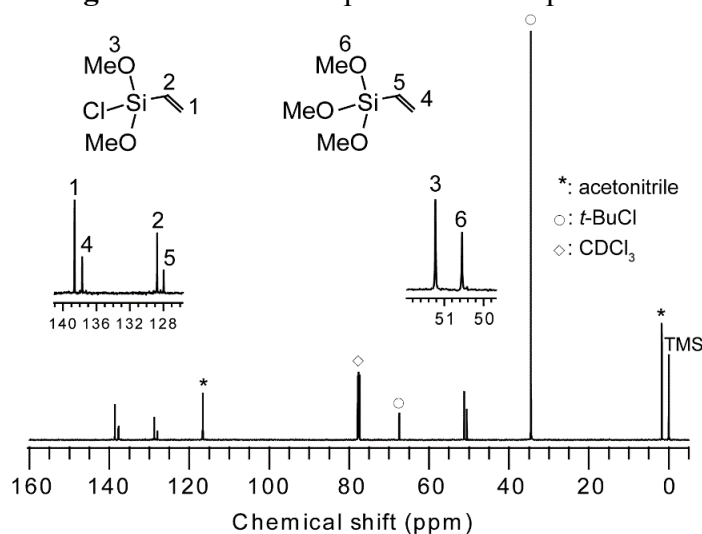


Figure 2.8. ^{13}C NMR spectrum of compound **2**.

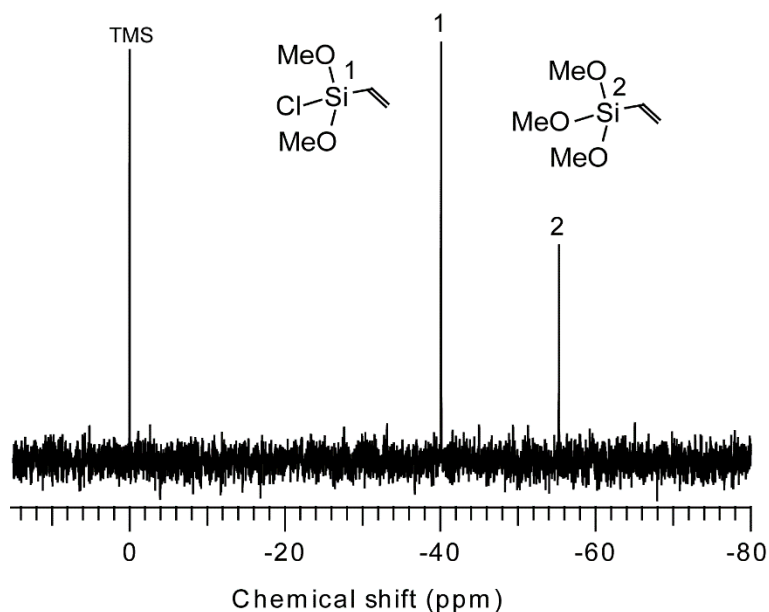


Figure 2.9. ^{29}Si NMR spectrum of compound **2**.

2.2.4 Synthesis of $(t\text{BuO})_2\text{MeSiOSi}(\text{CH}=\text{CH}_2)(\text{OMe})_2$ (**3**)

Compound **3** was synthesized by alkoxylation of **1** with **2**. Pyridine was added to the solution containing **2** described above (2.2.3). The mixture was cooled at 0 °C and a hexane solution of **1** (11.0 g, 0.053 mol) was dropped to the mixture. The molar ratio of **1/2** was 1/1.1. The mixture was stirred for 30 min at room temperature and excess pyridine and methanol were added for methoxylation of remaining SiCl groups. After stirring for 30 min at room temperature, the solvents (hexane and MeCN), *tert*-butyl chloride, remaining pyridine, and methanol were evaporated *in vacuo* and the solid residue was removed by filtration. Yellow clear liquid (**3**, 11.1 g, yield 64.6 %) was obtained after vacuum distillation. The ^1H , ^{13}C , and ^{29}Si NMR spectra of **3** are shown in Figures 2.10 to 2.12.

Compound 3. ^1H NMR (500 MHz; CDCl_3 ; 25 °C; TMS) δ = 6.10 (dd, J = 4.2, 14.5 Hz, 1H; SiCH=CH₂ (*trans* position to Si)), 6.02 (dd, J = 4.2, 20.5 Hz, 1H; SiCH=CH₂ (*cis* position to Si)), 5.91 (dd, J = 14.5, 20.5 Hz, 1H; SiCH=CH₂), 3.56 (s, 6H; SiOCH₃),

1.30 (s, 18H; C(CH₃)₃), 0.15 ppm (s, 3H; SiCH₃); ¹³C NMR (126 MHz, CDCl₃, 25 °C, TMS) δ = 136.5 (SiCH=CH₂), 129.7 (SiCH=CH₂), 72.7 (CMe₃), 50.4 (SiOMe), 31.7 (CMe₃), -0.3 ppm (SiMe); ²⁹Si (99 MHz; CDCl₃; 25 °C; TMS) δ = -61.7 (1Si, T¹; SiOSiMe(O*t*Bu)₂), -64.2 ppm (1Si, T¹; SiOSi(CH=CH₂)(OMe)₂) HRMS (ESI, 1.5 kV) calcd. for C₁₃H₃₀O₅Si₂Na⁺ [M+Na]⁺: 345.1524; found: 345.1524.

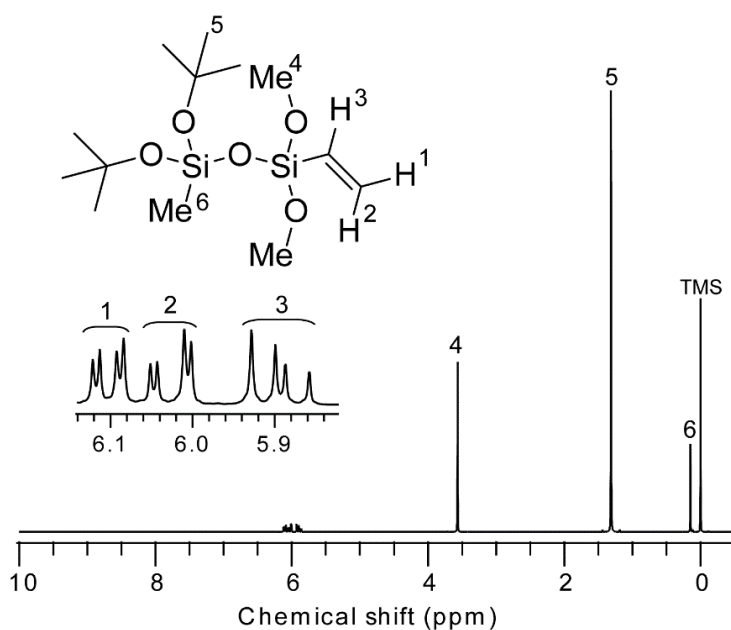


Figure 2.10. ¹H NMR spectrum of compound 3.

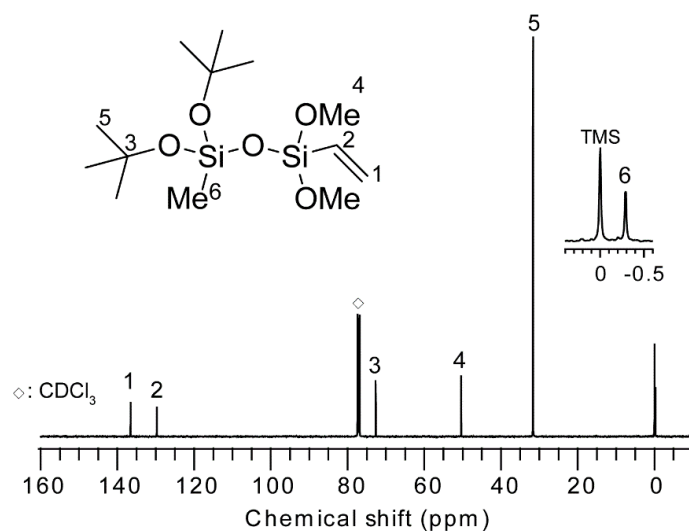


Figure 2.11. ¹³C NMR spectrum of compound 3.

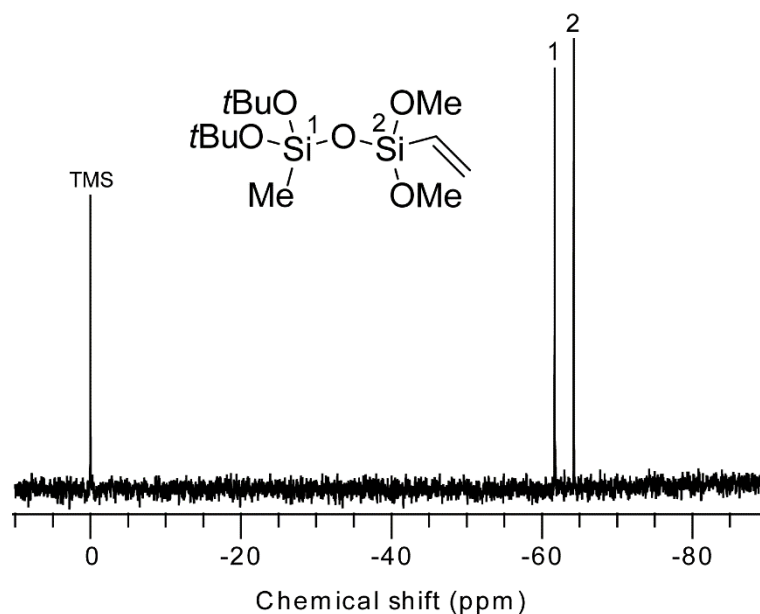


Figure 2.12. ^{29}Si NMR spectrum of compound **3**.

2.2.5 Synthesis of $\text{Cl}(\text{CH}_2)_3\text{SiCl}(\text{OMe})_2$ (**4**)

Compound **4** was synthesized according to a manner similar to the synthesis of **2**. $\text{Cl}(\text{CH}_2)_3\text{SiCl}_3$ was used instead of $(\text{CH}_2=\text{CH})\text{SiCl}_3$ in the synthesis of **2**. $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$ was also formed. As mentioned above for the synthesis of **2**, $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$ was not removed because $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$ does not affect the synthesis of compound **5**. The ^1H , ^{13}C , and ^{29}Si NMR spectra of **4** are shown in Figures 2.13 to 2.15.

Compound 4. ^1H NMR (500 MHz; CDCl_3 ; 25 °C; TMS) δ = 3.61 (s, 6H; SiOCH_3), 3.54 (m, 2H; $\text{Si}(\text{CH}_2)_2\text{CH}_2\text{Cl}$), 1.92 (m, 2H; $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 1.00 ppm (m, 2H; $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$); ^{13}C NMR (126 MHz; CDCl_3 ; 25 °C; TMS) δ = 51.3 (SiOMe), 46.8 ($\text{Si}(\text{CH}_2)_2\text{CH}_2\text{Cl}$), 25.9 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 12.0 ppm ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$); ^{29}Si (99 MHz; CDCl_3 ; 25 °C; TMS) δ = -27.0 ppm (1Si, D^0 ; $\text{O}_2\text{SiCl}((\text{CH}_2)_3\text{Cl})$)

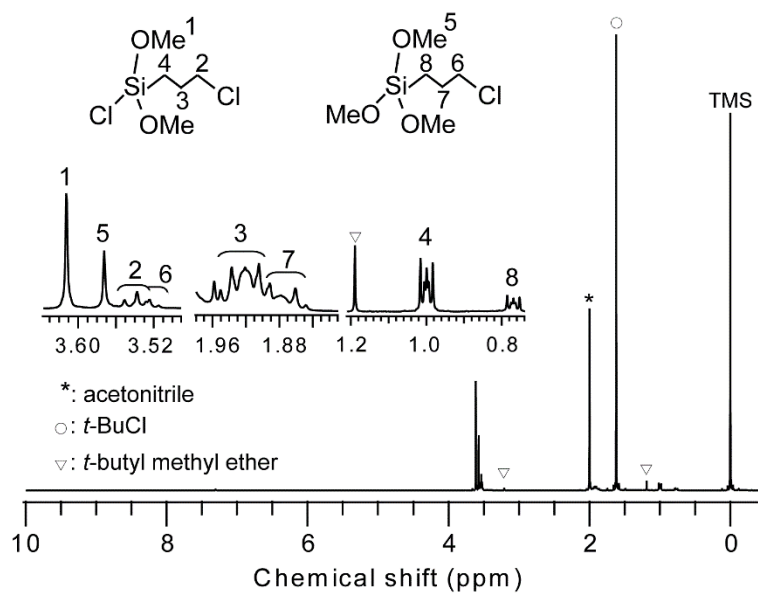


Figure 2.13. ^1H NMR spectrum of compound **4**.

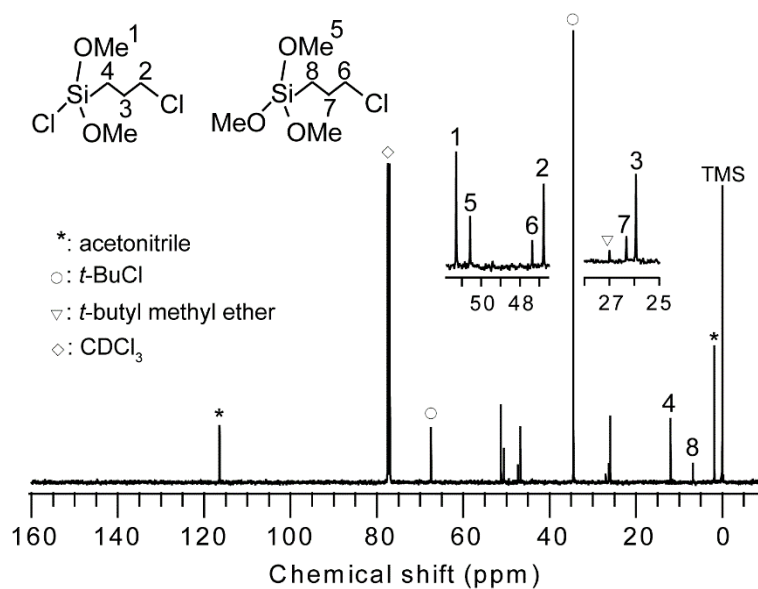


Figure 2.14. ^{13}C NMR spectrum of compound **4**.

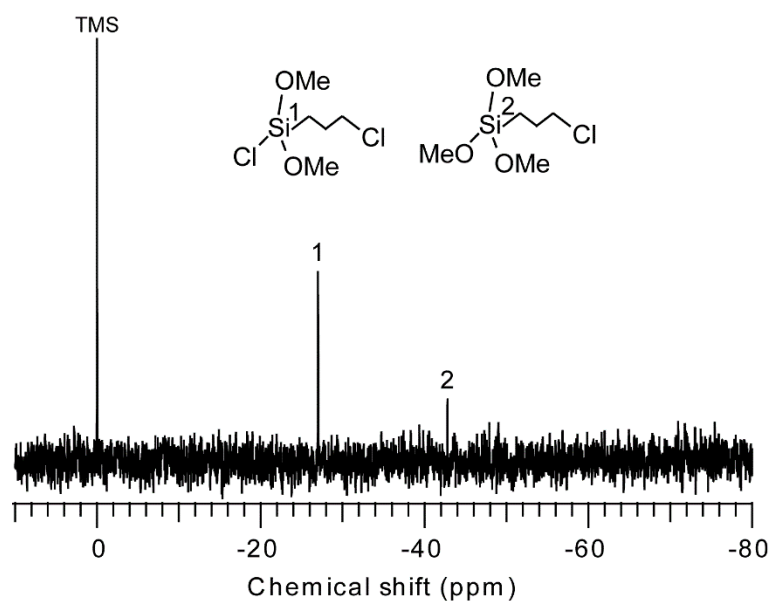


Figure 2.15. ^{29}Si NMR spectrum of compound **4**.

2.2.6 $\text{SiMe}[\text{OSi}(\text{CH}=\text{CH}_2)(\text{OMe})_2][\text{OSi}(\text{CH}_2)_3\text{Cl}(\text{OMe})_2]_2$ (**5**)

A solution of **3** (11.1 g, 32.2 mmol) in hexane (10 mL) was added to a solution of **4** and BiCl_3 in a 100 mL Schlenk flask. The molar ratio of **3**/**4**/ BiCl_3 was 1/3/0.033. The mixture was stirred at room temperature for 24 h under N_2 atmosphere. Pyridine and methanol were added into the mixture and the mixture was stirred for 30 min for methoxylation of SiCl groups formed by functional group exchange reaction between **4** and **5**. After the completion of the reaction, confirmed by ^1H and ^{13}C NMR, the solvents, $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$, *tert*-butyl chloride, remaining pyridine, and methanol were removed under reduced pressure. Then, colorless clear liquid **5** (4.1 g, 7.2 mmol, yield 23 %) was isolated by vacuum distillation after a solid residue was removed by filtration.

Compound 5. ^1H NMR (500 MHz; CDCl_3 ; 25 °C; TMS): δ = 6.14 (dd, J = 4.2, 14.4 Hz, 1H; $\text{SiCH}=\text{CH}_2$ (*trans* position to Si)), 6.02 (dd, J = 4.2, 20.7 Hz, 1H; $\text{SiCH}=\text{CH}_2$ (*cis* position to Si)), 5.88 (dd, J = 14.5, 20.7 Hz, 1H; $\text{SiCH}=\text{CH}_2$), 3.56 (s, 6H; $\text{Si}(\text{OCH}_3)_2(\text{CH}=\text{CH}_2)$), 3.55 (s, 12H; $\text{Si}(\text{OCH}_3)_2(\text{CH}_2)_3\text{Cl}$), 3.51 (t, J = Hz, 4H;

Si(CH₂)₂CH₂Cl), 1.88 (m, 4H; SiCH₂CH₂CH₂Cl), 0.76 (m, 4H; SiCH₂CH₂CH₂Cl), 0.27 ppm (s, 3H; SiCH₃); ¹³C NMR (126 MHz; CDCl₃; 25 °C; TMS) δ = 137.1 (SiCH=CH₂), 128.9 (SiCH=CH₂), 50.33 (Si(OMe)₂(CH=CH₂)), 50.30 (Si(OMe)₂(CH₂)₃Cl), 47.3 (Si(CH₂)₂CH₂Cl), 26.4 (SiCH₂CH₂CH₂Cl), 8.3 (SiCH₂CH₂CH₂Cl), -3.2 ppm (SiMe); ²⁹Si (99 MHz; CDCl₃; 25 °C; TMS) δ = -51.4 (2Si, T¹; (SiO)(MeO)₂Si((CH₂)₃Cl), -63.9 (1Si, T¹; (SiO)(MeO)₂Si(CH=CH₂)), -66.8 ppm (1Si, T³; (SiO)₃SiMe); HRMS (Electrospray Ionization, 2 kV) calcd. for C₁₅H₃₆O₉Cl₂Si₄Na⁺ [M+Na]⁺: 565.0707; found: 565.0706.

2.2.7 Hydrolysis and condensation of compound 5

Compound **5**, THF containing 10 vol% of THF-*d*₈, H₂O and HCl (0.01 mol/L) were mixed in a Teflon vessel and the mixture was stirred at room temperature. THF was used as the solvent because it is a compatible solvent for both compound **5** and H₂O. The molar ratio of compound **5**/THF/H₂O/HCl was 1/25/6/0.5 × 10⁻³. Hydrolysis and condensation behaviors of the oligomer were investigated by constantly following the evolution of the relevant ¹³C and ²⁹Si NMR signals. The details of the measurements are described in the characterization section.

2.2.8 Characterization

Solution ¹H, ¹³C and ²⁹Si NMR spectra were recorded on a Bruker AVANCE 500 spectrometer with resonance frequencies of 500.0 MHz, 125.7 MHz, and 99.3 MHz, respectively, at ambient temperature. Sample solutions were put in 5 mm glass tubes. The chemical shifts were referenced to internal tetramethylsilane (TMS) at 0 ppm. CDCl₃ and THF containing 10% of THF-*d*₈ were used to obtain lock signals. A small amount of Cr(acac)₃ (acac = acetylacetonate) was also added as a relaxation agent for ²⁹Si nuclei.

^{13}C NMR was measured with a recycle delay of 2 s. ^{29}Si NMR was measured with a recycle delay of 10 s. HR-ESI mass analysis was carried out with a JEOL JMS-T100 CS instrument. Samples were dissolved in methanol.

2.3 Results and Discussion

2.3.1 Characterizations of compound 5

The ^1H NMR spectrum of compound 5 (Figure 2.16) shows nine signals at 0.27 ($-\text{SiMe}$), 0.75 to 0.78 ($-\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-Cl}$), 1.86 to 1.91 ($-\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-Cl}$), 3.50 to 3.53 ($-\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-Cl}$), 3.55 ($-\text{Si}(\text{CH}_2)_3\text{Cl}(\text{OMe})_2$), 3.56 ($-\text{Si}(\text{CH}_2=\text{CH})(\text{OMe})_2$), 5.85 to 5.92 ($-\text{CH}=\text{CH}_2$), 6.00-6.05 ($-\text{CH}=\text{CH}_2$ (*cis* position to Si)), and 6.12 to 6.16 ppm ($-\text{CH}=\text{CH}_2$ (*trans* position to Si)). The integration ratio of these signals is 1.0:1.0:1.0:20.7*:3.8:3.8:3.0 and these correspond to the calculated ratio (1:1:1:22:4:4:3, *containing all the signals from 3s.50 ppm to 3.56 ppm because of the overlapping). On the other hand, there are no signals assigned to *t*BuO groups of the compound 3.

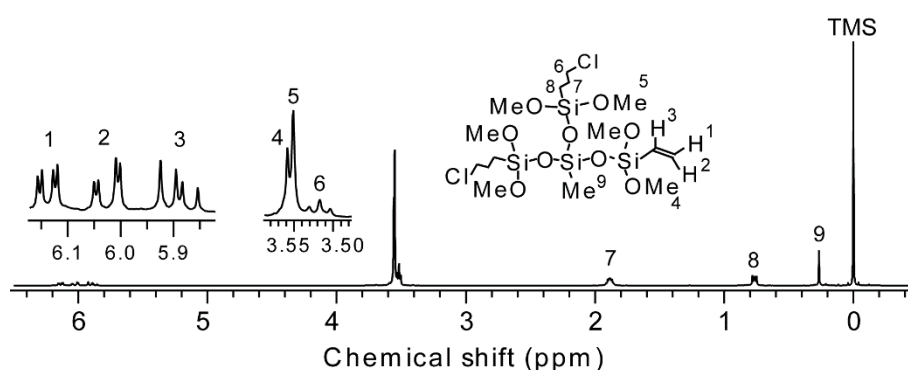


Figure 2.16. ^1H NMR spectrum of compound 5.

These results indicate the alkoxylation accompanied with complete elimination of *t*BuO groups. Furthermore, vinyl and chloropropyl groups are retained

without any side reactions. The ^{13}C NMR spectrum (Figure 2.17) also shows the presence of chloropropyl and vinyl groups and the absence of *t*BuO groups, which strongly supports this conclusion.

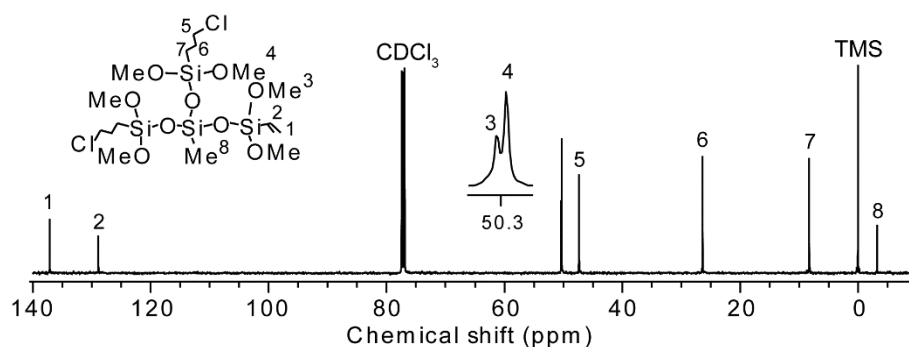


Figure 2.17. ^{13}C NMR spectrum of compound **5**.

The ^{29}Si NMR spectrum of compound **1** (Figure 2.18) shows three signals at -51.4 , -63.9 and -66.8 ppm and their intensity ratio is 1.9:1.1:1.0. The singlet signal at -51.4 ppm is assigned to $-\text{Si}(\text{CH}_2)_3\text{Cl}$, because the number of $-\text{Si}(\text{CH}_2)_3\text{Cl}$ group is twice as that of $-\text{Si}(\text{CH}=\text{CH}_2)$ or $-\text{SiMe}$ groups. The other two signals at -63.9 and -66.8 ppm are assigned to $-\text{Si}^{\text{T}1}(\text{CH}=\text{CH}_2)$ and $-\text{Si}^{\text{T}3}\text{Me}$, respectively, because of the following two reasons. i) The signal due to T^1 Si atoms possessing vinyl groups appears around -62 ppm.²⁵ ii) The signal due to T^3 Si atoms possessing methyl groups appears around -65 ppm.²⁶ These assignments are also supported by a computational analysis. The details on the method are shown in ref. 27. The results show that the signal due to Si of $\text{Si}^{\text{T}3}$ -methyl group appears at higher magnetic field by 4.02 ppm than that due to Si of $\text{Si}^{\text{T}1}$ -vinyl group. As mentioned above, the measured signal due to Si of $\text{Si}^{\text{T}3}$ -methyl appeared at higher magnetic field by 2.9 ppm than that due to Si of $\text{Si}^{\text{T}1}$ -vinyl. The high-resolution ESI-MS spectrum shows a peak at $m/z = 565.0706$ corresponding to $[\text{M}+\text{Na}^+]$ (calcd. mass: 565.0707). These results confirmed the synthesis of compound **5**.

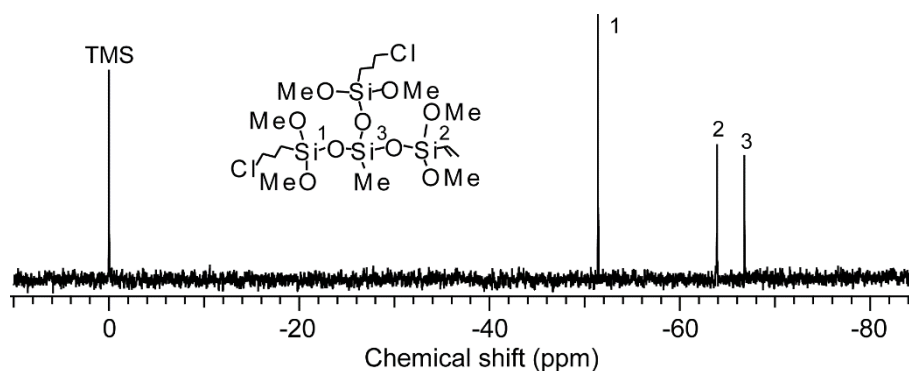


Figure 2.18. ^{29}Si NMR spectrum of compound **5**.

Therefore, it is successful to synthesize the siloxane oligomer which has alkoxy groups and plural functional groups. It is reasonably expected to synthesize siloxane oligomers which possess both acidic and basic functional groups by transforming the vinyl and chloropropyl groups of **5**, respectively. In addition, alkoxy siloxane oligomers which have other functional groups can be synthesized by changing the kind of alkoxychlorosilanes under the same reaction processes. Furthermore, the ratio of functional groups can be controlled by changing the order of the alkoxy silylation. Because alkoxychlorosilanes are easily synthesized from chlorosilanes, the synthetic method presented here is very versatile.

2.3.2 Hydrolysis and condensation of compound **5**

The solution ^{13}C NMR spectra of compound **5** hydrolyzed for different reaction times (Figure 2.19) indicate the complete hydrolysis between 2 - 3 h after the beginning of the reaction. Please note that the chemical shifts of ^{13}C NMR signals in Figure 2.19 (0 h) were slightly different from those in Figure 2.17 because THF- d_8 was used to obtain the spectra of Figure 2.19 (0 h) while CDCl_3 was used for the spectrum of Figure 2.17. THF- d_8 was chosen because THF is compatible with both **5** and H_2O .

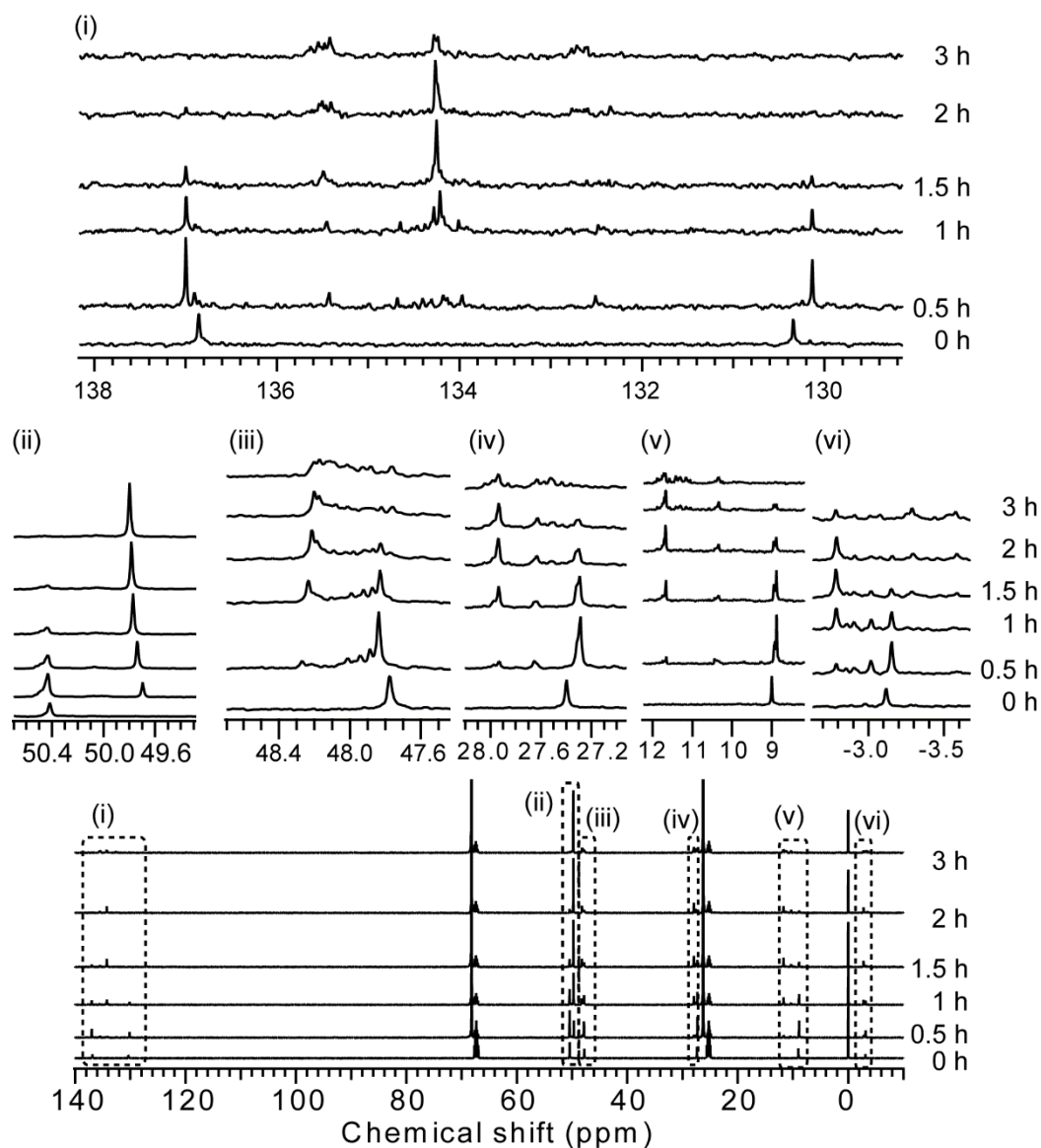
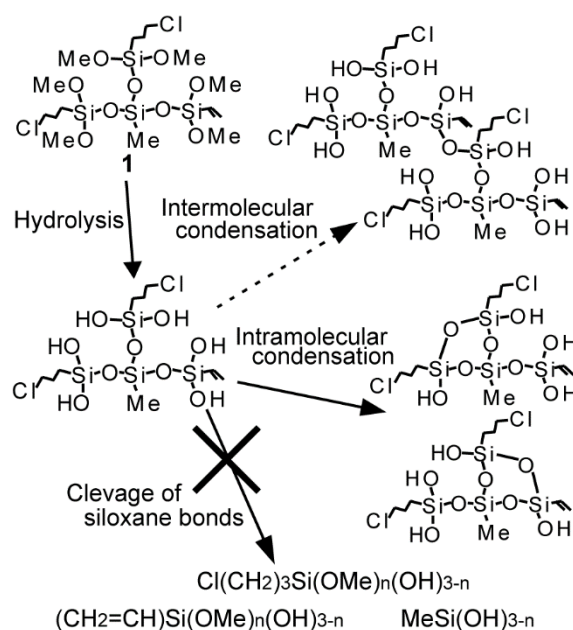


Figure 2.19. ^{13}C NMR ($\text{THF-}d_8$) of spectra of compound **5** hydrolyzed for different reaction times.

The signal intensity assigned to methoxy group (50.4 ppm) decreased steadily, and disappeared after 3 h. A new signal assigned to methanol simultaneously appeared at 49.7 to 49.8 ppm. In addition, all the signal intensities due to methyl (−3.1 ppm), vinyl (130.2 ppm and 136.4 ppm) and 3-chloropropyl groups (9.0 ppm, 27.4 ppm, and 47.8 ppm) of compound **5** are weakened with the time course of hydrolysis and condensation,

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while many new signals for the same functional groups appearing at chemical shifts similar to those for compound **5** (The magnified spectra are shown in Figure 2.19). These results are interpreted to mean that the environments of the carbon atoms of those groups change as hydrolysis and condensation progresses. The diversification of the environments is caused by the following factors. i) Because compound **5** contains hydrolysable six $-\text{SiOMe}$ groups, very many kinds of molecules will be generated by hydrolysis of **5**. ii) In the condensation process, two kinds of cyclic siloxane will be formed by intramolecular condensation (Scheme 2.2), and the stereoisomers will be generated when these molecules are formed. Detailed interpretation and assignments of ^{13}C NMR signals are shown from next paragraph.



Scheme 2.2 Proposed reaction processes for hydrolysis and condensation of compound **5**.

Interpretation of the ^{13}C NMR spectra of compound **5** hydrolyzed for different reaction times (Figure 2.19) and the assignment of signals are discussed here by focusing the signals due to vinyl group of compound **5**. The reason why vinyl group is chosen for

the discussion is as follows. Chemical shifts of two carbon atoms of vinyl group are affected by the variation in the environment of Si atom linked to vinyl group, and the degree of variation is different between $-\text{Si}\underline{\text{C}}\text{H}=\text{CH}_2$ and $-\text{SiCH}=\underline{\text{C}}\text{H}_2$. Therefore, vinyl group is suitable for discussing the structural transformations of compound **5** than methyl and chloropropyl groups.

Many signals due to vinyl groups around 130 ppm to 140 ppm and their variations in the chemical shifts during the hydrolysis and condensation are discussed as follows.

1) A. Gordillo *et al.* reported that the ^{13}C NMR signals due to $-\text{Si}\underline{\text{C}}\text{H}=\text{CH}_2$ and $-\text{SiCH}=\underline{\text{C}}\text{H}_2$ of triethoxyvinylsilane appeared at 129.2 ppm and 137.4 ppm, respectively.²⁸ When triethoxyvinylsilane is hydrolyzed to form monosodiumoxyvinylsilanediol the signals due to $-\text{Si}\underline{\text{C}}\text{H}=\text{CH}_2$ and $-\text{SiCH}=\underline{\text{C}}\text{H}_2$ shift to downfield and upfield by about 3 ppm and 1.5 ppm, respectively. It should be noted that in the case of ref. 28, the substance is monomeric. On the other hand, the substance studied here is oligomeric and the effect of neighboring Si on the chemical shift should be large, if the electron withdrawing effect of siloxane bond is considered,²⁹ though this is rather qualitative.

2) According to Cai and Weber,³⁰ the ^{13}C NMR signals due to $-\text{Si}\underline{\text{C}}\text{H}=\text{CH}_2$ and $-\text{SiCH}=\underline{\text{C}}\text{H}_2$ in 2,4,6-trivinyl-2,4,6-trimethylcyclotrisiloxane appeared at 134.2 to 134.4 ppm (the variation comes from *cis-trans* conformation) and 135.5 to 135.8 ppm (the same *cis-trans* conformation), respectively. And the two signals appeared at 133.3 to 133.5 ppm and 136.1 to 136.4 ppm for 2,4,6,8-tetravinyl-2,4,6,8-tetramethylcyclotetrasiloxane, respectively. Consequently, by the increase in the ring size, the upfield shift is observed for $-\text{Si}\underline{\text{C}}\text{H}=\text{CH}_2$ and the downfield shift is observed for $-\text{SiCH}=\underline{\text{C}}\text{H}_2$.

On the basis of these interpretations, the author consider the assignments of ^{13}C

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NMR signals around 130 ppm to 140 ppm.

i) The assignments for the signals

Many ^{13}C NMR signals observed around 132.6 ppm, around 134.2 ppm, and around 135.5 ppm can be assigned to $-\text{Si}\underline{\text{C}}\text{H}=\text{CH}_2$ (Si atoms do not participate in the trisiloxane ring formation), $-\text{Si}\underline{\text{C}}\text{H}=\text{CH}_2$ (Si atoms participate in the trisiloxane ring formation), and $-\text{SiCH}=\underline{\text{C}}\text{H}_2$, respectively. The reasons for these assignments are shown below.

a) Gordillo *et al.* reported that the ^{13}C NMR signals due to $-\text{Si}\underline{\text{C}}\text{H}=\text{CH}_2$ and $-\text{SiCH}=\underline{\text{C}}\text{H}_2$ of trialkoxyvinylsilane shift to downfield and upfield by hydrolysis, respectively.²⁸

b) The shift of $-\text{Si}\underline{\text{C}}\text{H}=\text{CH}_2$ is larger than that of $-\text{SiCH}=\underline{\text{C}}\text{H}_2$ because the distance from the hydrolysis reaction sites ($-\text{SiOMe}$) to $-\text{Si}\underline{\text{C}}\text{H}=\text{CH}_2$ is shorter than that of $-\text{SiCH}=\underline{\text{C}}\text{H}_2$.

c) On the basis of ^{29}Si NMR measurements (Fig. 3), compound **1** is converted to cyclic siloxanes by hydrolysis and intramolecular condensation.

d) By comparison the ^{13}C NMR signals reported by Cai and Weber³⁰ with data shown here, the author can conclude cyclotrisiloxanes are formed by hydrolysis of compound **1**.

e) As shown in Scheme 2, two kinds of cyclotrisiloxanes are formed, one contains Si atom having a vinyl group within the cyclic structure and the other does not.

f) According to the two papers^{28, 30}, the signals due to $-\text{SiCH}=\underline{\text{C}}\text{H}_2$ appear in almost same chemical shifts, irrespective the molecular structures (monomeric and cyclic compounds). On the other hand, the signals due to $-\text{Si}\underline{\text{C}}\text{H}=\text{CH}_2$ of monomeric compounds appear upfield than those of cyclic compounds. Therefore, the signals around 132.6 ppm are assigned to $-\text{Si}\underline{\text{C}}\text{H}=\text{CH}_2$ whose Si atoms are not involved in the trisiloxane ring

formation, and the signals around 134.2 ppm are assigned to $-\text{Si}\underline{\text{C}}\text{H}=\text{CH}_2$ whose Si atoms participate in the trisiloxane ring formation.

ii) The decrease in the number of signals can be explained as follows.

Because compound **5** contains six $-\text{SiOMe}$ groups, very many kinds of molecules will be generated by hydrolysis and intra/intermolecular condensation of compound **5**. In fact, the initial step of hydrolysis (0.5 h), a lot of signals are observed in the range of 130 ppm to 140 ppm. These signals can be assigned to molecules in which a few $-\text{SiOMe}$ groups are hydrolyzed. The decrease in the number of these signals in 1 h to 3 h is explained by the reduction of the kind of molecules after full hydrolysis of $-\text{SiOMe}$ groups. After 2 h to 3 h from the beginning of the hydrolysis, the formation of cyclic siloxanes is suggested by ^{29}Si NMR measurements. Therefore, the strongest peak (134.2 ppm) can be assigned to the cyclic siloxanes. The enlarged spectrum after 2 h from the beginning of hydrolysis showed that the signal at 134.2 ppm has a shoulder, and the enlarged spectrum after 3 h indicated the two signals at 134.2 ppm. These signals can be caused by the formation of stereoisomers of cyclic siloxanes.

Multiple signals are observed in the ^{29}Si NMR spectra (Figure 2.20) of hydrolyzed solutions of compound **5**, and assignments of these signals are shown in Table 2.1. (Please note that the chemical shifts of ^{29}Si NMR signals in Figure 2.20(0 h) were slightly different from those in Figure 2.18 because of the difference in deuterated solvent.) It is quite difficult to assign these signals precisely because their chemical shifts are very close together. Three signals appear at -49.9 ppm, -62.7 ppm, and -66.5 ppm in 0.5 h. As confirmed by the ^{13}C NMR (Figure 2.19), the hydrolysis is complete within 2 to 3 h. Therefore, these signals are assigned to $-\text{Si}\underline{\text{O}}\text{H}$ groups generated by hydrolysis

(Scheme 2.2). These three signals disappear steadily after 2 h, and new signals appear at -49.7 ppm to -50.5 ppm, -56.9 ppm to -57.4 ppm, and -63.1 ppm to -63.9 ppm. The assignments of these signals are discussed regarding as two types of molecules; i) molecules generated by cleavage of siloxane bonds of compound **5** or ii) molecules generated by intra- and inter-molecular condensation.

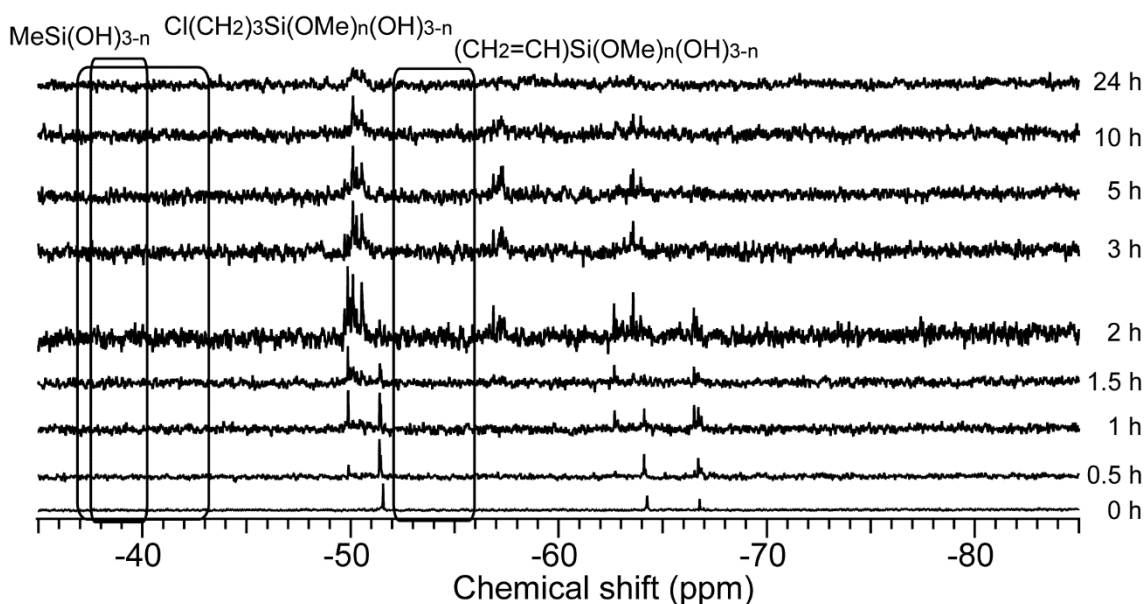


Figure 2.20. ^{29}Si NMR ($\text{THF-}d_8$) of spectra of compound **5** hydrolyzed for different reaction times.

Table 2.1: Assignments for ^{29}Si NMR signals of hydrolyzed **5**.

Time / h	Signals due to $-\text{Si}(\text{CH}_2)_3\text{Cl}$	Signals due to $-\text{Si}(\text{CH}=\text{CH}_2)$	Signals due to $-\text{SiMe}$
0	$\text{T}^1_{(\text{OMe})_2}$: -51.4 ppm	$\text{T}^1_{(\text{OMe})_2}$: -64.3 ppm	$\text{T}^3_{(\text{OSi})_2}$: -66.7 ppm
0.5 to 1.5	$\text{T}^1_{(\text{OH})_2}$: -49.9 ppm	$\text{T}^1_{(\text{OH})_2}$: -62.7 ppm	$\text{T}^3_{(\text{OSi})_2}$: -66.5 ppm to -66.7 ppm
2 to 10	$\text{T}^2_{\text{OH,OSi}}, \text{T}^3_{(\text{OSi})_2}$: -49.7 ppm to -50.5 ppm	$\text{T}^2_{\text{OH,OSi}}, \text{T}^3_{(\text{OSi})_2}$: -56.9 ppm to -57.4 ppm	$\text{T}^3_{(\text{OSi})_2}$: -63.1 ppm to -63.9 ppm

*Symbol T of T^n_x denotes three oxygen atoms on Si. The superscript n of T^n means the number of Si bonded to the central Si atom. The subscript x of T_x denotes the kind of functional groups linked to Si atom.

At first, the cleavage of siloxane bonds of compound **5** was examined. If the siloxane bonds of compound **5** are cleaved, $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{OMe})_n(\text{OH})_{3-n}$, $\text{MeSi}(\text{OMe})_n(\text{OH})_{3-n}$ and $(\text{CH}_2=\text{CH})\text{Si}(\text{OMe})_n(\text{OH})_{3-n}$ ($n = 0\sim 3$) would be generated (Scheme 2.2). However, there are no signals in the T^0 region corresponding to these molecules (-36 ppm to -44 ppm, -52 ppm to -56 ppm, and -38 ppm to -40 ppm,^{25, 31} respectively). Because these molecules are easily observed under acidic conditions,³¹ it is quite reasonable to conclude that the oligosiloxane structure of compound **5** is not degraded under the conditions used here.

Next, intramolecular condensation of compound **5** is discussed. The overlapped signals of the sample after the reaction for 2 h, appearing at -49.7 ppm to -50.5 ppm, -56.9 ppm to -57.4 ppm, and -63.1 ppm to -63.9 ppm, are assignable to $-\underline{\text{Si}}(\text{CH}_2)_3\text{Cl}$, $-\underline{\text{Si}}(\text{CH}=\text{CH}_2)$, and $-\underline{\text{Si}}\text{Me}$ of cyclotrisiloxanes, respectively (Table 2.1). Intramolecular condensation naturally forms cyclic siloxane structures and the terminal T^1 silicon atoms of compound **5** become T^2 silicon atoms. Signals corresponding to T^2 silicon atoms of cyclotrisiloxanes appear downfield from T^2 silicon atoms in non-cyclic compounds because of ring strain.³² The presence of too many signals can be explained by the formation of two types of cyclic siloxanes (Scheme 2.2) and their geometric isomers.³³⁻³⁵

Finally, intermolecular condensation of compound **5** is discussed. The signals in the ranges from -56.9 ppm to -57.4 ppm and from -62.8 ppm to -63.9 ppm might be assigned to *intermolecularly* condensed species of compound **5**, in which the hydroxy groups of $-\underline{\text{Si}}(\text{OH})_2(\text{CH}_2)_3\text{Cl}$ are used for condensation (Scheme 2.2), because it is known that signals corresponding to T^2 and T^3 silicon atoms of intermolecularly condensed species appear upfield than T^1 silicon atoms.³¹ However, there are no signals corresponding to intermolecularly condensed species derived by condensation of hydroxy groups of $-\underline{\text{Si}}(\text{OH})_2(\text{CH}=\text{CH}_2)$ around at -80 ppm. The absence of species resulting from

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intermolecular condensation of $-\text{Si}(\text{OH})_2(\text{CH}=\text{CH}_2)$ group can be explained by the following two reasons. At first, the intensity of the signals due to $-\text{Si}(\text{OH})_2(\text{CH}=\text{CH}_2)$ is lower than that of $-\text{Si}(\text{OH})_2(\text{CH}_2)_3\text{Cl}$ because the number of $-\text{Si}(\text{CH}=\text{CH}_2)$ group is half of $-\text{Si}(\text{CH}_2)_3\text{Cl}$ group. Second, the signal intensity of each silicon atom is weakened because the environment of silicon atoms is diversified and the molecular mobility is decreased by intermolecular condensation. The same reasons can be applied to explain the absence of the signals assigned to $-\text{SiMe}$ groups after 3h. For these reasons, signals due to intermolecularly condensed species are normally observed to much lesser degrees. Therefore, the possibility of intermolecular condensation cannot be excluded completely in the initial stage of sol-gel reaction of compound **5** (Intermolecular condensation progressed by evaporating the solvent from the reaction mixture after 24 h from the reaction and a transparent gel was formed.). However, the observed signals are clearly assigned as the progress of intramolecular condensation, which leads us to conclude that the last one proceeds preferentially rather than intermolecular condensation.

As shown above, the siloxane linkages are not broken, which indicates that the incorporated functional groups are located at the original positions. This means that the method presented here is quite useful for the design of precursors for the preparation of hybrid materials as well as mesostructured materials possessing functional groups distributed homogeneously with some fixed distance. This is superior to the grafting method³⁻⁵ using two kinds of reagents, which provide hybrids with only locally distributed functional groups.

The preference of cyclization should be attributed to the branched oligosiloxane structure of compound **5**. In the case of linear oligosiloxane, it is reported that intramolecular condensation is competed with intermolecular condensation except for in a dilute solution.^{36,37} In comparison with a linear oligosiloxane, silanol groups generated

by hydrolysis of alkoxy groups of compound **5** are sterically close to one another. Therefore, it is quite reasonable that intramolecular condensation proceeds preferentially because silanol groups generated by hydrolysis of alkoxy groups are close to each other and condense easily. Cyclic siloxanes generated by intramolecular condensation possess four silanol groups which are not used for intramolecular condensation. After the formation of cyclic siloxanes, Si–O–Si networks can be constructed by intermolecular condensation among these silanols. The formation of Si–O–Si networks by intermolecular condensation should result in the broadening of NMR signals and the decrease in their intensities because the environment of Si atoms is diversified and the molecular mobility is decreased by the Si–O–Si network formation. In fact, the signals in the spectra of the products reacted for 10 h and 24 h after the beginning of hydrolysis were broadened and also the intensity of signals in those spectra decreased (Figure 2.20). Hybrid materials prepared using branched oligomers are expected to possess unique features in terms of porosity and density because the position of silanol groups is so restricted that they are not able to react freely with neighboring silanol groups. The study on the relationship between the properties of hybrids and siloxane structures in various length scales is challenging for future design of siloxane-based materials.

2.4 Conclusions

Alkoxysiloxane oligomer **5** possessing plural different functional groups has been successfully synthesized by combining a conventional silylation with non-hydrolytic silylation which does not involve the formation of silanol group during the reaction. The siloxane bonds are not cleaved during hydrolysis and condensation of compound **5**, as judged by ^{29}Si NMR data. It is indicated that intramolecular condensation proceeds more preferentially than intermolecular condensation. Therefore, compound **5**

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can be used as a building block to prepare hybrid materials via the sol-gel process. The distribution and separation between individual functional groups can be controlled by using this type of oligomer. Reactive functional groups are appended to vinyl and 3-chloropropyl group in this study. The extension of the kinds of functional groups that could be used to prepare hybrid materials with controlled functionalities will be a fruitful area of future research in sol-gel chemistry.

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Chapter 3

Protecting and Leaving Functions of Trimethylsilyl Groups in Trimethylsilylated Silicates for the Synthesis of Oligosiloxanes Possessing Alkoxy Groups

Adapted with permission from M. Yoshikawa, Y. Tamura, R. Wakabayashi, M. Tamai, A. Shimojima, K. Kuroda, “Protecting and Leaving Functions of Trimethylsilyl Groups in Trimethylsilylated Silicates for the Synthesis of Alkoxysiloxane Oligomers”, *Angew. Chem. Int. Ed.* **2017**, *56*, 13990-13994. Copyright 2017 John Wiley & Sons, Ltd.

3.1 Introduction

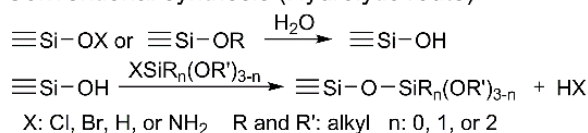
In organic synthesis, precise molecular design has been widely developed by using protection and deprotection of functional groups.¹ Silyl groups, most typically trimethylsilyl, are commonly used as protecting groups for -COH groups because C-O-Si bonds can be easily cleaved at the O-Si bond. We were inspired to apply this methodology to siloxane-based inorganic synthetic chemistry in order to advance and stimulate the field. It is well known that trialkylsilyl (-SiR_3) groups are useful for capping SiOH/SiO^- groups; however, their use as protecting groups for the controlled synthesis of siloxane-based compounds has not been reported. One of the more challenging and unprecedented issues requiring investigation is the selective cleavage of the Si-O-SiR_3 linkages (deprotection) for subsequent reactions in multistep synthesis.

The target molecules in this study are well-defined oligosiloxanes used as building blocks for siloxane-based materials. Silicone, silsesquioxanes, and silica have applications in a wide range of fields. Using building blocks for the preparation of these materials is an effective methodology to construct siloxane structures that cannot be achieved by using monomeric silanes, which enables the development of materials with novel properties and functionalities.² In particular, oligosiloxanes possessing alkoxy groups (hereafter called alkoxy siloxane oligomers) are important because of their ability to form Si-O-Si networks with controlled nanostructures by hydrolysis and polycondensation of the alkoxy groups.³⁻⁵ However, selective synthetic methods for alkoxy siloxane oligomers are quite limited.

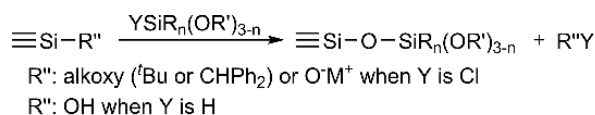
Alkoxy siloxane oligomers are generally synthesized by alkoxy silylation of monomeric silanes or oligosiloxanes (Scheme 3.1a). The formation of siloxane bonds and the introduction of alkoxy groups are conducted simultaneously in these reactions.⁶⁻¹¹ However, the instability of the alkoxy groups against hydrolysis limits the reaction

conditions and types of precursors available. Additionally, the synthesis and isolation of the reactants containing Si–OH groups are difficult. Although non-hydrolytic routes containing chapter 2 in this thesis (Scheme 3.1b) have also been developed,¹²⁻¹⁶ the structures of the alkoxy siloxane oligomers reported so far have been limited. To address these issues, the author propose a new synthetic route in which the formation of siloxane bonds and the introduction of alkoxy groups are done separately, as shown in Scheme 3.1c. The terminal reactive sites (SiOH/SiO⁻) of oligosiloxanes are first protected with trimethylsilyl groups, allowing the facile isolation of a variety of oligosiloxanes as stable compounds. The trimethylsilyl groups are then substituted with alkoxy silyl groups (deprotection). Trimethylsilylated derivatives of oligosiloxanes are rich in diversity, and various structural types such as linear, branched, ladder, and cubic have been reported. However, methods for the substitution step have not been developed yet. Although the substitution reaction of dimethylsilyl groups with other trialkylsilyl groups was reported,¹⁷ this reaction cannot be adopted for the synthesis of alkoxy siloxane oligomers because the reaction is conducted under hydrolytic conditions.

(a) Conventional synthesis (Hydrolytic route)

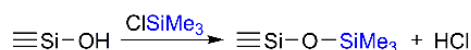


(b) Conventional synthesis (Non-hydrolytic route)

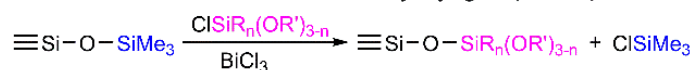


(c) This study

1. Formation of SiOSi with TMS: Protection



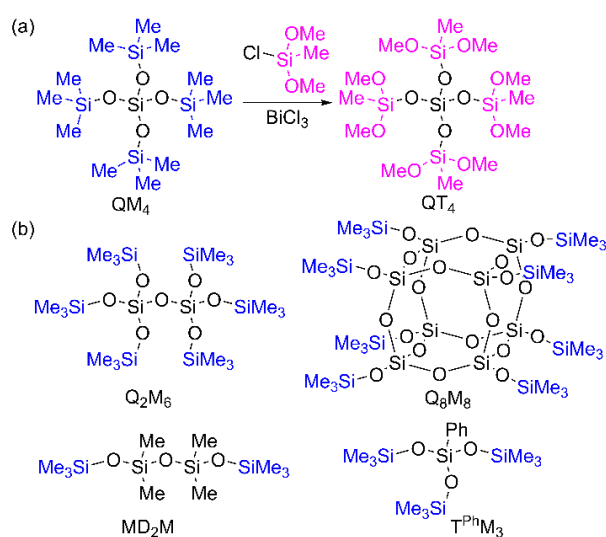
2. Substitution of TMS with alkoxy silyl groups: Deprotection



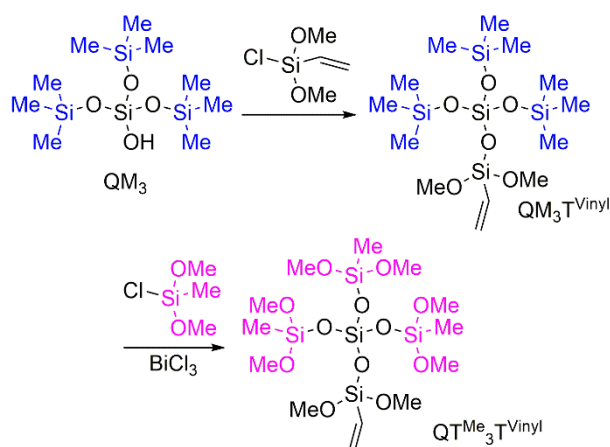
Scheme 3.1. Conventional synthetic routes to alkoxy siloxane oligomers and a novel route proposed in this study.

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This chapter shows the nucleophilic substitution reaction of TMS groups with alkoxy-silyl groups as a novel synthetic method for the synthesis of alkoxy-siloxane oligomers (Scheme 3.1c). The author confirmed the leaving group ability of the TMS groups of QM_4^\dagger by substituting with dimethoxy(methyl)silyl groups using a Lewis acid catalyst ($BiCl_3$) (Scheme 3.2a). The scope of the reaction was then investigated by using several oligosiloxanes possessing TMS groups as starting materials (Scheme 3.2a, b). Finally, we synthesized tris(dimethoxy(methyl)siloxy)(vinyl dimethoxysiloxy)-silane ($QT^{Me_3}T^{Vinyl}$) from tris(trimethylsiloxy)silanol (QM_3) (Scheme 3.3). QM_3 can be considered as the protected compound of $Si(OH)_4$ with three TMS groups. To the best of my knowledge, this is the first report where the concept of protecting and leaving groups is applied to the synthesis of siloxane-based compounds.



Scheme 3.2. (a) Syntheses of alkoxy-siloxane oligomer based on the substitution reaction of TMS groups with alkoxy-silyl groups. (b) Oligosiloxanes possessing TMS groups used as starting materials.



Scheme 3.3. Synthesis of an alkoxy-siloxane oligomer with a vinyl group using TMS groups as protecting and leaving groups.

3.2 Experimental and Characterization of starting materials

3.2.1 Materials

(i) General

Acetone (> 99.0%), acetonitrile (MeCN, dehydrated > 99.0%), amberlyst-15(H), *tert*-butyl methyl ether (MTBE, dehydrated, > 99.0%), concentrated hydrochloric acid (conc. HCl), hexane (> 99.8%), methanol (dehydrated, > 99.8%), pyridine (dehydrated, > 99.5%), 2-propanol (> 99.7%), tetrahydrofuran (THF, dehydrated, > 99.5%, stabilizer free), and xylene (dehydrated, > 80%, mixture of *o*-xylene, *m*-xylene and *p*-xylene) were purchased from Wako Pure Chemical Industries, Ltd. and used as received. Chlorotrimethylsilane (TMCS, > 98.0%), decamethyltetrasiloxane (MD₂M, > 97.0%), palladium hydroxide (Pd(OH)₂/C, 20% of Pd(OH)₂ on carbon, wetted with *ca.* 50% water), phenyltris(trimethylsiloxy)silane (> 98.0%), potassium *tert*-butoxide (*t*BuOK, > 97.0%), tetrachlorosilane (SiCl₄, > 98.0%), tetraethoxysilane (TEOS, > 96.0%), trichloromethylsilane (Cl₃SiMe, > 98.0%), and trichlorovinylsilane (Cl₃Si(CH=CH₂), > 98.0%) were purchased from Tokyo Chemical Industry Co., Ltd. and used as received.

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Tetramethylammonium hydroxide pentahydrate (TMAOH·5H₂O, > 97.0%) and tris(trimethylsiloxy)silane (> 98.0%) were purchased from Sigma-Aldrich Co., LLC. and used as received. Bismuth(III) chloride (BiCl₃, > 98.0%) and magnesium sulfate (anhydrous, > 95.0%) were purchased from Kanto Chemical Co., Ltd. and used as received. Ethanol (EtOH, > 99.5%) was purchased from Junsei Chemical Co., Ltd., and used as received.

(ii) Silicates

Natural hemimorphite (Ojuela Mine, Mapimi, Durango, Mexico, the purity was checked by powder X-ray diffraction.) and sodium metasilicate nonahydrate¹⁸ (Sigma-Aldrich Co., > 98.0%), as disilicate and monosilicate sources, respectively, were used as received.

3.2.2 Synthesis of starting materials

(i) Chlorodimethoxy(methyl)silane ((MeO)₂MeSiCl)¹⁹

Bismuth (III) chloride (BiCl₃) was dried under reduced pressure in a Schlenk flask for 30 min. Dehydrated acetonitrile (MeCN) was added to the flask under N₂ atmosphere, and the mixture was stirred until dissolving of BiCl₃. Trichloromethylsilane (Cl₃SiMe) was added to the solution at 0 °C, and dehydrated *t*-butyl methyl ether (MTBE) was added dropwise to the mixture. The molar ratio of Cl₃SiMe/MTBE/BiCl₃ was 1/2.2/0.01. After stirring the mixture at room temperature for 8 h, colorless clear liquid was obtained and this liquid was measured by liquid-state NMR. Although trimethoxymethylsilane and *t*-butyl chloride remained as by-products, the obtained mixture was used for the following alkoxy-silylations without any purification because such by-products, containing no –SiCl groups, do not affect the reactions.

(MeO)₂MeSiCl. ¹H NMR (500.13 MHz; CDCl₃; 25 °C; TMS) δ = 3.60 (s, 6H; OCH₃) and 0.42 ppm (s, 3H; SiCH₃); ¹³C NMR (126.76 MHz; CDCl₃; 25 °C; TMS) δ = 51.1 (OCH₃) and -2.1 ppm (SiCH₃); ²⁹Si (99.36 MHz; CDCl₃; 25 °C; TMS) δ = -24.6 ppm (1Si, D⁰).

(ii) Tetrakis(trimethylsiloxy)silane (QM₄)²⁰

Sodium metasilicate nonahydrate (142.2 g) was dissolved to deionized water (419 mL), and 1 M sodium metasilicate aq. was prepared. Deionized water (125 mL), conc. HCl (150 mL), 2-propanol (300 mL), and hexamethyldisiloxane (200 mL) were mixed in a 1 L flask at room temperature for 1 h. 1 M sodium metasilicate aq. (100 mL) was added to the mixture, and the mixture was stirred at room temperature for 1 h. After separation of the aqueous layer, the organic layer was washed with deionized water twice. Then, 2.5 g of Amberlyst-15 was added to the organic layer. After stirring the mixture at room temperature for 2 h, Amberlyst-15 was removed by filtration and the solvents was evaporated *in vacuo*. Then, colorless clear liquid was isolated by vacuum distillation (5 mmHg, 75 °C).

QM₄. ¹H NMR (500.13 MHz; CDCl₃; 25 °C; TMS) δ = 0.10 ppm (s, 36H; Si(CH₃)₃); ¹³C NMR (126.76 MHz; CDCl₃; 25 °C; TMS) δ = 1.6 ppm (Si(CH₃)₃); ²⁹Si (99.36 MHz; CDCl₃; 25 °C; TMS) δ = 8.4 (4Si, M¹; SiOSiMe₃) and -104.6 ppm (1Si, Q⁴; Si(OSi)₄); HRMS (Electrospray Ionization, 2 kV) calcd. for C₁₂H₃₆O₄Si₅Na⁺ [M+Na]⁺: 407.1352; found: 407.1354.

(iii) Tetra-*tert*-butoxysilane (Si(O^{*t*}Bu)₄)²¹

Potassium *t*-butoxide (KO^{*t*}Bu, 50 g) was added to a 500 mL three neck flask, and dried under reduced pressure. After the addition of dehydrated xylene (250 mL) under N₂

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atmosphere, tetrachlorosilane (SiCl_4 , 11.6 mL) was added dropwise to the mixture at 0 °C. The molar ratio of $\text{SiCl}_4/\text{KO}^t\text{Bu}$ was 1/4.4. After stirring the mixture for 1 h, the mixture was refluxed overnight. The precipitates were removed by centrifugation, and the solvent was evaporated *in vacuo* at 40 °C. Then, colorless clear liquid was obtained by vacuum distillation (6 mmHg, 100 °C). This colorless clear liquid was solidified at room temperature.

Si(O^tBu)₄. ¹H NMR (500.13 MHz; CDCl_3 ; 25 °C; TMS) $\delta = 1.29$ ppm (s, 36H; CH_3); ¹³C NMR (126.76 MHz; CDCl_3 ; 25 °C; TMS) $\delta = 72.2$ (CMe_3) and 31.4 ppm ($\text{C}(\text{CH}_3)_3$); ²⁹Si (99.36 MHz; CDCl_3 ; 25 °C; TMS) $\delta = -98.0$ ppm (1Si, Q^0).

(iv) Synthesis of QT₄ from Si(O^tBu)₄¹⁵

QT₄ was synthesized by alkoxylation of $\text{Si}(\text{O}^t\text{Bu})_4$ with $(\text{MeO})_2\text{MeSiCl}$ according to the previous report.¹⁵ A solution of $\text{Si}(\text{O}^t\text{Bu})_4$ (14.2 g) in hexane was added to a solution of $(\text{MeO})_2\text{MeSiCl}$ and BiCl_3 in anhydrous MeCN, and the mixture was stirred at room temperature for 1 d under N_2 atmosphere. The molar ratio of $\text{Si}(\text{O}^t\text{Bu})_4/(\text{MeO})_2\text{MeSiCl}$ was 1/8. Excess of pyridine and methanol were added to the residual solution for methoxylation of SiCl groups formed by functional group exchange reaction between SiOMe groups and SiCl groups. The mixture was stirred at room temperature for 30 min, and the solvents, remaining pyridine and methanol were removed under reduced pressure. After a solid residue was removed by filtration, colorless clear liquid was obtained by vacuum distillation.

QT₄. ¹H NMR (500.13 MHz; CDCl_3 ; 25 °C; TMS) $\delta = 3.55$ (s, 24H; OCH_3), 0.16 ppm (s, 12H; SiCH_3); ¹³C NMR (126.76 MHz; CDCl_3 ; 25 °C; TMS) $\delta = 50.1$ (OCH_3), -7.0 ppm (SiCH_3); ²⁹Si NMR (99.36 MHz; CDCl_3 ; 25 °C; TMS) $\delta = -48.1$ (4Si, T^1 ; $\text{SiOSiMe}(\text{OMe})_2$), -110.7 ppm (1Si, Q^4 ; $\text{Si}(\text{OSi})_4$); HRMS (Electrospray Ionization, 2

kV) calcd. for $C_{12}H_{36}O_{12}Si_5Na^+$ $[M+Na]^+$: 535.0940; found: 535.0945.

(v) Hexakis(trimethylsiloxy)disiloxane (Q₂M₆)²²

Hexamethyldisiloxane (9 mL), dehydrated acetone (1 mL), and chlorotrimethylsilane (5 mL) were mixed in a 50 mL round-bottomed flask. After stirring at room temperature for 5 min, 0.5 g of hemimorphite (The purity was checked by powder XRD.) was added to the mixture and the mixture was stirred at room temperature for 3 min. Then, a solid residue was removed by filtration and the solvent and the remaining silylating agents were evaporated to obtain a viscous liquid.

Q₂M₆. ¹H NMR (500.13 MHz; CDCl₃; 25 °C; TMS) δ = 0.10 ppm (s, 54H; Si(CH₃)₃); ¹³C NMR (126.76 MHz; CDCl₃; 25 °C; TMS) δ = 1.6 ppm (Si(CH₃)₃); ²⁹Si (99.36 MHz; CDCl₃; 25 °C; TMS) δ = 8.6 (6Si, M¹; SiOSiMe₃) and -107.1 ppm (2Si, Q⁴; Si(OSi)₄); HRMS (Electrospray Ionization, 2 kV) calcd. for $C_{18}H_{54}O_7Si_8Na^+$ $[M+Na]^+$: 629.1916; found: 629.1915.

(vi) Si₈O₂₀(NMe₄)₈·nH₂O (TMA₈D4R)⁷

Tetramethylammonium hydroxide pentahydrate (TMAOH·5H₂O, 27.7 g), deionized water (13.8 mL), ethanol (86.8 mL), and tetraethoxysilane (TEOS, 34.0 mL) were mixed in a round-bottomed flask at room temperature. The molar ration of TMAOH/H₂O/EtOH/TEOS was 1/10/10/1. After stirring the mixture for 3 d, the solvent was evaporated by boiling until the volume was reduced by half. The remaining solution was cooled to room temperature, and almost of the solution was solidified. The precipitates were separated from the remaining solution, and dried *in vacuo* at 60 °C to obtain TMA₈D4R.

TMA₈D4R. ¹H NMR (500.13 MHz; EtOH-*d*₆; 25 °C; TMS) δ = 3.30 ppm (s,

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96H; N(CH₃)₄); ¹³C NMR (126.76 MHz, EtOH-*d*₆, 25 °C; TMS) δ = 56.3-56.4 ppm (N(CH₃)₄); ²⁹Si (99.36 MHz; EtOH-*d*₆; 25 °C; TMS) δ = -99.0 ppm (8Si, Q³; Si(O⁻)(OSi)₃).

(vii) Trimethylsilylated double-four-ring silicate (Q₈M₈)²³

TMA₈D4R (5 g) was dissolved in methanol (5 mL), and the solution was added dropwise to a mixture of hexane (16.5 mL) and chlorotrimethylsilane (12.0 mL). The mixture was stirred at room temperature for 12 h, and the hexane layer was separated and evaporated. The white solid residue was washed with MeCN to obtain Q₈M₈.

Q₈M₈. ¹H NMR (500.13 MHz; CDCl₃; 25 °C; TMS) δ = 0.15 ppm (s, 72H; Si(CH₃)₃); ¹³C NMR (126.76 MHz; CDCl₃; 25 °C; TMS) δ = 1.2 ppm (Si(CH₃)₃); ²⁹Si (99.36 MHz; CDCl₃; 25 °C; TMS) δ = 12.5 ppm (8Si, M¹; SiOSiMe₃), -108.9 ppm (8Si, Q⁴; Si(OSi)₄).

(viii) Tris(trimethylsiloxy)silanol (QM₃)²⁴

Tris(trimethylsiloxy)silane ((Me₃SiO)₃SiH, 10 mL) was mixed with dehydrated tetrahydrofuran (20 mL), 0.05 g of palladium hydroxide was added to the mixture. Then, deionized water (1.2 mL) was added to the mixture, and the mixture was stirred at 50 °C for 1 d. The molar ratio of (Me₃SiO)₃SiH/H₂O was 1/2.3. After cooling to room temperature, excess water was removed with anhydrous magnesium sulfate. Then, palladium hydroxide and magnesium sulfate were removed by filtration through celite, and the filtrate was evaporated to obtain (Me₃SiO)₃SiOH.

QM₃. ¹H NMR (500.13 MHz; CDCl₃; 25 °C; TMS) δ = 0.13 ppm (s, 27H; Si(CH₃)₃); ¹³C NMR (126.76 MHz; CDCl₃; 25 °C; TMS) δ = 1.5 ppm (Si(CH₃)₃); ²⁹Si (99.36 MHz; CDCl₃; 25 °C; TMS) δ = 9.7 (3Si, M¹; OSiMe₃) and -96.1 ppm (1Si, Q³);

$\text{Si}(\text{OH})(\text{OSi})_3$; HRMS (Electrospray Ionization, 2 kV) calcd. for $\text{C}_9\text{H}_{28}\text{O}_4\text{Si}_4\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 335.0957; found: 335.0957.

(ix) Chlorodimethoxy(vinyl)silane ((MeO)₂(CH₂=CH)SiCl)¹⁹

(MeO)₂(CH₂=CH)SiCl was synthesized according to a way similar to that of (MeO)₂MeSiCl. Trichlorovinylsilane was used instead of Cl₃SiMe, and trimethoxyvinylsilane was formed. As noted above for the synthesis of (MeO)₂MeSiCl, trimethoxyvinylsilane was not removed.

(MeO)₂(CH₂=CH)SiCl. ¹H NMR (500.13 MHz; CDCl₃; 25 °C; TMS) δ = 6.20 (dd, J = 12.5, 2.5 Hz, 1H; SiCH=CH₂ (*trans* position to Si)), 6.10 (dd, J = 17.0, 2.5 Hz, 1H; SiCH=CH₂ (*cis* position to Si)), 5.94 (dd, J = 17.0, 12.5 Hz, 1H; SiCH=CH₂) and 3.61 ppm (s, 6H; OCH₃); ¹³C NMR (126.76 MHz; CDCl₃; 25 °C; TMS) δ = 138.6 (SiCH=CH₂), 128.7 (SiCH=CH₂) and 51.2 ppm (OCH₃); ²⁹Si (99.36 MHz; CDCl₃; 25 °C; TMS) δ = -40.1 ppm (Si, D⁰).

(x) QM₃T^{vinyl}

Excess of dehydrated pyridine was added to the mixture containing (MeO)₂(CH₂=CH)SiCl mentioned above. A hexane solution of (Me₃SiO)₃SiOH was added to the mixture at 0 °C, and the mixture was stirred for 30 min. Excess of dehydrated methanol was added to the mixture for transformation of remaining -SiCl groups into -SiOMe groups. After stirring for 30 min at room temperature, the solvents, trimethoxyvinylsilane, and remaining methanol were removed *in vacuo*, and the solid residue was removed by filtration. Then, colorless clear liquid was isolated by vacuum distillation (9 mmHg, 135 °C).

QM₃T^{vinyl}. ¹H NMR (500.13 MHz; CDCl₃; 25 °C; TMS) δ = 6.10 (dd, J = 15.0,

4.0 Hz, 1H; SiCH=CH₂ (*trans* position to Si)), 6.00 (dd, $J = 20.5, 4.0$ Hz, 1H; SiCH=CH₂ (*cis* position to Si)), 5.86 (dd, $J = 20.5, 15.0$ Hz, 1H; SiCH=CH₂), 3.54 (s, 6H; OCH₃) and 0.12 ppm (s, 27H; Si(CH₃)₃); ¹³C NMR (126.76 MHz; CDCl₃; 25 °C; TMS) $\delta = 136.7$ (SiCH=CH₂), 129.3 (SiCH=CH₂), 50.3 (OCH₃) and 1.5 ppm (Si(CH₃)₃); ²⁹Si (99.36 MHz; CDCl₃; 25 °C; TMS) $\delta = 9.3$ (3Si, M¹; SiOSiMe₃), -64.2 (1Si, T¹; SiOSi(CH=CH₂)(OMe)₂) and -106.2 ppm (1Si, Q⁴; SiO₄); HRMS (Electrospray Ionization, 2 kV) calcd. for C₁₃H₃₆O₆Si₅Na⁺ [M+Na]⁺: 451.1250; found: 451.1252.

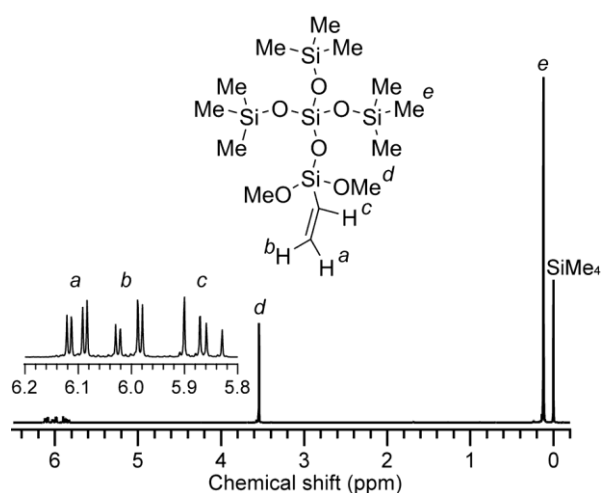


Figure 3.1. ¹H NMR spectrum of (MeO)₂(CH₂=CH)SiOSi(OSiMe₃)₃.

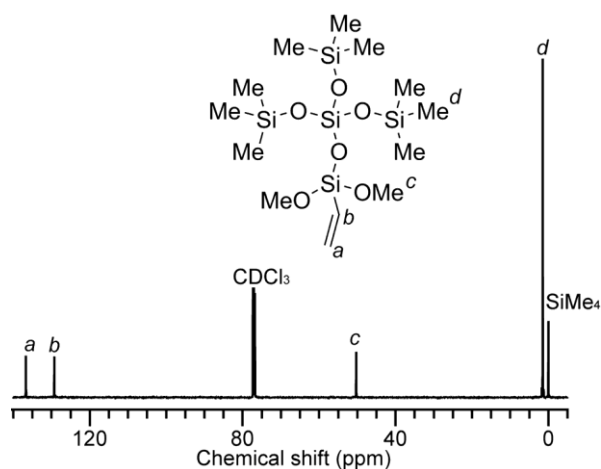


Figure 3.2. ¹³C NMR spectrum of (MeO)₂(CH₂=CH)SiOSi(OSiMe₃)₃.

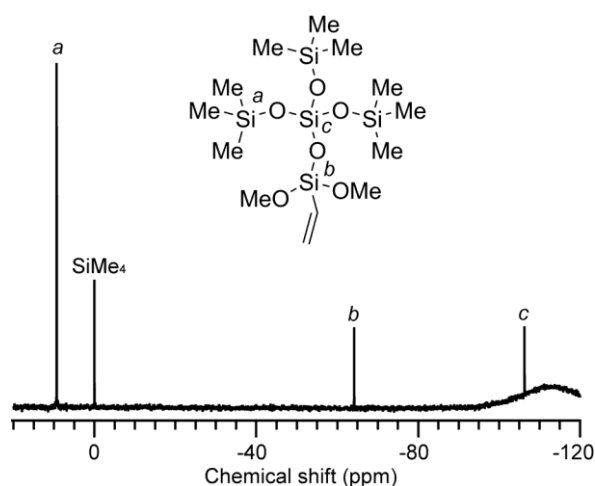


Figure 3.3. ^{29}Si NMR spectrum of $(\text{MeO})_2(\text{CH}_2=\text{CH})\text{SiOSi}(\text{OSiMe}_3)_3$.

3.2.3 Substitution of TMS groups of various compounds

(i) QM₄

QM₄ (3.4 mL) was added to a solution of $(\text{MeO})_2\text{MeSiCl}$ and BiCl_3 in anhydrous MeCN under N_2 atmosphere, and the mixture was stirred under various reaction condition as shown in Table 3.1. The molar ratio of QM₄/ $(\text{MeO})_2\text{MeSiCl}$ was 1/8. In the case of entry 1, the crude sample was measured by liquid-state ^1H , ^{13}C , ^{29}Si NMR after stirring. After the evaporation of the solvent and the remaining $(\text{MeO})_2\text{MeSiCl}$ *in vacuo*, excess of pyridine and methanol were added to the residual solution for methoxylation of SiCl groups formed by functional group exchange reaction between SiOMe groups and SiCl groups. The mixture was stirred at room temperature for 30 min, and remaining pyridine and methanol were removed under reduced pressure. Then, colorless clear liquid was obtained after removing a solid residue by filtration. The solution was measured by liquid-state ^1H , ^{13}C , ^{29}Si NMR and HRMS.

In addition, to confirm the catalysis of BiCl_3 for substitution of TMS groups, QM₄ and $(\text{MeO})_2\text{MeSiCl}$ were mixed without BiCl_3 at room temperature or 60 °C for one week.

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(ii) Q₂M₆, MD₂M, and T^{Ph}M₃

The experiment was conducted as the same way of the substitution reaction of QM₄. Q₂M₆, MD₂M, and T^{Ph}M₃ were used instead of OM₄, respectively. The molar ratio of TMS groups/(MeO)₂MeSiCl was 1/1.5. The reaction was conducted at 60 °C for one week.

(iii) Q₈M₈

The experiment was conducted as the same way of the substitution reaction of QM₄. A THF solution of Q₈M₈ was used in place of OM₄, and the molar ratio of Q₈M₈/(MeO)₂MeSiCl was 1/40. After the reaction was conducted at 60 °C for one week, excess of pyridine and methanol were added and the mixture was stirred at room temperature for 30 min. THF, and remaining silylating agent, pyridine, and methanol were removed under reduced pressure to obtain a solid residue. The reaction product and unreacted Q₈M₈ were extracted from solid residue with hexane, and the hexane solution was evaporated by a rotary evaporator. The reaction product was obtained by extraction with MeCN.

(iv) Investigation of the reverse reaction of the substitution reaction of TMS groups

BiCl₃ (0.23 g) was dried in a Schlenk flask under reduced pressure. Anhydrous MeCN (10 mL) was added to the flask under N₂ atmosphere, and the mixture was stirred until BiCl₃ was dissolved. QT₄ (3.4 g, synthesized from Si(O^tBu)₄) and Me₃SiCl (3.5 mL) were added to the mixture, and the mixture was stirred at room temperature for one week. The molar ration of QT₄/Me₃SiCl/BiCl₃ was 1/4/0.1. Excess of pyridine and methanol were added to the mixture at 0 °C for methoxylation of SiCl groups, and the mixture was stirred for 30 min. The colorless clear liquid was obtained by filtration to remove a solid

residue. The solution was measured by liquid-state ^1H , ^{13}C , and ^{29}Si NMR.

(v) Comparison of the leaving group abilities between TMS and $t\text{Bu}$

For comparison of the leaving group abilities between TMS and $t\text{Bu}$ groups, $\text{Si}(\text{O}t\text{Bu})_4$ was reacted with $(\text{MeO})_2\text{MeSiCl}$ in the presence of BiCl_3 . The product was purified as the same way of the alkoxylation of QM_4 .

(vi) $\text{QM}_3\text{T}^{\text{vinyl}}$

The experiment was conducted as the same way of the substitution reaction of QM_4 . $\text{QM}_3\text{T}^{\text{vinyl}}$ was used instead of OM_4 , and the molar ratio of $\text{QM}_3\text{T}^{\text{vinyl}}/(\text{MeO})_2\text{MeSiCl}$ was 1/6. The reaction was conducted at $60\text{ }^\circ\text{C}$ for 4 d.

$\text{QT}^{\text{Me}_3}\text{T}^{\text{vinyl}}$. ^1H NMR (500.13 MHz; CDCl_3 ; $25\text{ }^\circ\text{C}$; TMS) $\delta = 6.14$ (dd, $J = 15.0$, 4.5 Hz, 1H; $\text{SiCH}=\text{CH}_2$ (*trans* position to Si)), 6.05 (dd, $J = 21.0$, 4.5 Hz, 1H; $\text{SiCH}=\text{CH}_2$ (*cis* position to Si)), 5.90 (dd, $J = 21.0$, 15.0 Hz, 1H; $\text{SiCH}=\text{CH}_2$), 3.58 (s, 6H; $\text{Si}(\text{CH}=\text{CH}_2)(\text{OCH}_3)_2$), 3.55 (s, 18H; $\text{SiMe}(\text{OCH}_3)_2$) and 0.16 ppm (s, 9H; SiCH_3); ^{13}C NMR (126.76 MHz; CDCl_3 ; $25\text{ }^\circ\text{C}$; TMS) $\delta = 137.2$ ($\text{SiCH}=\text{CH}_2$), 128.7 ($\text{SiCH}=\text{CH}_2$), 50.1 (OCH_3) and -7.0 ppm (SiCH_3); ^{29}Si (99.36 MHz; CDCl_3 ; $25\text{ }^\circ\text{C}$; TMS) $\delta = -48.2$ (3Si , T^1 ; $\text{SiOSiMe}(\text{OMe})_2$), -64.0 (1Si , T^1 ; $\text{SiOSi}(\text{CH}=\text{CH}_2)(\text{OMe})_2$) and -110.8 ppm (1Si , Q^4 ; SiO_4); HRMS (Electrospray Ionization, 2 kV) calcd. for $\text{C}_{13}\text{H}_{36}\text{O}_{12}\text{Si}_5\text{Na}^+$ [$\text{M}+\text{Na}$] $^+$: 547.0945 ; found: 547.0944 .

$\text{QMT}^{\text{Me}_2}\text{T}^{\text{vinyl}}$. ^1H NMR (500.13 MHz; CDCl_3 ; $25\text{ }^\circ\text{C}$; TMS) $\delta = 6.13$ (dd, $J = 15.0$, 4.0 Hz, 1H; $\text{SiCH}=\text{CH}_2$ (*trans* position to Si)), 6.04 (dd, $J = 21.5$, 4.0 Hz, 1H; $\text{SiCH}=\text{CH}_2$ (*cis* position to Si)), 5.89 (dd, $J = 21.5$, 15.0 Hz, 1H; $\text{SiCH}=\text{CH}_2$), 3.57 (s, 6H; $\text{Si}(\text{CH}=\text{CH}_2)(\text{OCH}_3)_2$), 3.54 (s, 12H; $\text{SiMe}(\text{OCH}_3)_2$), 0.16 ppm (s, 6H; SiCH_3) and 0.14 ppm (s, 9H; $\text{Si}(\text{CH}_3)_3$); ^{13}C NMR (126.76 MHz; CDCl_3 ; $25\text{ }^\circ\text{C}$; TMS) $\delta = 137.0$

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(SiCH=CH₂), 128.9 (SiCH=CH₂), 50.3 (OCH₃), 1.4 (Si(CH₃)₃), and -6.9 ppm (SiCH₃); ²⁹Si (99.36 MHz; CDCl₃; 25 °C; TMS) δ = 10.8 (1Si, M¹; SiOSiMe₃), -48.3 (2Si, T¹; SiOSiMe(OMe)₂), -64.1 (1Si, T¹; SiOSi(CH=CH₂)(OMe)₂) and -109.3 ppm (1Si, Q⁴; SiO₄); HRMS (Electrospray Ionization, 2 kV) calcd. for C₁₃H₃₆O₁₀Si₅Na⁺ [M+Na]⁺: 515.1047; found: 515.1047.

3.2.4 Characterization

Liquid-state ¹H, ¹³C and ²⁹Si NMR spectra were recorded on a Bruker AVANCE 500 spectrometer with resonance frequencies of 500.13 MHz, 125.76 MHz, and 99.36 MHz, respectively at ambient temperature. Samples were dissolved in CDCl₃, and small amounts of TMS and Cr(acac)₃ (acac = acetylacetonate) were added as an internal reference of chemical shift at 0 ppm and a relaxation agent for ²⁹Si nuclei, respectively. CDCl₃ was used to obtain lock signals. The solutions were put in 5 mm glass tubes. ¹³C spectra were recorded with a recycle delay of 2 s. ²⁹Si NMR spectra were recorded with a 45° pulse and a recycle delay of 10 s. High-resolution ESI mass analysis was conducted by using an Exactive Plus instrument (Thermo Fisher Scientific). Low resolution electrospray ionization mass analysis was conducted by using a JMS-T100 CS AccuTOF (JEOL) instrument. Samples were dissolved in ethanol.

3.3 Results and Discussion

3.3.1 Leaving group ability of TMS group

The fact that TMS groups act as a leaving group in the substitution reaction of QM₄ with dimethoxy(methyl)silyl groups was confirmed by the following evidence. The formation of trimethylchlorosilane (TMCS) as a byproduct and the formation of QM₂T₂, QMT₃, and QT₄ as products were confirmed by NMR spectroscopy of the reaction

mixture (Figures 3.4a–3.6a).

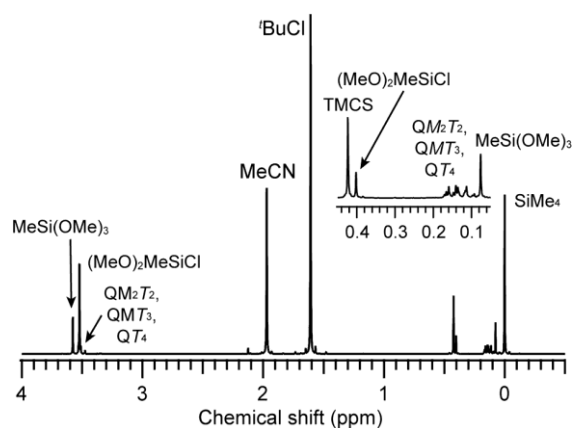


Figure 3.4. ^1H NMR spectrum of the crude sample of the $\text{QM}_4/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system after stirring at room temperature for one day (entry 1).

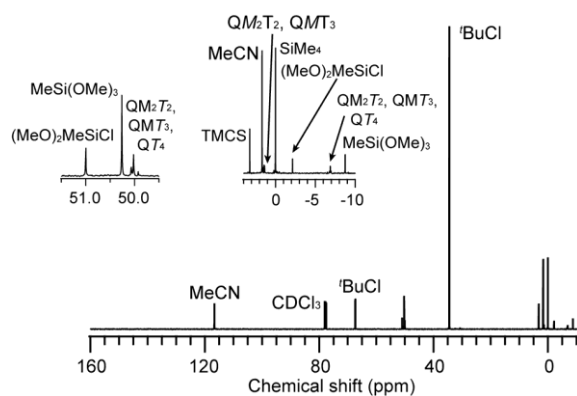


Figure 3.5. ^{13}C NMR spectrum of the crude sample of the $\text{QM}_4/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system after stirring at room temperature for one day (entry 1).

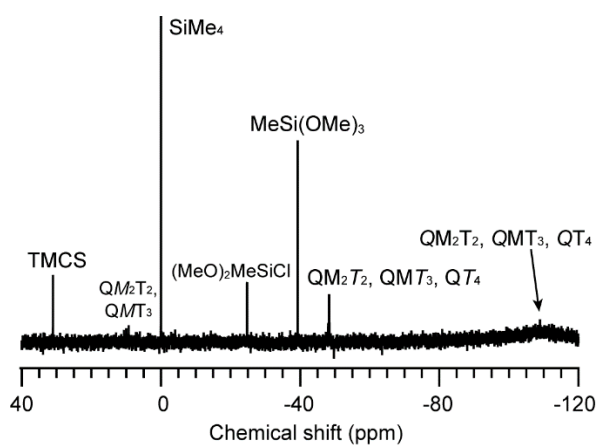


Figure 3.6. ^{29}Si NMR spectrum of the crude sample of the $\text{QM}_4/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system after stirring at room temperature for one day (entry 1).

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The ^{29}Si NMR spectrum of the purified sample derived from the $\text{QM}_4/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system (Table 3.1, entry 1, Figure 3.7a) shows signals corresponding to QM_2T_2 , QMT_3 , and QT_4 . The starting QM_4 was not observed. The formation of these compounds is also supported by their ^1H and ^{13}C NMR spectra (Figures 3.8 and 3.9), and high-resolution ESI-MS data (Table 3.2). The conversion ratio of TMS groups is 84%, which is calculated by Eq. (1) based on the signal intensities of M and T silicon atoms.

$$\text{Conversion (\%)} = \frac{\text{Sum of signal intensities of T silicon atoms}}{\text{Sum of signal intensities of M and T silicon atoms}} \times 100 \quad \text{Eq. (1)}$$

Table 3.1: Reaction conditions for the substitution of TMS group of QM_4 .

Entry	Temperature / °C	Time / d	Product	Conversion of TMS groups / %
1	25	1	QM_2T_2 , QMT_3 , QT_4	84
2	25	7	QM_2T_2 , QMT_3 , QT_4	84
3	60	7	QMT_3 , QT_4	98

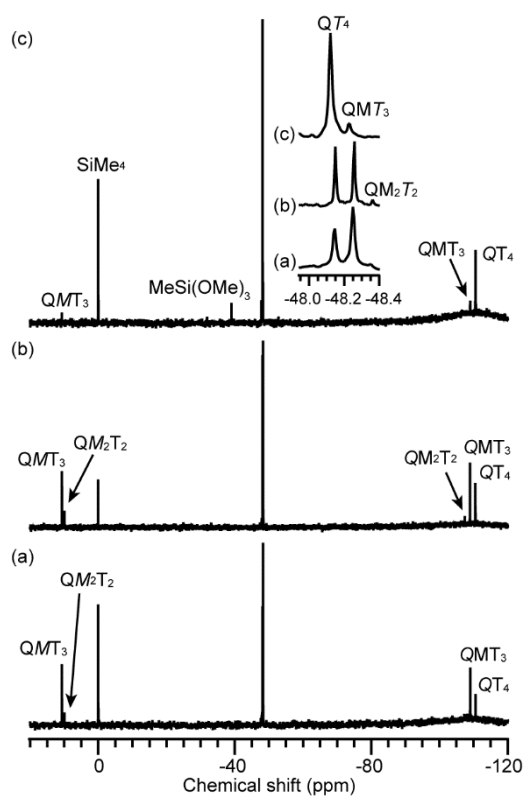


Figure 3.7. ^{29}Si NMR spectra of the obtained colorless clear liquid from the $\text{QM}_4/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system for various reaction times and temperatures. (a) entry 1, (b) entry 2, (c) entry 3.

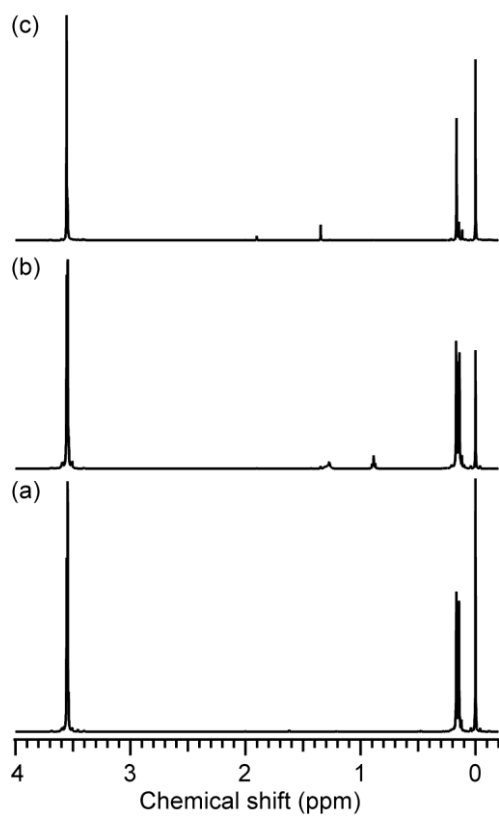


Figure 3.8. ^1H NMR spectra of the obtained colorless clear liquid from the $\text{QM}_4/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system for various reaction times and temperatures. (a) Entry 1, (b) entry 2, and (c) entry 3.

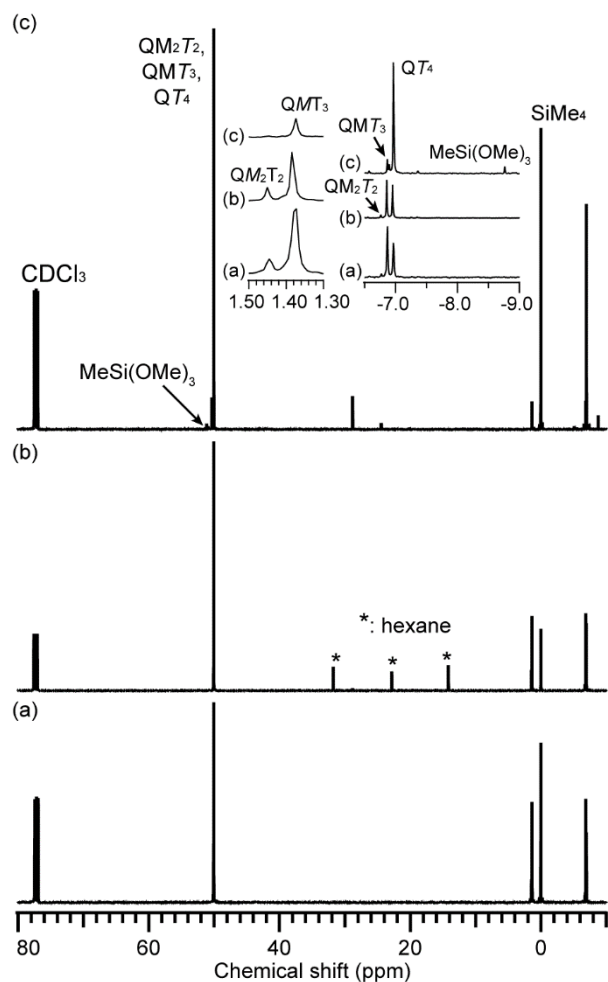


Figure 3.9. ^{13}C NMR spectra of the obtained colorless clear liquid from the $\text{QM}_4/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system for various reaction times and temperature. (a) Entry 1, (b) entry 2, and (c) entry 3.

Table 3.2: Observed fragments by the MS measurement in the $\text{QM}_4/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system.

Molecule	Calculated for $[\text{M}+\text{Na}]^+$	Found as $[\text{M}+\text{Na}]^+$
QM_2T_2	471.1149	471.1147
QMT_3	503.1047	503.1042
QT_4	535.0945	535.0940

The conversion did not change (84%) when the reaction time was increased from 1 day to 7 days (Table 3.1, entry 2, Figure 3.7b). This result can be attributed to the

equilibrium of the substitution reaction. The conversion of TMS groups was much lower (3%) without the presence of BiCl_3 under otherwise identical conditions (Figures 3.10–3.12), indicating that BiCl_3 catalyzes the substitution reaction of TMS groups.

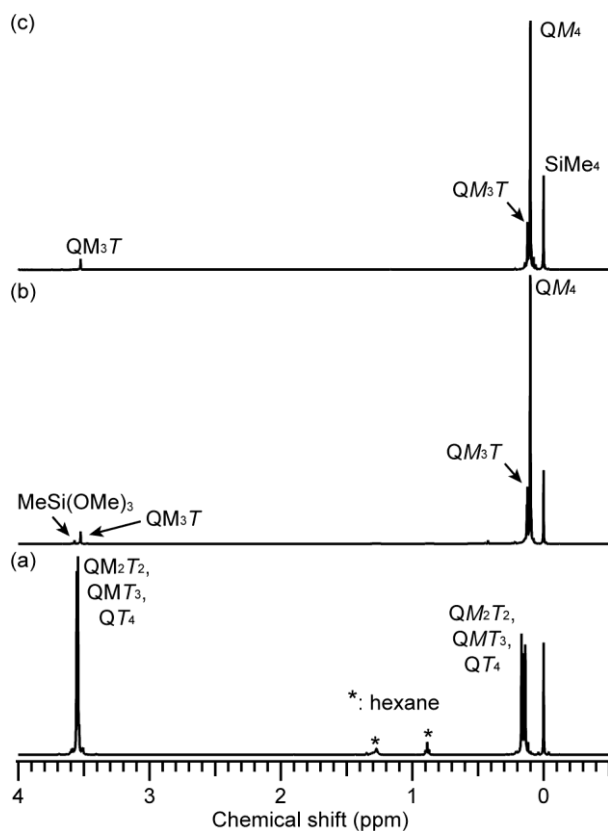


Figure 3.10. ^1H NMR spectra of the $\text{QM}_4/(\text{MeO})_2\text{MeSiCl}$ reaction system. (a) Entry 2 for comparison (with BiCl_3 at room temperature), (b) without BiCl_3 at room temperature, and (c) without BiCl_3 at $60\text{ }^\circ\text{C}$.

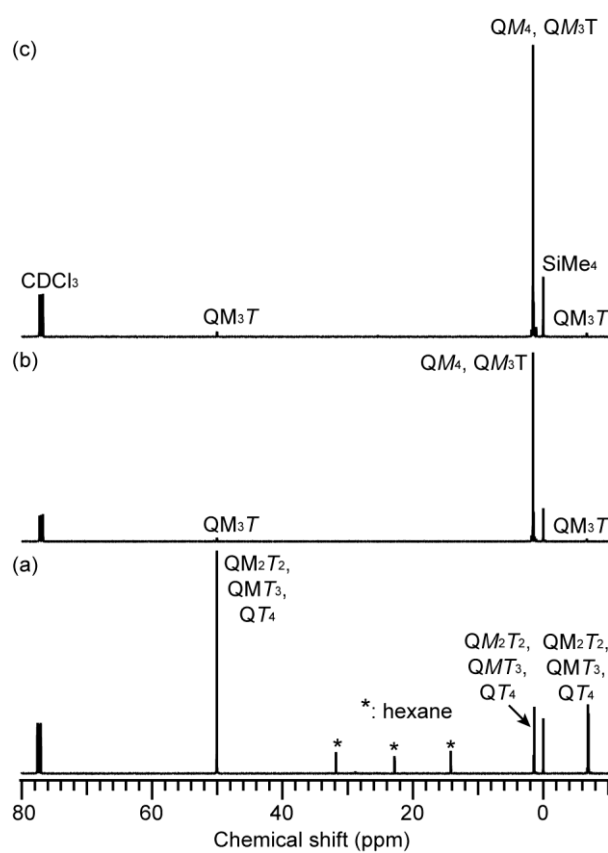


Figure 3.11. ^{13}C NMR spectra of the $\text{QM}_4/(\text{MeO})_2\text{MeSiCl}$ reaction system. (a) Entry 2 for comparison (with BiCl_3 at room temperature), (b) without BiCl_3 at room temperature, and (c) without BiCl_3 at 60°C .

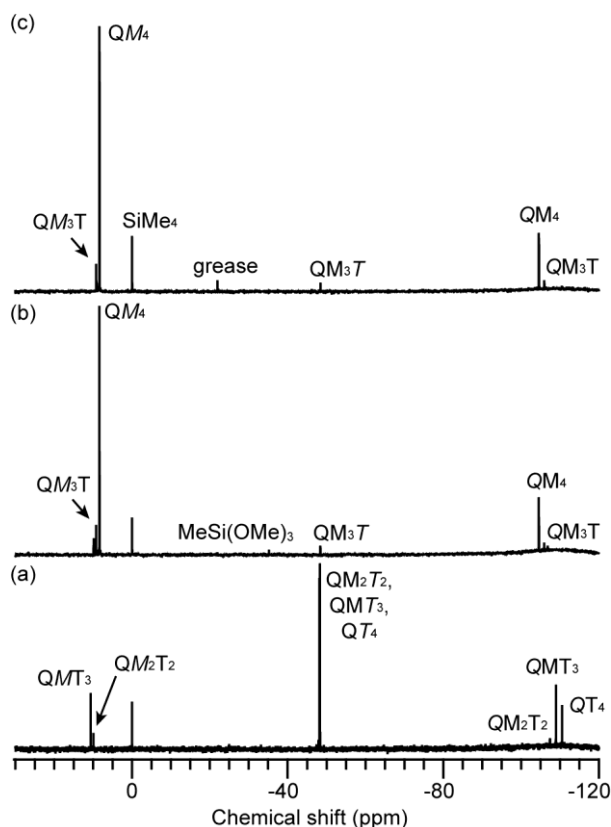


Figure 3.12. ^{29}Si NMR spectra of the $\text{QM}_4/(\text{MeO})_2\text{MeSiCl}$ reaction system. (a) Entry 2 for comparison (with BiCl_3 at room temperature), (b) without BiCl_3 at room temperature, and (c) without BiCl_3 at 60°C .

To determine whether the substitution reaction of TMS groups is an equilibrium reaction or not, the reverse reaction of the substitution of TMS group of QM_4 with $(\text{MeO})_2\text{MeSiCl}$ was conducted by reacting QT_4 , which was synthesized in a different manner (see the Experimental Section 3.2.2 (iv)), with TMCS. The ^1H , ^{13}C , and ^{29}Si NMR spectra (Figures 3.13–3.15) of the obtained mixture show signals corresponding to a large amount of unchanged QT_4 and a small amount of QMT_3 , suggesting that the reverse reaction only proceeded slightly. These results explain why some of the TMS groups were not substituted with alkoxy groups in the $\text{QM}_4/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system.

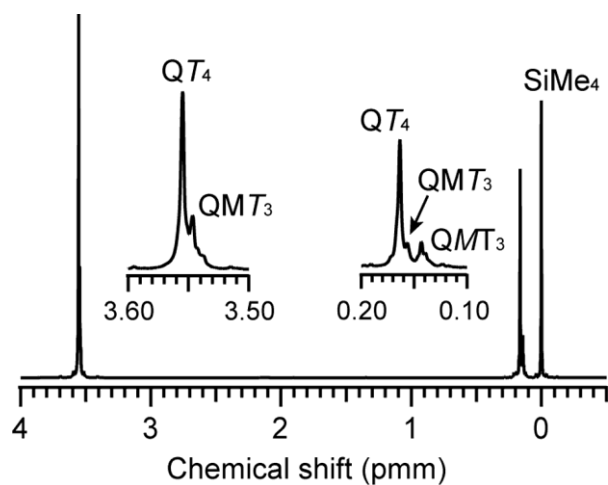


Figure 3.13. ^1H NMR spectrum of the $\text{QT}_4/\text{TMCS}/\text{BiCl}_3$ reaction system.

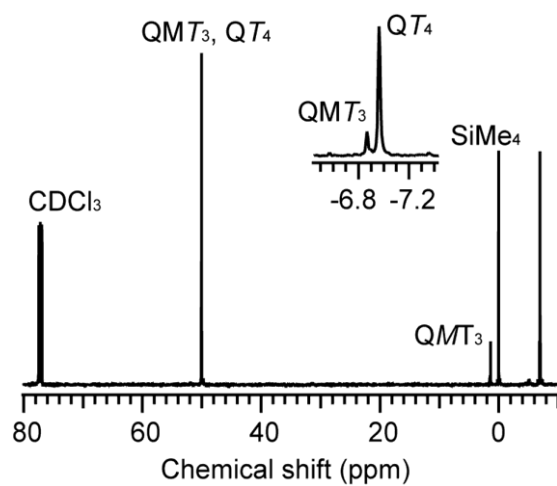


Figure 3.14. ^{13}C NMR spectrum of the $\text{QT}_4/\text{TMCS}/\text{BiCl}_3$ reaction system.

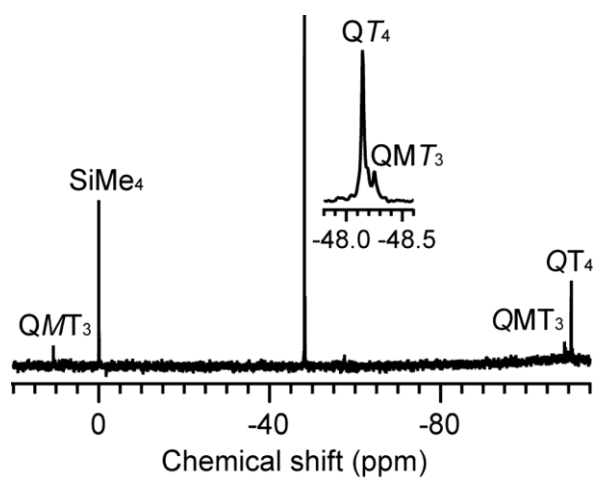


Figure 3.15. ^{29}Si NMR spectrum of the $\text{QT}_4/\text{TMCS}/\text{BiCl}_3$ reaction system.

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To improve the conversion of TMS groups, the substitution reaction was conducted at the boiling point of the byproduct (TMCS) to bias the reaction equilibrium by removing TMCS from the reaction mixture (Table 3.1, entry 3). The ^1H , ^{13}C , and ^{29}Si NMR spectra of the liquid, removed from the reaction mixture, show signals corresponding to TMCS, suggesting that it was successfully removed from the reaction mixture (Figures 3.16–3.18). The ^{29}Si NMR spectrum of the purified sample (Table 3.1, entry 3, Figure 3.7c) shows signals corresponding to QMT₃ and QT₄, whereas the signal from QM₂T₂ has disappeared. The conversion of TMS groups was 98%, indicating that the reaction equilibrium was successfully biased by removing the TMCS from the mixture.

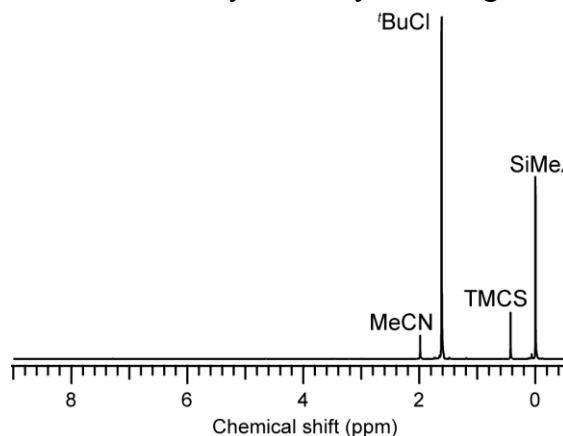


Figure 3.16. ^1H NMR spectrum of the liquid removed from the QM₄/(MeO)₂MeSiCl/BiCl₃ reaction system at 60 °C for a week (entry 3).

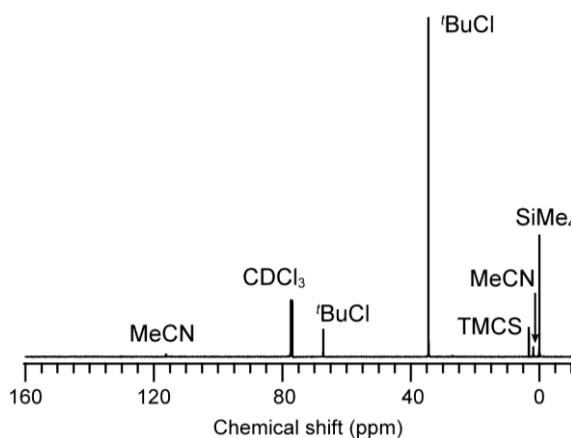


Figure 3.17. ^{13}C NMR spectrum of the liquid removed from the QM₄/(MeO)₂MeSiCl/BiCl₃ reaction system at 60 °C for one week (entry 3).

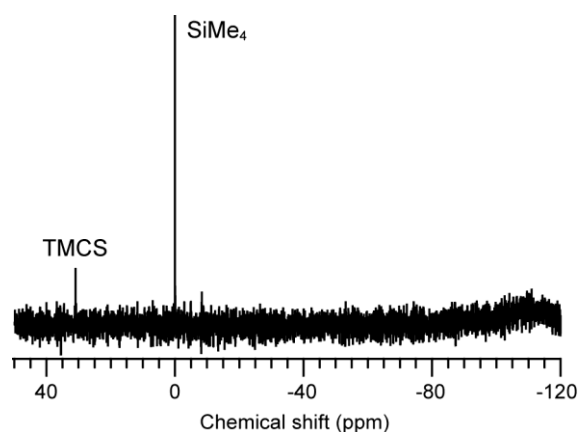


Figure 3.18. ^{29}Si NMR spectrum of the liquid removed from the $\text{QM}_4/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system at 60 °C for a week (entry 3).

3.3.2 Investigation of substrate tolerance

The substrate versatility of the substitution reaction of TMS groups was investigated by using Q_2M_6 and Q_8M_8 . Q_2M_6 and Q_8M_8 were reacted with $(\text{MeO})_2\text{MeSiCl}$ in the presence of BiCl_3 at 60 °C for a week. In both cases, although the substitution reaction proceeded, TMS groups partially remained, as determined by NMR and MS spectroscopies (Q_2M_6 : Figures 3.19–3.21 and Table 3.3; Q_8M_8 : Figures 3.22–3.24 and Table 3.4). The conversions of TMS groups for Q_2M_6 and Q_8M_8 were 34% and 39%, respectively, and were not improved by increasing the reaction time. Such conversions may be caused by the increase in the steric hindrance around the oxygen atoms linked to the TMS groups as the substitution reaction proceeds, as described later in the reaction mechanism section. These results suggest that the substrate tolerance of the substitution reaction of TMS groups is limited.

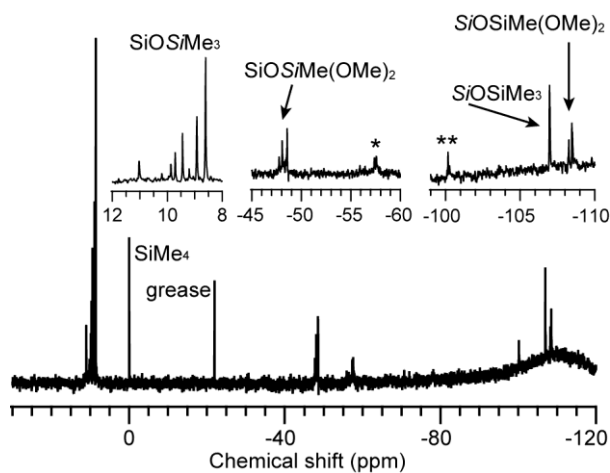


Figure 3.19. ^{29}Si NMR spectrum of the $\text{Q}_2\text{M}_6/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system. *: polymerized compounds in the reaction products. **: intramolecular polymerized compounds via functional group exchange reaction (The details are shown in Scheme S1).

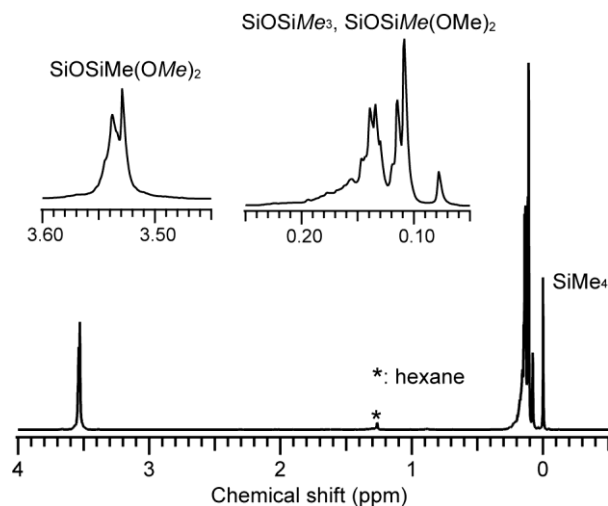


Figure 3.20. ^1H NMR spectrum of the $\text{Q}_2\text{M}_6/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system.

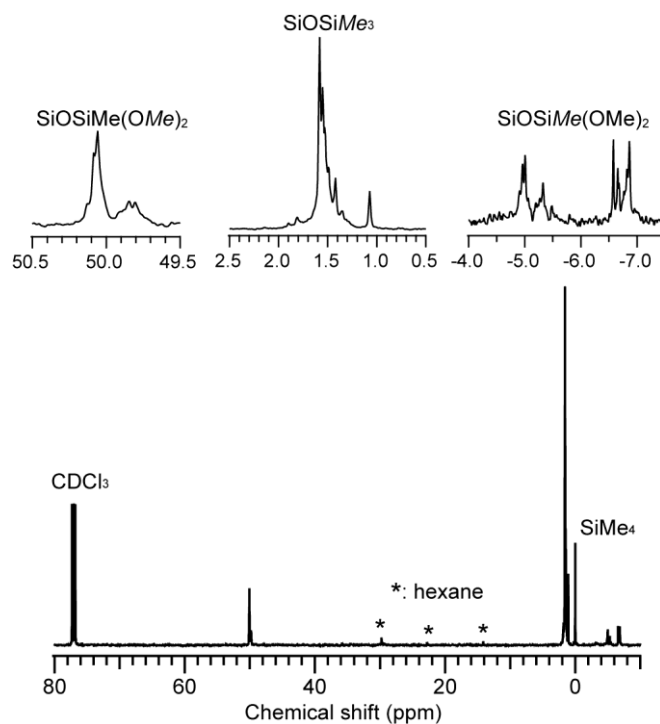
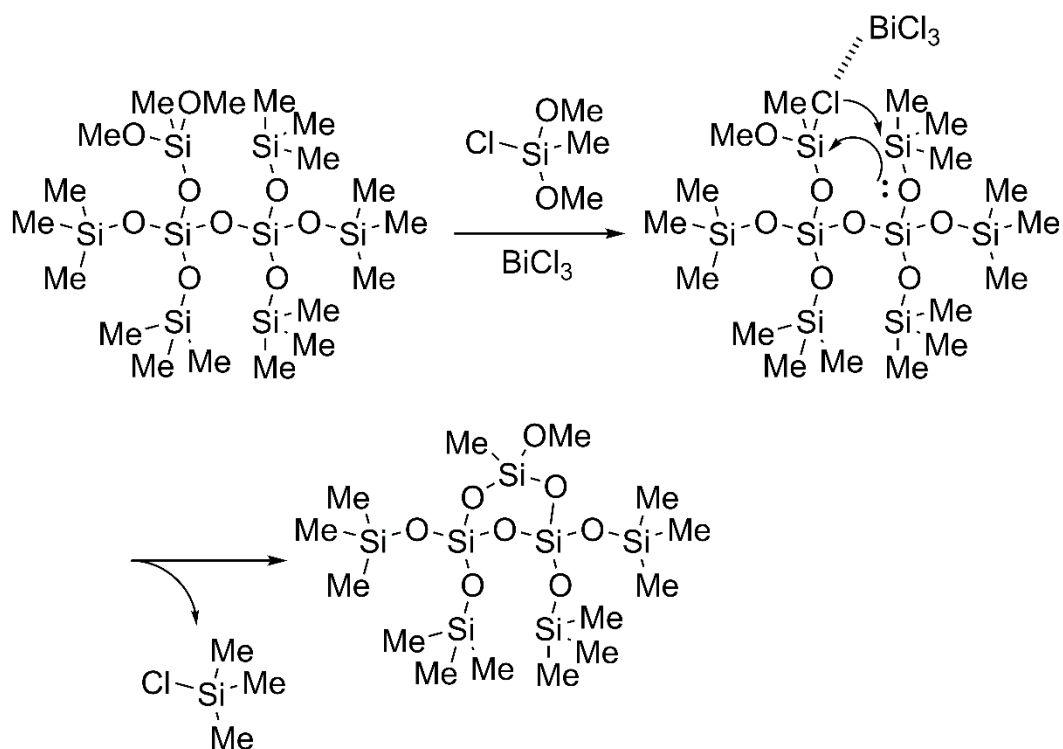


Figure 3.21. ^{13}C NMR spectrum of the $\text{Q}_2\text{M}_6/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system.

Table 3.3: Observed fragments by the MS measurement in the $\text{Q}_2\text{M}_6/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system.

Molecule	Calculated for $[\text{M}+\text{Na}]^+$	Found as $[\text{M}+\text{Na}]^+$
$\text{Q}_2\text{M}_5\text{T}_1$	661.1	661.1
$\text{Q}_2\text{M}_4\text{T}_2$	693.1	693.1
$\text{Q}_2\text{M}_3\text{T}_3$	725.1	725.1
$\text{Q}_2\text{M}_2\text{T}_4$	757.1	757.1
$\text{Q}_2\text{M}_1\text{T}_5$	789.1	789.1



Scheme 3.4. Reaction scheme for the formation of the supposed byproduct assigned to the signal at -100.0 ppm in Figure 3.19.

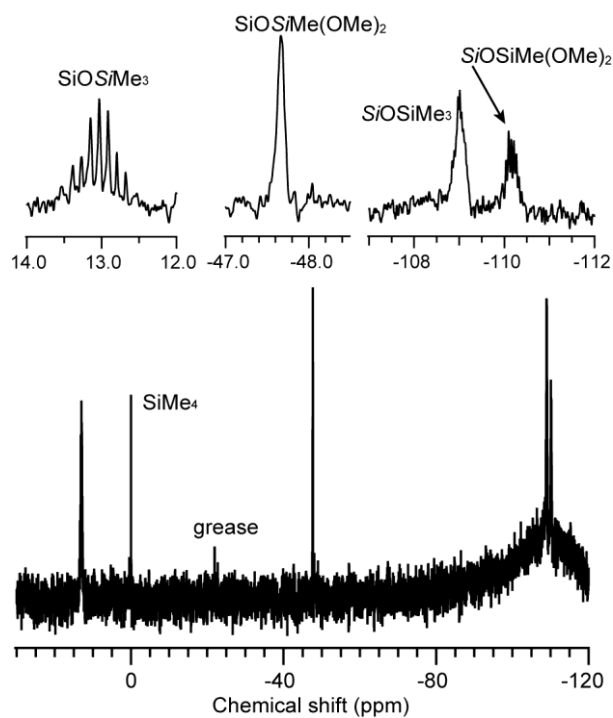


Figure 3.22. ^{29}Si NMR spectrum of the $\text{Q}_8\text{M}_8/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system.

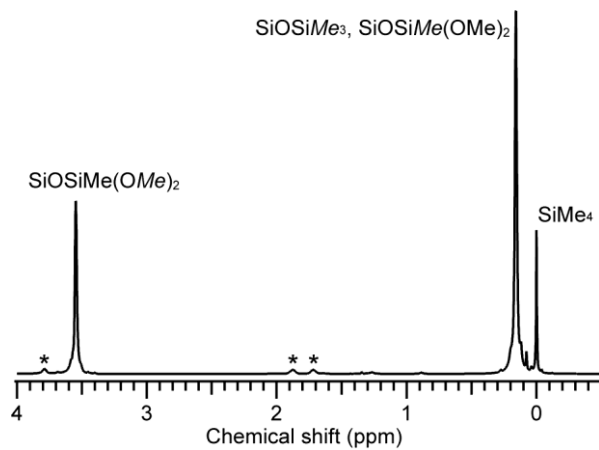


Figure 3.23. ^1H NMR spectrum of the $\text{Q}_8\text{M}_8/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system.
*Polymerized compounds of THF.

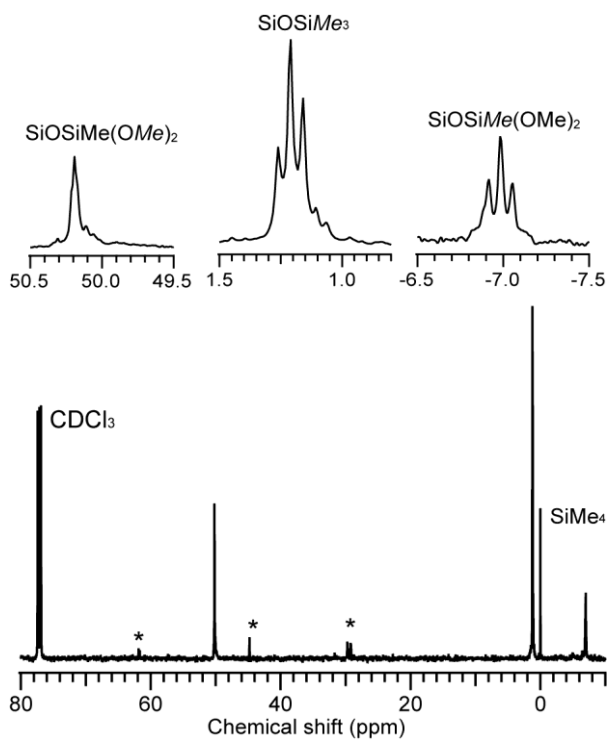
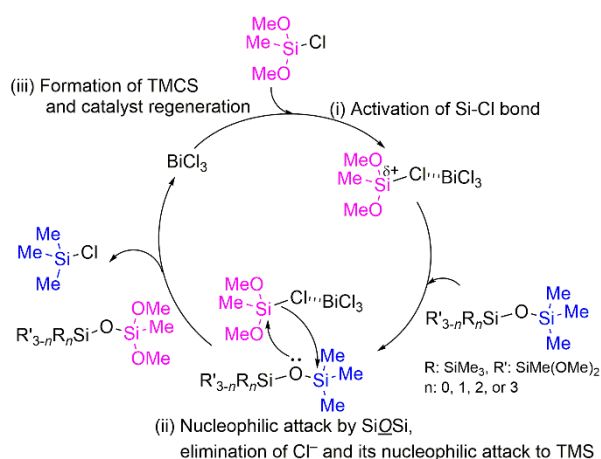


Figure 3.24. ^{13}C NMR spectrum of the $\text{Q}_8\text{M}_8/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system.
*Polymerized compounds of THF.

Table 3.4: Observed fragments by the MS measurement in the $Q_8M_8/(MeO)_2MeSiCl/BiCl_3$ reaction system.

Molecule	Calculated for $[M+Na]^+$	Found as $[M+Na]^+$
$Q_8M_7T_1$	1183.1	1183.1
$Q_8M_3T_5$	1311.0	1311.1
$Q_8M_2T_6$	1345.0	1345.1
$Q_8M_1T_7$	1375.0	1375.0

The proposed reaction mechanism of the substitution reaction of TMS groups with alkoxysilyl groups is shown in Scheme 3.5, in which the $QM_4/(MeO)_2MeSiCl/BiCl_3$ reaction system is used as a model case. This mechanism is based on previous mechanistic studies of Lewis acid-catalyzed siloxane-bond-formation reactions between SiOR (R = Me or Et) and SiX (X = Cl or Br).^{25, 26} This reaction mechanism consists of the following three steps: (i) the Si–Cl bond of the alkoxychlorosilane is activated by $BiCl_3$; (ii) an oxygen atom of QM_4 attacks the silicon atom of the alkoxychlorosilane and a chloride ion is eliminated to attack the silicon atom of a trimethylsilyl group; (iii) TMCS is formed and eliminated, and $BiCl_3$ is regenerated.

**Scheme 3.5.** Proposed reaction mechanism of the substitution reaction of TMS groups with alkoxysilyl groups.

In the cases of Q_2M_6 and Q_8M_8 as starting materials, the oxygen atoms that are not linked to TMS groups (Si_Q-O-Si_Q), were not involved in the reaction, as suggested by the lack of signals in the NMR and MS spectra corresponding to the molecules formed by cleaving the Si_Q-O-Si_Q bonds. The oxygen atoms of Si_Q-O-Si_Q bonds are more sterically hindered and more electron poor than those of $Si_Q-O-Si_M(TMS)$ bonds; therefore, the oxygen atoms in Si_Q-O-Si_Q bonds are less capable of nucleophilic attack.

The relatively low reactivities of Q_2M_6 and Q_8M_8 in the substitution reactions may be due to the steric hindrance around the oxygen atoms linked directly to TMS groups, which reduces their ability to attack the alkoxychlorosilane nucleophilically. In fact, when MD₂M, a compound with decreased steric hindrance than Q_2M_6 , was used as a starting material, the conversion of TMS groups was 100% based on the ^{29}Si NMR spectrum (Figure 3.25). However, the reaction products were partially polymerized (details are shown below.).

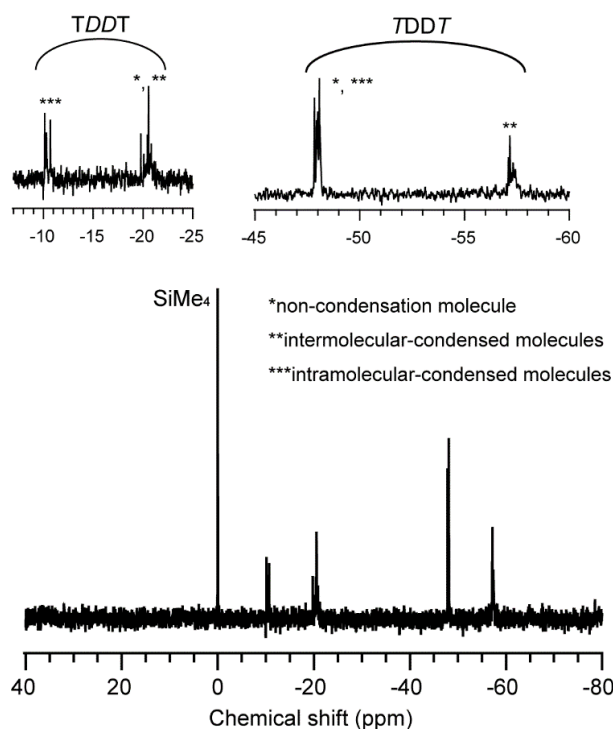


Figure 3.25. ^{29}Si NMR spectrum of the MD₂M/(MeO)₂MeSiCl/BiCl₃ reaction system.

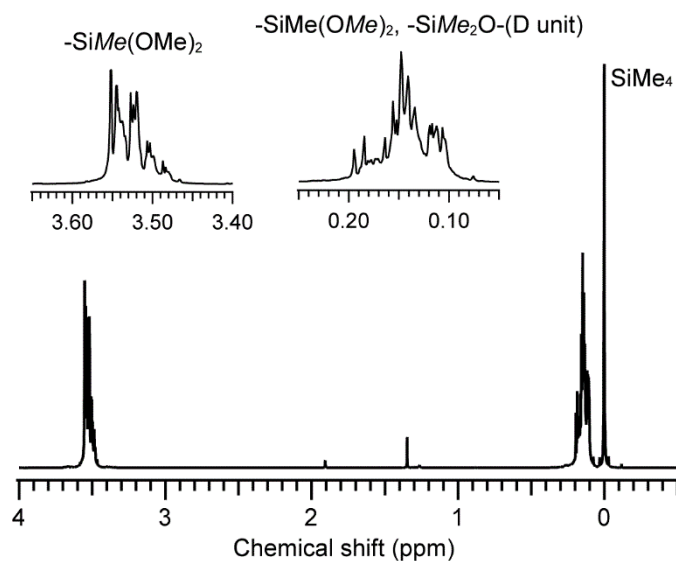


Figure 3.26. ^1H NMR spectrum of the $\text{MD}_2\text{M}/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system.

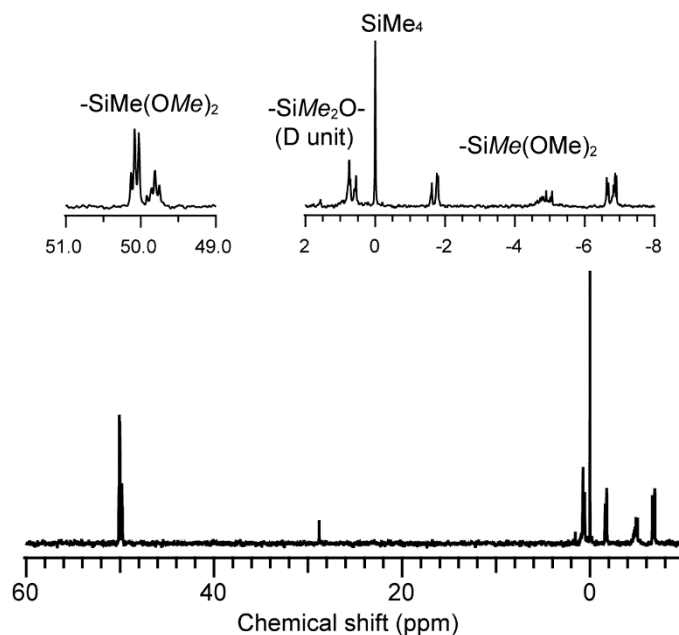


Figure 3.27. ^{13}C NMR spectrum of the $\text{MD}_2\text{M}/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system.

To investigate the effects of the electron density, the TMS groups of $\text{T}^{\text{Ph}}\text{M}_3$ were substituted with dimethoxy(methyl)silyl groups. The Si atom linked to TMS groups of $\text{T}^{\text{Ph}}\text{M}_3$ is more electron rich than those of QM_4 and Q_2M_6 . The conversion of TMS groups

of $T^{\text{Ph}}M_3$ was higher (100%) than those of QM_4 and Q_2M_6 , based on the ^{29}Si NMR spectrum (Figure 3.28). This finding suggests that the nucleophilic attack of the oxygen atoms linked to TMS groups is the key step of the substitution.

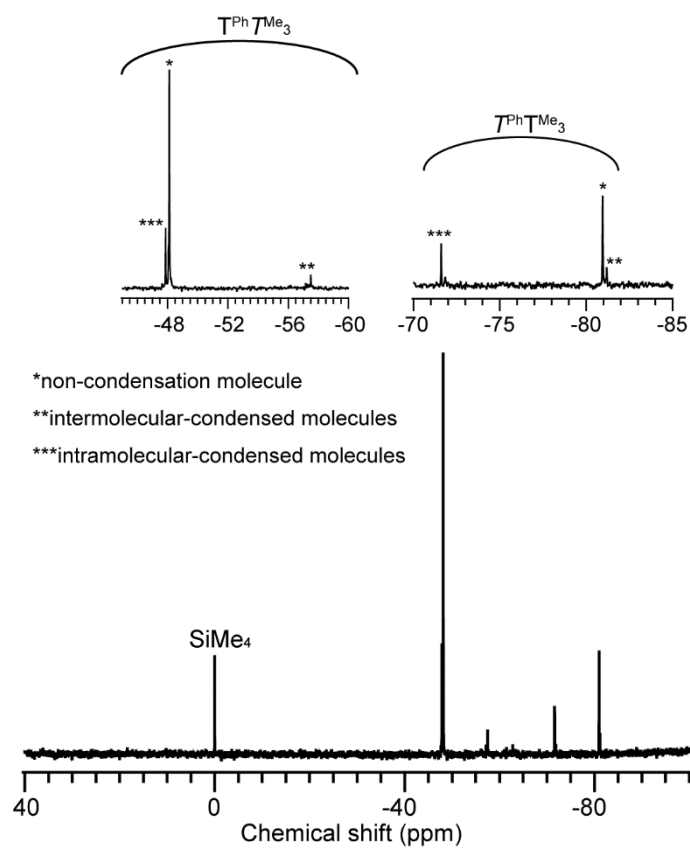


Figure 3.28. ^{29}Si NMR spectrum of the $T^{\text{Ph}}M_3/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system.

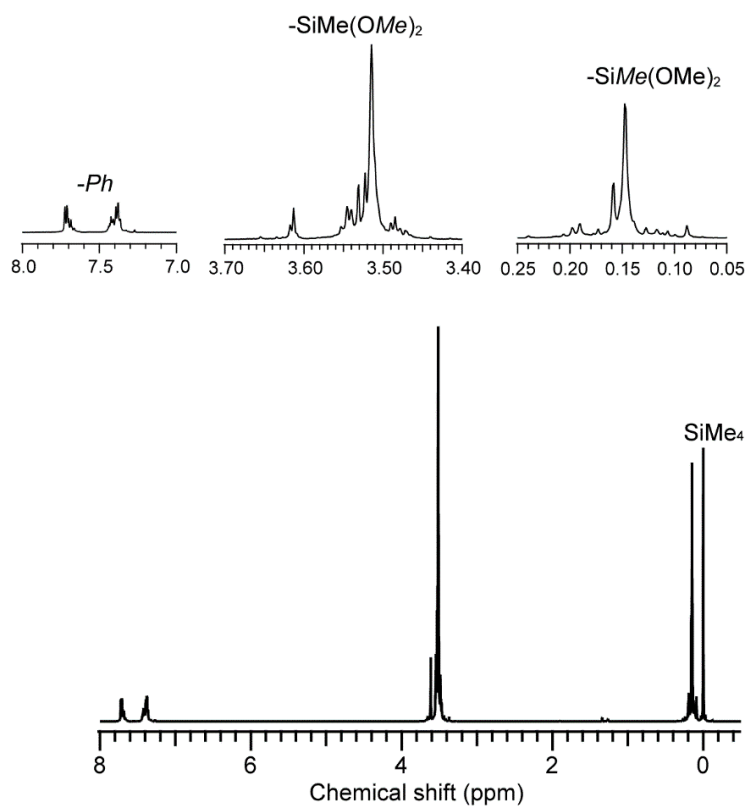


Figure 3.29. ^1H NMR spectrum of the $\text{T}^{\text{Ph}}\text{M}_3/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system.

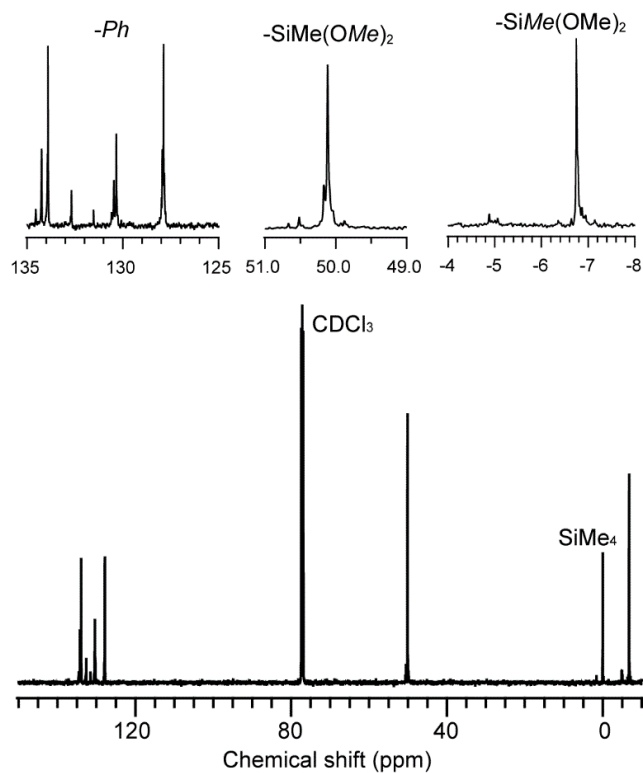
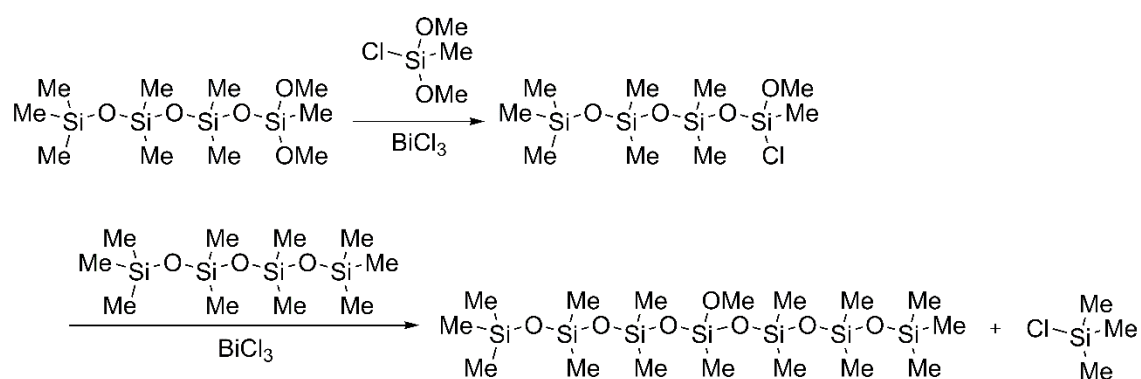


Figure 3.30. ^{13}C NMR spectrum of the $\text{T}^{\text{Ph}}\text{M}_3/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system.

The conversions of TMS groups of MD₂M and T^{Ph}M₃ were high, however, partial polymerization of the reaction products was confirmed by NMR spectroscopy (Figures 3.25–3.27 and 3.28–3.30, respectively). Partial polymerization could not be confirmed for QM₄. This polymerization may be caused by a functional-group-exchange reaction between the incoming -SiMe(OMe)₂ and -SiCl groups of dimethoxy(methyl)chlorosilane, and the subsequent substitution reaction of TMS groups (Scheme 3.6). Alkoxy groups linked to electron-rich Si atoms are more easily exchanged with chloro groups than those linked to electron-poor Si atoms;²⁶ therefore, polymerized compounds were formed in the reactions of MD₂M and T^{Ph}M₃. Despite the low stability of the reaction products in the cases of MD₂M and T^{Ph}M₃, the concept of this study, that is the substitution of TMS groups with alkoxy groups, was demonstrated.



Scheme 3.6. Reaction scheme for the formation of the polymerized product in the MD₂M and T^{Ph}M₃ reaction system (MD₂M is used as a model).

3.3.3 Utilization of TMS group as a protecting group

The leaving group ability of TMS groups linked to -OSi was confirmed as mentioned above, therefore, the synthesis of alkoxy siloxane oligomers was conducted with TMS groups as protecting and leaving groups. As shown in Scheme 3.3, tris(trimethylsiloxy)silanol (QM₃) was chosen as a starting material because it can be

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considered as the protected compound of $\text{Si}(\text{OH})_4$ with three TMS groups. Firstly, the remaining silanol group of QM_3 was alkoxy-silylated with chlorodimethoxy(vinyl)silane to obtain $\text{QM}_3\text{T}^{\text{Vinyl}}$. Then, the TMS groups of $\text{QM}_3\text{T}^{\text{Vinyl}}$ were substituted with dimethoxy(methyl)silyl groups while retaining the vinyl dimethoxysilyl group. The formations of the target compound and the molecule with one remaining TMS group were confirmed by ^{29}Si NMR spectroscopy (Figure 3.31). These results were also supported by ^1H , ^{13}C NMR (Figures 3.32 and 3.33), and MS analysis. The reason for this selective substitution of TMS groups can be explained by lower nucleophilicity of $-\text{OSi}(\text{CH}=\text{CH}_2)(\text{MeO})_2$ group than that of TMS group at the second stage in Scheme 3.5. The conversion of TMS groups was calculated to be 97% and the synthesis of the target compound was achieved in high yield (94%); therefore, TMS groups can be used as protecting and leaving groups for the synthesis of siloxane-based molecules. Although the substrate scope of the reaction for oligosiloxanes composed of SiO_4 units is still limited, because the conversion ratio depends on the structure of the starting trimethylsilylated silicates, the concept of utilizing protecting groups has been achieved by using this reaction. This approach is a novel synthetic strategy for the synthesis of alkoxy-siloxane oligomers by using designed precursors for siloxane-based materials.

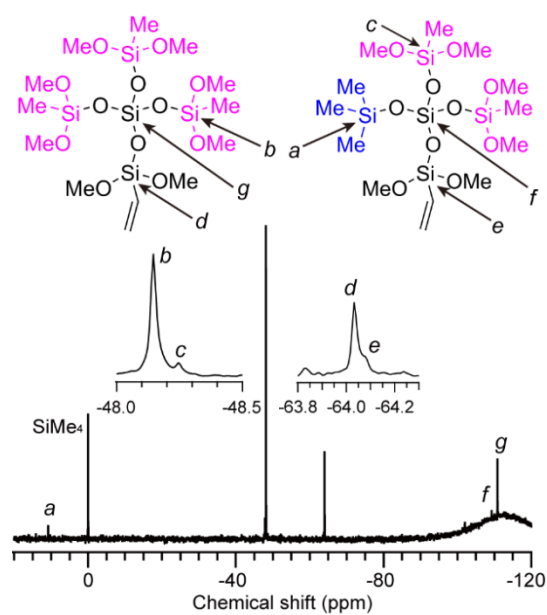


Figure 3.31. ^{29}Si NMR spectrum of the $\text{QM}_3\text{T}^{\text{vinyl}}/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system.

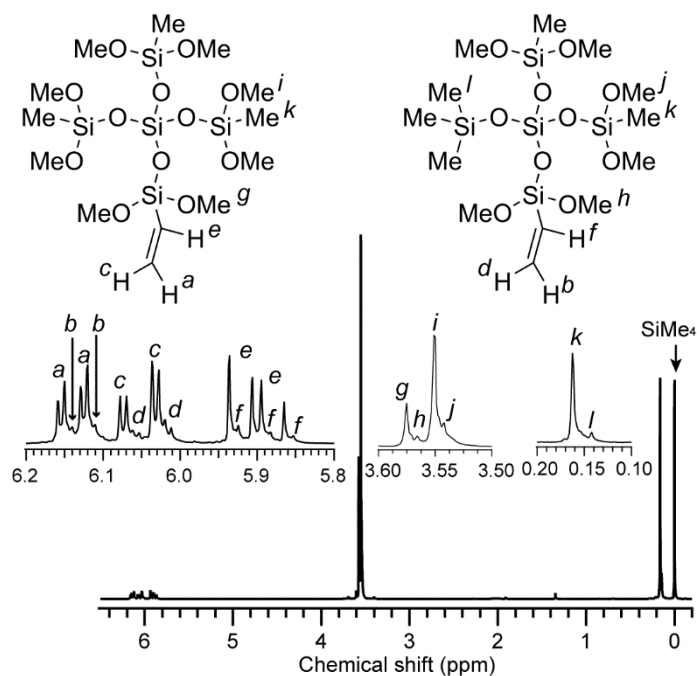


Figure 3.32. ^1H NMR spectrum of the $\text{QM}_3\text{T}^{\text{vinyl}}/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system.

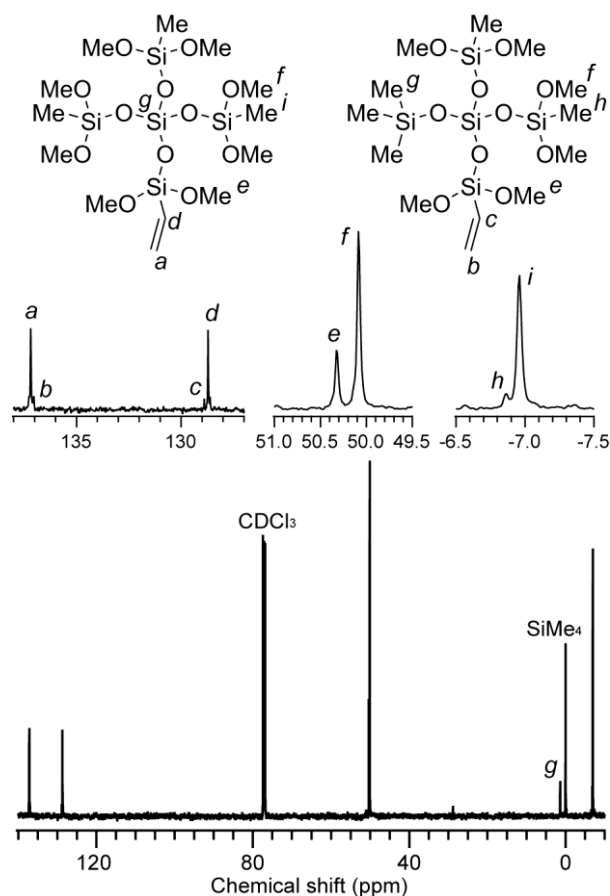


Figure 3.33. ^{13}C NMR spectrum of the $\text{QM}_3\text{T}^{\text{vinyl}}/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system.

3.3.4 Comparison with substitution reaction of $t\text{Bu}$ groups as a leaving group

The substitution reaction of TMS groups is similar to the alkoxylation of *tert*-butoxysilane with alkoxychlorosilane.^{15, 16} Leaving groups are substituted with alkoxy silyl groups in both reactions. The difference in conversion for these two reactions was investigated by reacting $(\text{MeO})_2\text{MeSiCl}$ with QM_4 or $\text{Si}(\text{O}^t\text{Bu})_4$ under the same conditions (room temperature for one day). The ^1H , ^{13}C , and ^{29}Si NMR spectra show that all the $t\text{Bu}$ groups are substituted with dimethoxy(methyl)silyl groups (Figures 3.34–3.36). However, some TMS groups remained after the substitution reaction as mentioned above. This difference is due to the fact that the substitution of TMS groups progresses in a reversible manner. In the case of $t\text{Bu}$ groups, the reverse reaction does not occur because

the tertiary carbon atom of $t\text{BuCl}$ (byproduct of the reaction) is not reactive under substitution conditions owing to steric hindrance. In this sense, $t\text{Bu}$ group has an advantage over TMS group in terms of conversions; however, there are a couple of concerns regarding the use of $t\text{BuO}$ groups. Functional-group exchange between $t\text{BuO}$ and chloro groups in starting materials unavoidably occurs, lowering the yields of target molecules. As mentioned in the introduction, trimethylsilylated oligosiloxanes are rich in diversity. These compounds can be used as building blocks for siloxane-based materials by the introduction of alkoxyethyl groups by using the reaction developed herein. Therefore, this synthetic method could become a fruitful methodology for the synthesis of siloxane compounds and siloxane-based materials derived from those compounds.

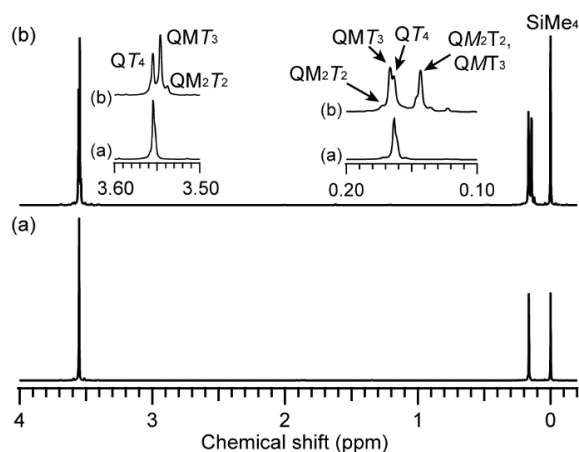


Figure 3.34. ^1H NMR spectra of the $\text{Si}(\text{OR})_4/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system. (a) $\text{R} = t\text{Bu}$ and (b) $\text{R} = \text{TMS}$ (entry 1).

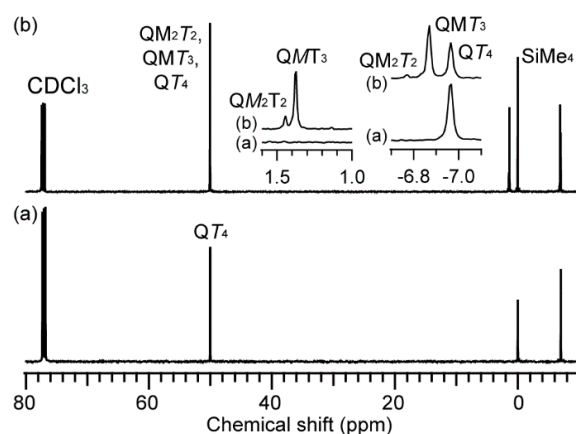


Figure 3.35. ^{13}C NMR spectra of the $\text{Si}(\text{OR})_4/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system. (a) $\text{R} = \text{}^t\text{Bu}$ and (b) $\text{R} = \text{TMS}$ (entry 1).

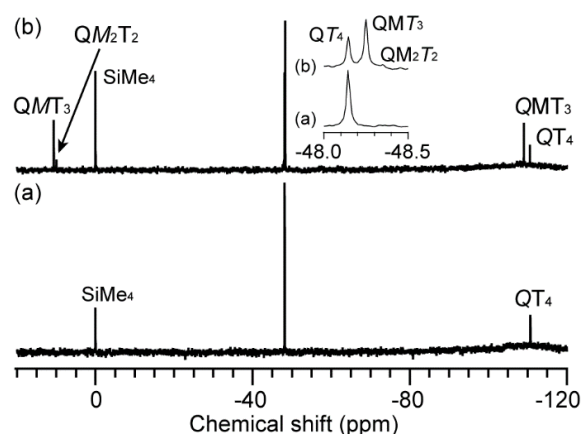


Figure 3.36. ^{29}Si NMR spectra of the $\text{Si}(\text{OR})_4/(\text{MeO})_2\text{MeSiCl}/\text{BiCl}_3$ reaction system. (a) $\text{R} = \text{}^t\text{Bu}$ and (b) $\text{R} = \text{TMS}$ (entry 1).

3.4 Conclusions

In conclusion, the leaving-group ability of TMS groups in oligosiloxanes was confirmed by the reaction of several oligosiloxanes possessing TMS groups with alkoxychlorosilane in the presence of BiCl_3 as catalyst. The TMS groups of oligosiloxanes were substituted with alkoxy-silyl groups, and alkoxy-siloxane oligomers were successfully synthesized. Trimethylsilyl-terminated oligosiloxanes can be synthesized from natural and synthetic silicates, and their siloxane structures are rich in diversity (linear, branched, cyclic, and cubic). The expansion of the substrate scope of

this reaction in future studies will lead to a novel synthetic method for alkoxy siloxane oligomers. The present work demonstrates that the concept of protecting groups in synthetic organic chemistry is applicable to siloxane-based molecules. Further studies on the viability of this reaction will contribute to the precise synthesis of siloxane-based molecules.

3.5 Note and References

† Symbols Q^n , T^n , D^n , and M^n denote the bonding state of Si atoms; Q^n : $Si(OSi)_n(OH, OR, \text{ or } O^-)_{4-n}$ ($n = 0, 1, 2, 3, \text{ or } 4$), T^n : $R'Si(OSi)_n(OH, OR, \text{ or } O^-)_{3-n}$ ($n = 0, 1, 2, \text{ or } 3$), D^n : $R'_2Si(OSi)_n(OH, OR, \text{ or } O^-)_{2-n}$ ($n = 0, 1, \text{ or } 2$), and M^n : $R'_3Si(OSi)_n(OH, OR, \text{ or } O^-)_{1-n}$ ($n = 0 \text{ or } 1$). In addition, the superscripts of these symbols, such as T^{Me} and T^{Ph} , denote the functional groups linked to the Si atoms (R') in this chapter.

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Chapter 4

Synthesis of a Cyclododecasiloxane Possessing Alkoxysilyl Groups as a Nanobuilding Block and Its Use for Preparation of Gas Permeable Membranes

Adapted from Masashi Yoshikawa, Hiroya Shiba, Masakoto Kanezashi, Hiroaki Wada, Atsushi Shimojima, Toshinori Tsuru, and Kazuyuki Kuroda, “Synthesis of a 12-membered cyclic siloxane possessing alkoxysilyl groups as a nanobuilding block and its use for preparation of gas permeable membranes”, *RSC Adv.* **2017**, *7*, 48683 with permission from The Royal Society of Chemistry.

4.1 Introduction

Siloxane-based porous materials have been used in practical applications, such as catalysis, separation, and adsorption,^{1,2} because of their thermal and chemical stability and high compatibility with other materials (such as polymers, metals, and metal oxides) for composite formation. The properties of such materials depend on the structure of the siloxane network; therefore, the structural control at a molecular level is important.

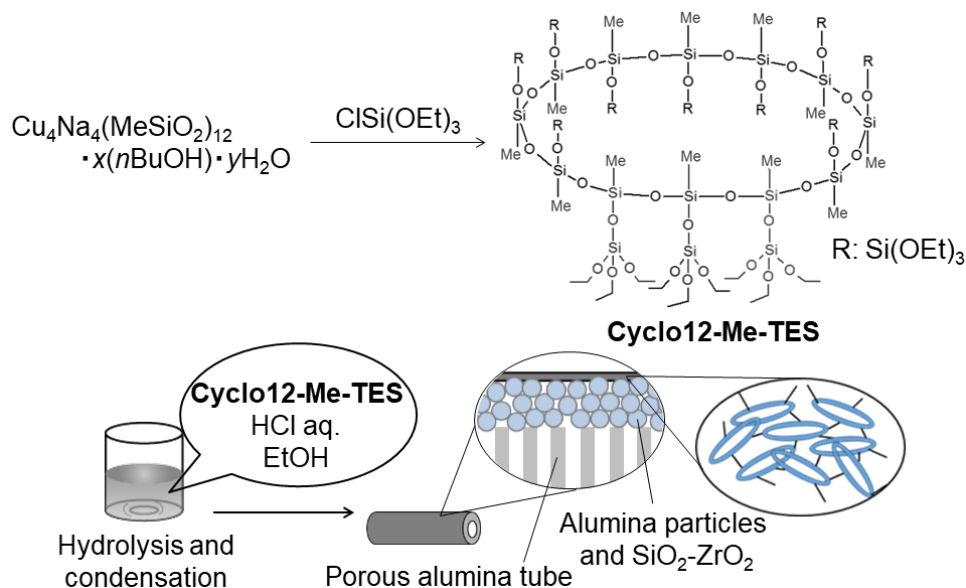
The use of nanobuilding blocks with defined oligosiloxane structures is quite effective for controlling siloxane networks at the molecular level.³ This pathway provides unique materials that cannot be obtained from monomeric silicon compounds. Branched, cyclic, and cage-type oligosiloxanes have been synthesized and used as nanobuilding blocks for various siloxane-based nanomaterials.^{4,5} Among them, cyclic siloxanes are expected to act as nanobuilding blocks possessing inclusion properties similar to cyclic organic compounds such as cyclodextrins and crown ethers.⁶ Actually, inclusion compounds composed of cyclic penta-, hexa-, and hepta-siloxanes and metal ions have been reported,⁷⁻⁹ which indicates that the cavity within cyclic siloxanes is accessible to some guest species. The inner spaces provided by larger cyclic siloxanes are expected to show unique host-guest interactions with various molecular species. In contrast to many reports concerning the use of organic host compounds (carbon based), the effective utilization of the cavity of cyclic siloxanes remains largely unexplored.

There have been many reports concerning the synthesis of cyclic siloxanes with various ring sizes. In this study, the author has chosen a cyclododecasiloxane as a nanobuilding block. The inside diameter of the cyclododecasiloxane is roughly estimated to be *ca.* 0.9 nm when the ring structure is fully extended and planar,[‡] and the ring is larger than that of a benzene ring. The cyclododecasiloxanes are easily obtained as complexes with metal cations by the hydrolysis and condensation of

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organotrialkoxysilanes in the presence of alkali metal hydroxide and transition metal cations.^{10,11} Despite the attractiveness of cyclic siloxanes, cyclododecasiloxanes have rarely been used as nanobuilding blocks for the formation of siloxane-based materials to the best of my knowledge. Shchegolikhina *et al.*^{12,13} reported the preparation of layered compounds by the solid-phase condensation of cyclododecasiloxanes possessing both hydroxy and phenyl groups. Zheng *et al.* prepared a porous polymer by the hydrosilylation polymerization of a cyclododecasiloxane possessing both vinyl and hydrosilyl groups.¹⁴ Zheng *et al.* also reported a polymer by thiol-ene polymerization of a cyclododecasiloxane possessing both vinyl and thiol groups.¹⁵ Unfortunately, these reports did not clarify the retention of the cyclic siloxane structures in the products.

This chapter describes the synthesis of a cyclododecasiloxane with alkoxyethyl groups as side groups as a new nanobuilding block by alkoxyethylation of the complex between cyclododecasiloxane and metal cations (Scheme 4.1). Hereafter, the obtained compound is referred to as **Cyclo12-Me-TES** (based on Cyclododecasiloxane possesses Methyl groups and TriEthoxySilyloxy (TES) groups as side groups). The hydrolysis and polycondensation processes of this compound were studied in detail by NMR spectroscopies to confirm that the ring structure was retained after the reaction. Furthermore, the cyclic siloxane was hydrolyzed and polycondensed onto a porous alumina tube to prepare composite membranes, and the membrane gas permeation properties were investigated to discuss the usefulness of the cyclic siloxane as a nanobuilding block.



Scheme 4.1. Synthesis of the cyclic siloxane with alkoxyethyl groups and the membrane preparation.

4.2 Experimental

4.2.1 Materials

1-Butanol (> 99.0%), chloroform (> 99.0%), deuterated ethanol (EtOH-*d*₆ > 99.5%), ethanol (dehydrated > 99.5%), hydrochloric acid (6 mol/L HCl aq.), sodium hydroxide (NaOH > 97.0%), toluene (dehydrated > 99.5%), and pyridine (dehydrated > 99.5%) were purchased from Wako Pure Chemical Industries, Ltd. and used as received. Chlorotrimethylsilane (> 98.0%), tetrachlorosilane (SiCl₄ > 98.0%), tetraethoxysilane (TEOS > 96.0%), triethoxymethylsilane (MTES > 98.0%), and zirconium tetrabutoxide (80% ZrBT in 1-butanol) were purchased from Tokyo Chemical Industry Co., Ltd. and used as received. Copper(II) chloride (CuCl₂ > 97 %) was purchased from Sigma-Aldrich Co., LLC. and used as received. The α-alumina powders were purchased from Sumitomo Chemical Co., Ltd. The SiO₂-ZrO₂ sol was obtained by hydrolysis and condensation of tetraethoxysilane and zirconium tetrabutoxide. The detailed sol preparation procedure has

been described previously.^{16,17} Porous α -alumina tubes (HU-A01, average pore size: 2.1 μm , outside diameter: 10 mm) were kindly supplied by the NIKKATO CORPORATION.

4.2.2 Synthesis of $\text{Cu}_4\text{Na}_4(\text{MeSiO}_2)_{12}\cdot x(n\text{BuOH})\cdot y\text{H}_2\text{O}$

$\text{Cu}_4\text{Na}_4(\text{MeSiO}_2)_{12}\cdot x(n\text{BuOH})\cdot y\text{H}_2\text{O}$ was synthesized according to the literature reported by Shchegolikhina *et al.*¹⁸ 1-Butanol (80 mL), NaOH (2.01 g, 50.2 mmol), and water (2.72 mL, 150.9 mmol) were mixed in a three-neck flask equipped with a reflux condenser. After stirring the mixture for 30 min at room temperature, a solution of MTES (10 mL, 50.3 mmol) in 20 mL of 1-butanol was added to the mixture with vigorous stirring. Then, 7.24 mL of water was added to the mixture, and it was heated to reflux. A solution of CuCl_2 (2.24 g, 16.7 mmol) in 60 mL of 1-butanol was added dropwise over ca. 20 min, and the mixture was refluxed for an additional 30 min. The hot solution was filtered to remove precipitates, and the filtrate was cooled to room temperature. The filtrate was evaporated in a rotary evaporator, and then the residue was dried *in vacuo* at 90 °C. A blue powder ($\text{Cu}_4\text{Na}_4(\text{MeSiO}_2)_{12}\cdot x(n\text{BuOH})\cdot y\text{H}_2\text{O}$) was obtained. The X-ray diffraction (XRD) pattern of the obtained blue powder was not consistent with that of $\text{Cu}_4\text{Na}_4(\text{MeSiO}_2)_{12}\cdot x(n\text{BuOH})\cdot y\text{H}_2\text{O}$ reported by Shchegolikhina *et al.*¹⁸ (Figure 4.1), probably because of the difference in the number of solvated molecules (1-butanol and/or H_2O). To confirm the formation of the cyclododecasiloxane structure, the product was silylated with chlorotrimethylsilane (detailed method and characterization are shown in next paragraph). The ^1H , ^{13}C , and ^{29}Si NMR and MS data of the trimethylsilylated compound coincided with those of the reported compound;¹⁸ therefore, the author concluded that the blue powder synthesized here possessed the cyclododecasiloxane structure.

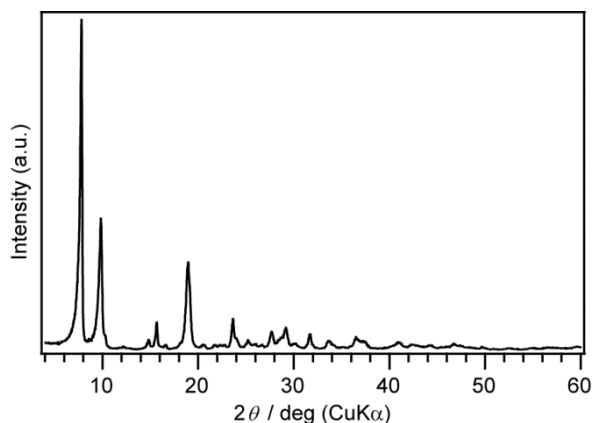


Figure 4.1. Powder XRD pattern of $\text{Cu}_4\text{Na}_4(\text{MeSiO}_2)_{12} \cdot x(n\text{BuOH}) \cdot y\text{H}_2\text{O}$.

4.2.3 Experimental procedure for trimethylsilylation of $\text{Cu}_4\text{Na}_4(\text{MeSiO}_2)_{12} \cdot x(n\text{BuOH}) \cdot y\text{H}_2\text{O}$

$\text{Cu}_4\text{Na}_4(\text{MeSiO}_2)_{12} \cdot x(n\text{BuOH}) \cdot y\text{H}_2\text{O}$ (0.1 g) was added to a mixture of dehydrated toluene (20 mL) and dehydrated pyridine (0.58 mL, 7.2 mmol). After stirring until homogenization at room temperature under N_2 atmosphere, chlorotrimethylsilane (0.91 mL, 7.2 mmol) was added to the mixture and blue green precipitates were formed. After stirring the mixture at 40 °C for 24 h, dehydrated ethanol (0.42 mL, 7.2 mmol) was added to the mixture for alkoxylation of remaining chlorotrimethylsilane. The mixture was stirred at room temperature for 30 min, and the precipitates were removed by suction filtration with Celite®. The filtrate was evaporated to obtain a colorless viscous liquid.

Trimethylsilylated cyclododecasiloxane: ^1H NMR (500.13 MHz; CDCl_3 ; 25 °C; TMS) δ = 0.11 (s, 108H; $\text{OSi}(\text{CH}_3)_3$), 0.08 ppm (s, 36H; O_3SiCH_3); ^{13}C NMR (125.76 MHz; CDCl_3 ; 25 °C; TMS) δ = 1.84 ($\text{OSi}(\text{CH}_3)_3$), 1.81 ($\text{OSi}(\text{CH}_3)_3$), -2.01 (SiCH_3), -2.06 ppm (SiCH_3); ^{29}Si NMR (99.36 MHz; CDCl_3 ; 25 °C; TMS) δ = 7.67 (M^1 , 4Si; OSiMe_3), 7.61 (M^1 , 8Si; OSiMe_3), -67.2 (T^3 , 8Si; O_3SiMe), -67.5 ppm (T^3 , 4Si; O_3SiMe); MS (ESI, 2 kV): calcd. for $\text{C}_{48}\text{H}_{144}\text{O}_{24}\text{Si}_{24}\text{Na}^+ [\text{M}+\text{Na}]^+$: 1799.4; found: 1799.3.

4.2.4 Synthesis of chlorotriethoxysilane (ClSi(OEt)₃)

ClSi(OEt)₃ was synthesized by the alkoxylation of SiCl₄ with ethanol under a nitrogen atmosphere. Tetrachlorosilane (16.5 mL, 143.7 mmol) was added to a Schlenk flask under a N₂ atmosphere, and the flask was cooled to 0 °C. Dehydrated ethanol (29.3 mL, 501.8 mmol) was added dropwise with stirring at 0 °C. After the ethanol had been added, the mixture was stirred at 0 °C for 1 h and at room temperature for 4 h. A colorless clear liquid was obtained. In this procedure, an excess of ethanol (3.5 eq.) was used to avoid the formation of diethoxydichlorosilane (Cl₂Si(OEt)₂) because Cl₂Si(OEt)₂ leads to intermolecular crosslinking between Cu₄Na₄(MeSiO₂)₁₂·x(nBuOH)·yH₂O at the silylation step. Although tetraethoxysilane (TEOS) was also formed with ClSi(OEt)₃ (approximately TEOS:ClSi(OEt)₃ = 1:1), the mixture was used for the silylation without purification because TEOS is much less reactive than ClSi(OEt)₃. The formation of ClSi(OEt)₃ was confirmed by ¹H, ¹³C, and ²⁹Si NMR spectroscopies.

4.2.5 Synthesis of Cyclo12-Me-TEOS

Cu₄Na₄(MeSiO₂)₁₂·x(nBuOH)·yH₂O was alkoxy-silylated with ClSi(OEt)₃. Dehydrated toluene (40 mL) and dehydrated pyridine (17 mL, 210.6 mmol) were added to ClSi(OEt)₃ in a Schlenk flask. Then, Cu₄Na₄(MeSiO₂)₁₂·x(nBuOH)·yH₂O (1.06 g) was added to the solution, and blue–green colored precipitates were formed. The mixture was stirred for 48 h at room temperature under N₂ atmosphere. Then, an excess of dehydrated pyridine and dehydrated ethanol were added to the mixture for the ethoxylation of the remaining ClSi(OEt)₃. The precipitates were filtered with a glass filter under N₂ atmosphere. Then, the solvent, unreacted pyridine, ethanol, and the following two byproducts ((1) TEOS, generated by the ethoxylation of ClSi(OEt)₃, and (2) hexaethoxydisiloxane, formed by the reaction between ClSi(OEt)₃ and adsorbed water

from $\text{Cu}_4\text{Na}_4(\text{MeSiO}_2)_{12} \cdot x(n\text{BuOH}) \cdot y\text{H}_2\text{O}$) were removed *in vacuo*. A small amount of the precipitate was removed by syringe filtration. Finally, the alkoxy-silylated cyclododecasiloxane was isolated by gel permeation chromatography (GPC) using chloroform as an eluent (colorless clear viscous liquid, 1.8902 g, yield: 78%).

Cyclo12-Me-TES. ^1H NMR (500.13 MHz; CDCl_3 ; 25 °C; TMS) δ = 3.81 (q, J = 7.0 Hz, 71H; OCH_2CH_3), 1.21 (t, J = 7.0 Hz, 108H; OCH_2CH_3), 0.26 (s, 12H; SiCH_3), 0.25 ppm (s, 24H; SiCH_3); ^{13}C NMR (125.76 MHz; CDCl_3 ; 25 °C; TMS) δ = 58.9 (OCH_2CH_3), 18.1 (OCH_2CH_3), -2.8 ppm (SiCH_3); ^{29}Si NMR (99.36 MHz; CDCl_3 ; 25 °C; TMS) δ = -67.43 to -67.45 (T^3 , 12Si; O_3SiMe (overlapping two signals)), -88.95, (Q^1 , 4Si; $\text{SiOSi}(\text{OEt})_3$), -89.04 ppm (Q^1 , 8Si; $\text{SiOSi}(\text{OEt})_3$); HRMS (ESI, 2 kV): calcd. for $\text{C}_{84}\text{H}_{216}\text{O}_{60}\text{Si}_{24}\text{Na}^+ [\text{M}+\text{Na}]^+$: 2879.8205; found: 2879.8320.

4.2.6 Hydrolysis and polycondensation of Cyclo12-Me-TES

Cyclo12-Me-TES was dissolved in a mixture of dehydrated ethanol and deuterated ethanol (40 vol% of $\text{EtOH-}d_6$). Then, water and 6 M hydrochloric acid were added to the solution. The molar ratio of **Cyclo12-Me-TES**: $\text{EtOH}+\text{EtOH-}d_6$: H_2O :HCl was 1:96:36:0.4. The mixture was analyzed by NMR spectroscopies after 1 h, 3 h, and 6 h of reaction.

4.2.7 Preparation of Cyclo12-Me-TES-derived gel

Cyclo12-Me-TES was dissolved in dehydrated ethanol. Then, water and 6 M hydrochloric acid were added to the solution. The molar ratio of **Cyclo12-Me-TES**: EtOH : H_2O :HCl was 1:6006:360:0.4 ($\text{EtO}:\text{H}_2\text{O} = 10$), and the concentration of **Cyclo12-Me-TES** was 1 wt%. Please note that the molar ratio among those compounds is different from that for the investigation of hydrolysis and polycondensation process of

Cyclo12-Me-TES. After the mixture had been stirred at 1200 rpm at room temperature for 24 h, the solution was cast on a Petri dish. Then, a colorless transparent xerogel was formed by drying at 100 °C for 10 min in air. A white powder was obtained by scraping the gel from the Petri dish for analysis (**Cyclo12-gel-as**). The white powder was heated under an argon atmosphere at 100 °C, 200 °C, or 300 °C for 1 h (**Cyclo12-gel-heat100**, **Cyclo12-gel-heat200**, and **Cyclo12-gel-heat300**, respectively) to investigate the possible structural changes of the siloxane network.

4.2.8 Preparation of TEOS–MTES-derived gel

The mixture of TEOS, MTES, ethanol, water, and 6 M hydrochloric acid was stirred at 1200 rpm at room temperature for 24 h. The molar ratio of TEOS:MTES:H₂O:HCl was 1:1:70:0.4. The EtO:H₂O molar ratio and mass concentration of alkoxides (TEOS + MTES) were the same as those for the aforementioned system of **Cyclo12-Me-TES** (EtO:H₂O = 10 and 1 wt%, respectively). The hydrolyzed solution was cast on a Petri dish, and a colorless transparent gel was formed by drying at 100 °C for 10 min in air. A white powder was obtained by scraping from the Petri dish for analysis (**TEOS-MTES-gel**). The powder was heated under an argon atmosphere at 100 °C, 200 °C, or 300 °C for 1 h (**TEOS-MTES-gel-heat100**, **TEOS-MTES-gel-heat200**, and **TEOS-MTES-gel-heat300**, respectively).

4.2.9 Fabrication of membranes from Cyclo12-Me-TES or mixed TEOS-MTES

α -Alumina particles (a mixture of two types of particles with average diameters of 0.2 and 1.9 μm) were coated onto the outside of porous α -alumina tube by using a SiO₂–ZrO₂ sol as a binder. To obtain a smooth surface, the tube was calcined in air at 550–600 °C for 30 min. These procedures were repeated several times to prevent the

formation of pinholes in the final membrane. Then, the diluted SiO₂–ZrO₂ sol (*ca.* 0.5 wt%) was coated onto the tube to form an intermediate layer (pore size: 2–3 nm).¹⁹ After calcination of the tube in air at 550–600 °C for 30 min, the **Cyclo12-Me-TEES**-derived layer was fabricated by coating with the hydrolyzed solution of **Cyclo12-Me-TEES**, which was prepared as the same way as **Cyclo12-gel-as**. Finally, the tube was dried and heated at 100 °C for 1 h under N₂ atmosphere. A TEOS–MTES-derived membrane was fabricated in the same way as the **Cyclo12-Me-TEES**-derived membrane by using the TEOS–MTES sol instead of **the Cyclo12-Me-TEES** sol. The TEOS–MTES sol was prepared as shown above.

4.2.10 Evaluation of single-gas permeation property

The experimental apparatus for a single-gas permeation measurement is shown in Figure 4.2 as a schematic. A single gas (He, H₂, CO₂, N₂, CH₄, CF₄, or SF₆) was fed to the outside surface (upstream) of a cylindrical membrane at 200 kPa, and the downside was kept at atmospheric pressure. At first, the values for the single gas permeances were measured at 100 °C, and then the membrane was heat-treated at 200–300 °C under a N₂ atmosphere. After confirming the attainment of a steady state at each temperature by measuring the time course of N₂ permeance, the temperature was cooled to 100 °C and the gas permeance was measured. The permeation rate was measured by a bubble film meter. The deviation of the permeation data was less than 5%.

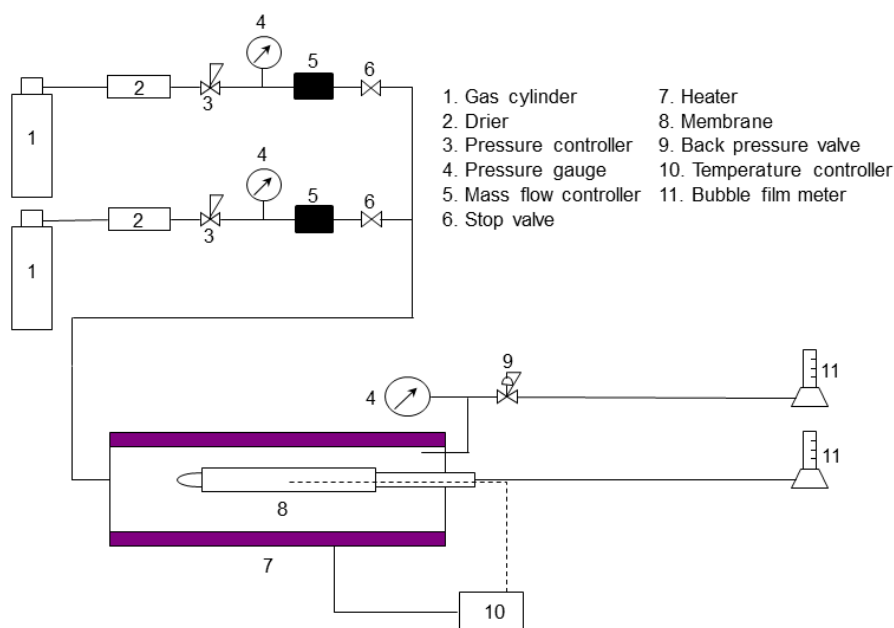


Figure 4.2. Experimental apparatus for a single-gas permeation measurement.

4.2.11 Characterization

Solution ^1H , ^{13}C , and ^{29}Si NMR spectra were recorded on AVANCE 500 (Bruker) or JNM-ECZ 500 (JEOL) spectrometers with resonance frequencies of 500.13 MHz, 125.76 MHz, and 99.36 MHz, respectively, at room temperature using 5-mm glass tubes. Tetramethylsilane (TMS) was used as an internal reference at 0 ppm. CDCl_3 and ethanol- d_6 were used to obtain lock signals. A small amount of $\text{Cr}(\text{acac})_3$ (acac: acetylacetonate) was added as a relaxation agent for ^{29}Si nuclei. ^{13}C NMR spectra were measured with a recycle delay of 2 s. ^{29}Si NMR spectra were measured with a 45° pulse and a recycle delay of 10 s. Solid-state ^{29}Si MAS NMR spectra were recorded on a JNM-ECX 400 (JEOL) spectrometer with a resonance frequency of 78.7 MHz at room temperature with a 45° pulse and a recycle delay of 250 s. The recycle delay was set at five times as long as longitudinal relaxation time (T_1) to complete the relaxation of all nuclear spins. The samples were placed in 4-mm zirconia tubes and spun at 6 kHz. The chemical shifts were

externally referenced to poly(dimethylsilane) at -33.8 ppm. Solid-state ^{13}C CP/MAS NMR spectra were also recorded on a JNM-ECX 400 (JEOL) spectrometer with a resonance frequency of 99.5 MHz at room temperature with a recycle delay of 10 s and a contact time of 5 ms. The samples were put in 4 -mm silicon nitride tubes and spun at 10 kHz. The chemical shifts were externally referenced to the methyl groups of hexamethylbenzene at 17.4 ppm. High-resolution electrospray ionization mass (HRMS) analysis was conducted by using an Exactive Plus (Thermo Fisher Scientific) instrument. Low-resolution electrospray ionization mass analysis was conducted by using a JMS-T100 CS AccuTOF (JEOL) instrument. Samples were dissolved in ethanol. Gel permeation chromatography (GPC) was carried out using a LC-9100 with a recycling preparative HPLC system, a refractive index (RI) detector (Japan Analytical Industry Co., Ltd.) and two types of crosslinked polystyrene packed columns (JAIGEL-1H and JAIGEL-2H; exclusion limits of 1000 and 2000 , respectively, and theoretical plate of 13000). Chloroform was used as an eluent with a flow rate of 3.5 mL/min. FT-IR spectra were recorded on a FT/IR-6100 (JASCO) spectrometer at ambient temperature. The FT-IR spectra were measured using KBr disk technique under vacuum conditions. Powder XRD patterns were recorded on a RINT-Ultima III (RIGAKU) diffractometer with $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA.

4.3 Results and Discussion

4.3.1 Characterization of Cyclo12-Me-TES

Figure 4.3a shows the ^{29}Si NMR spectrum of **Cyclo12-Me-TES**. The two T^3 signals (Figure 4.3a, A and B) observed at -67.43 ppm and -67.45 ppm can be assigned to the Si atoms constituting the cyclododecasiloxane. No signal of the complex was observed in the T^2 region (typically -56.8 ppm to -58.8 ppm²⁰⁻²²). The two Q^1 signals

(Figure 4.3a, C and D) at -88.95 ppm and -89.04 ppm are due to the Si atoms of the TES groups. The two slightly different environments for both T^3 and Q^1 units can be attributed

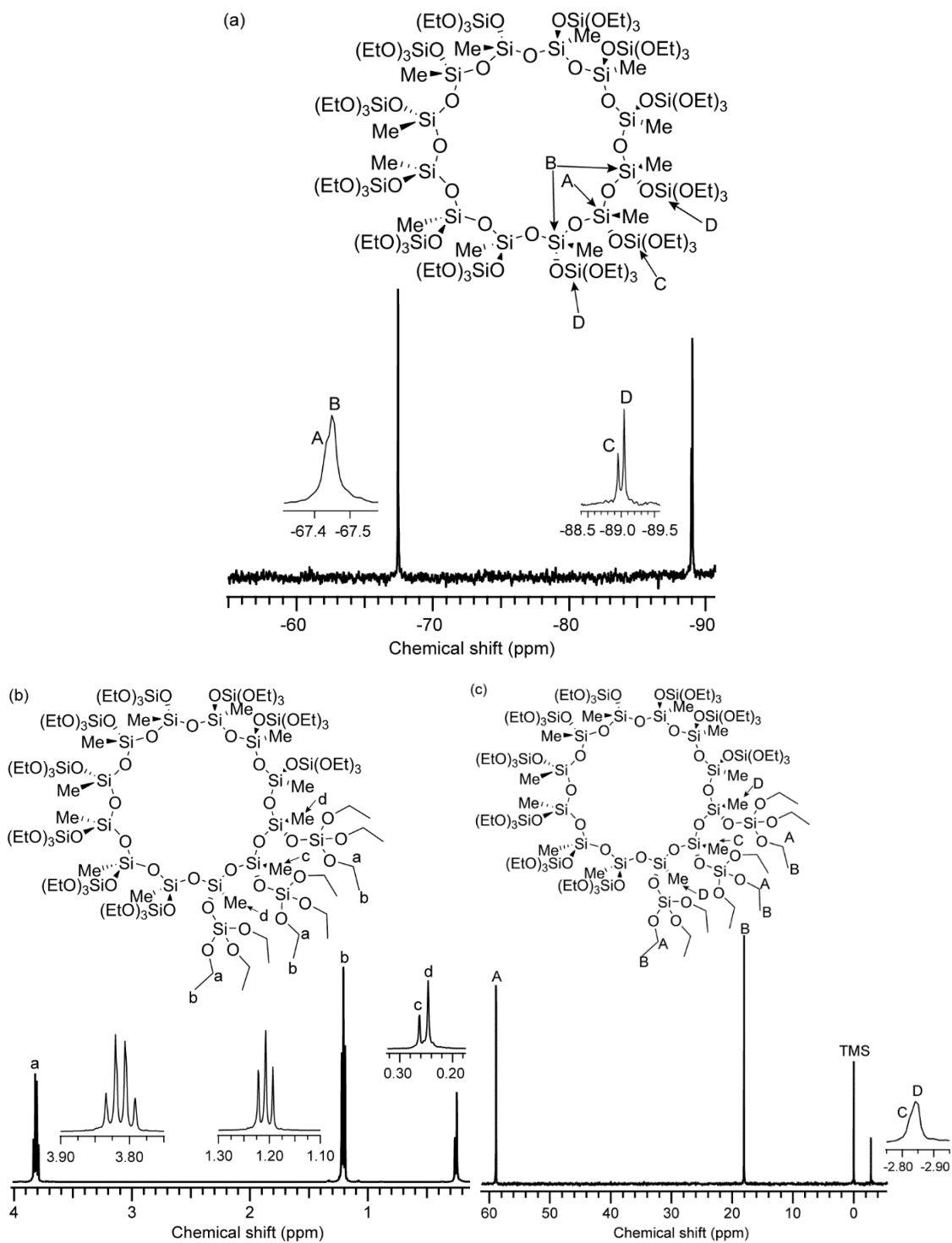


Figure 4.3. NMR spectra of Cyclo12-Me-TES. (a) ^{29}Si , (b) ^1H , and (c) ^{13}C .

to the up-and-down arrangement of the side TES groups on the cyclododecasiloxane, as shown in Figure 4.3a. Please note that the arrangement of side groups against the cyclododecasiloxane plane switches every three Si–O bonds. The intensity ratio of the ^{29}Si NMR signals ((A + B):C:D = 12:4:8) is consistent with the structure.[§] These results strongly suggest that the alkoxylation of $\text{Cu}_4\text{Na}_4(\text{MeSiO}_2)_{12}\cdot x(n\text{BuOH})\cdot y\text{H}_2\text{O}$ proceeds with the retention of the cyclododecasiloxane structure, including the up-and-down arrangement of side groups.

The ^1H NMR spectrum of **Cyclo12-Me-TES** (Figure 4.3b) shows four signals assigned to ethoxy groups (3.83–3.79 ppm for $-\text{OCH}_2\text{CH}_3$, 1.22–1.19 ppm for $-\text{OCH}_2\text{CH}_3$) and methyl groups (0.26 ppm and 0.25 ppm). The intensity ratio of these signals is in accordance with the calculated ratio. The two different environments for the methyl carbons are consistent with the structure, as mentioned above. Regarding the ethoxy groups, the separation of the signals was too small to be observed clearly. These ^1H NMR results, together with the ^{13}C NMR results (Figure 4.3c), also support the formation of **Cyclo12-Me-TES**.

The high-resolution ESI-MS spectrum of **Cyclo12-Me-TES** shows a peak at $m/z = 2879.8320$, corresponding to the sodium adduct of **Cyclo12-Me-TES** (calcd. for 2879.8205), confirming that **Cyclo12-Me-TES** had been successfully synthesized. This is the first report concerning the synthesis of a cyclododecasiloxane possessing alkoxyethyl groups that is available as a sol–gel precursor of siloxane-based materials. This synthetic procedure is applicable to the alkoxylation of metalorganosiloxanes possessing cyclic siloxane structures other than cyclododecasiloxanes,^{23–27} which could result in the variation of bond densities and angles of the formed siloxane networks.

4.3.2 Hydrolysis and polycondensation of Cyclo12-Me-TES

To investigate the behavior of **Cyclo12-Me-TES** in the sol-gel process, the hydrolysis and polycondensation of **Cyclo12-Me-TES** in solution was analyzed by liquid-state NMR spectroscopies. Figure 4.4 shows the ^{13}C NMR spectra of the hydrolyzed solution of **Cyclo12-Me-TES**. The signal intensity arising from the methylene carbon of the TES groups at 59.6 ppm decreased, and the intensity of the signal corresponding to the methylene carbon of ethanol (57.7 ppm) increased as the reaction time progressed. The signals arising from the TES groups almost disappeared after 3 h, which indicates the complete hydrolysis of the TES groups of **Cyclo12-Me-TES**. The signal arising from the $-\text{SiMe}$ groups broadened with reaction time. The signal broadening is also confirmed by the ^{29}Si NMR data (next paragraph).

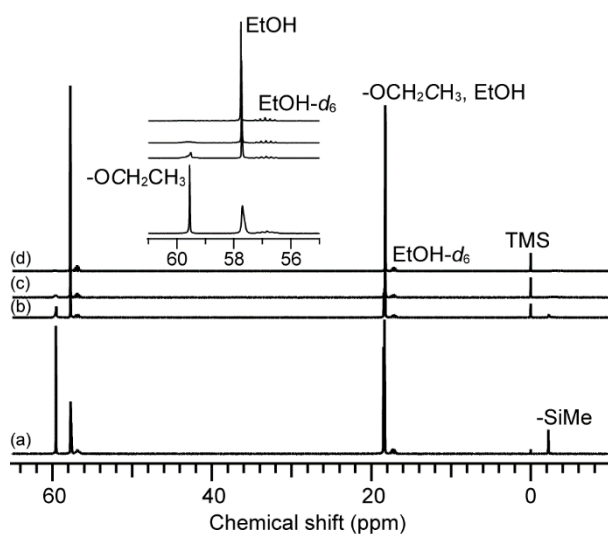


Figure 4.4. ^{13}C NMR spectra of the hydrolyzed solution of **Cyclo12-Me-TES**. (a) 0 h, (b) 1 h, (c) 3 h, and (d) 6 h.

Figure 4.5 shows the ^{29}Si NMR spectra of the hydrolyzed solution of **Cyclo12-Me-TES**. Three new signals are observed in the Q region (-85 ppm to -93 ppm) after 1 h, in addition to the original signal arising from the TES groups of **Cyclo12-Me-TES** ($-$

88.8 ppm). The new signals at -86.3 ppm, -90.7 ppm, and -92.8 ppm can be assigned to $-\text{SiOSi}(\text{OEt})_2(\text{OH})$, $-\text{SiOSi}(\text{OEt})(\text{OH})(\text{OSi})$, and $-\text{SiOSi}(\text{OH})_2(\text{OSi})$, respectively,^{21,28} which indicates that the partial hydrolysis and condensation of the TES groups of **Cyclo12-Me-TES** had occurred. Meanwhile, the T^3 signals corresponding to the Si atoms of the cyclododecasiloxane are observed. After 3 h and 6 h, all signals had weakened and broadened. This is caused by the following two factors: (i) the types of hydrolyzed and condensed molecules become more diverse with the progress of hydrolysis and condensation, and (ii) the molecular mobility of the condensed species is decreased by the increasing molecular weight as intermolecular condensation progresses or the rigidity of the cyclic siloxane increases through intramolecular condensation. During the reaction, no T^2 signals arising from the cleavage of the Si–O–Si bonds appeared (the T^2 signal of the Si atom possessing methyl group is generally observed at -56 ppm to -58 ppm), which suggests that the cyclic structure of **Cyclo12-Me-TES** is retained without rearrangement. Even if the rearrangement occurred too rapidly to observe by NMR spectroscopy, chemical shift of T^3 silicon in reformed siloxanes bonds would not be shifted to downfield by 3 ppm. Regarding to the downfield shift of T^3 signals, there are a couple of explanations. One probable reason is cyclization of adjacent TES groups to form cyclotetrasiloxanes. The other probable reason is the gradual progress of hydrolysis and condensation of TES groups, and this variation in the Q units must affect the electronic states of linked neighboring T^3 silicons. Because $-\text{SiOH}$ and $-\text{SiOSi}$ groups show a more electron-withdrawing effect than TES group, the signals due to T^3 silicon can be shifted to downfield. Therefore, the downfield shift observed in this study can be explained by the variations in the electron density during the sol-gel reaction. These results indicate that the cyclic structure of **Cyclo12-Me-TES** is retained after the sol-gel reactions, which is important for the preparation of separation/adsorption media using siloxane oligomers.

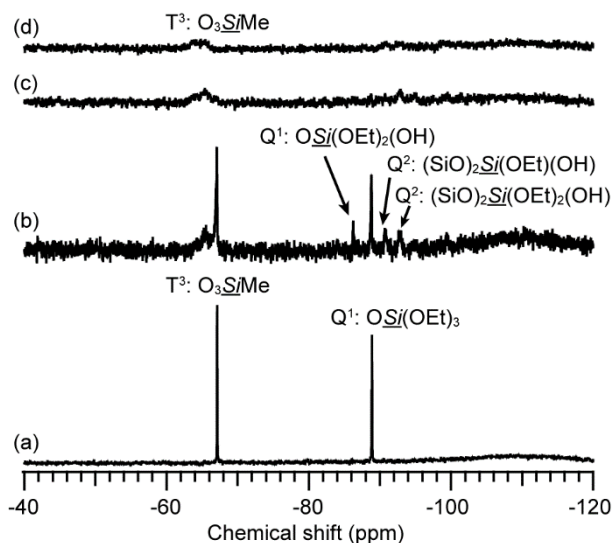


Figure 4.5. ^{29}Si NMR spectra of the hydrolyzed solution of **Cyclo12-Me-TES**. (a) 0 h, (b) 1 h, (c) 3 h, and (d) 6 h.

4.3.3 Characterization of the Cyclo12-Me-TES-derived gels and tetraethoxysilane–methyltriethoxysilane-derived gels

The stability of the cyclododecasiloxane units in the gels derived from **Cyclo12-Me-TES** was investigated. The hydrolyzed solution of **Cyclo12-Me-TES** was dried to obtain a xerogel (**Cyclo12-gel-as**). Subsequently, the obtained gel was heated at 100 °C, 200 °C, or 300 °C under an argon atmosphere (**Cyclo12-gel-heat100**, **Cyclo12-gel-heat200**, and **Cyclo12-gel-heat300**, respectively). These samples were analyzed by solid-state ^{29}Si NMR spectroscopy. **Cyclo12-gel-as** was obtained by drying the solution containing hydrolyzed and partially polycondensed **Cyclo12-Me-TES**. Please note that the reaction conditions were different from those used for the investigation of hydrolysis process described in the previous section. The hydrolysis conditions in this section were the same conditions as those for the preparation of the **Cyclo12-Me-TES**-derived membrane precursor sol. The larger amount of solvent (ethanol) in these systems is favorable for the suppression of the hydrolytic cleavage of the cyclododecasiloxane. The

^{29}Si magic angle spinning (MAS) NMR spectrum of **Cyclo12-gel-as** shows T and Q signals (Figure 4.6a). Three signals are observed in the Q region (Q^2 , Q^3 , and Q^4), indicating the progress of hydrolysis and polycondensation of **Cyclo12-Me-TES**; however, the appearance of Q^2 and Q^3 signals indicates these reactions had not completed and $-\text{SiOEt}$ and $-\text{SiOH}$ groups remained. In the T region, only the T^3 signal corresponding to the Si atoms in the cyclododecasiloxanes was observed, suggesting that the cyclododecasiloxane structure of **Cyclo12-Me-TES** had been retained.

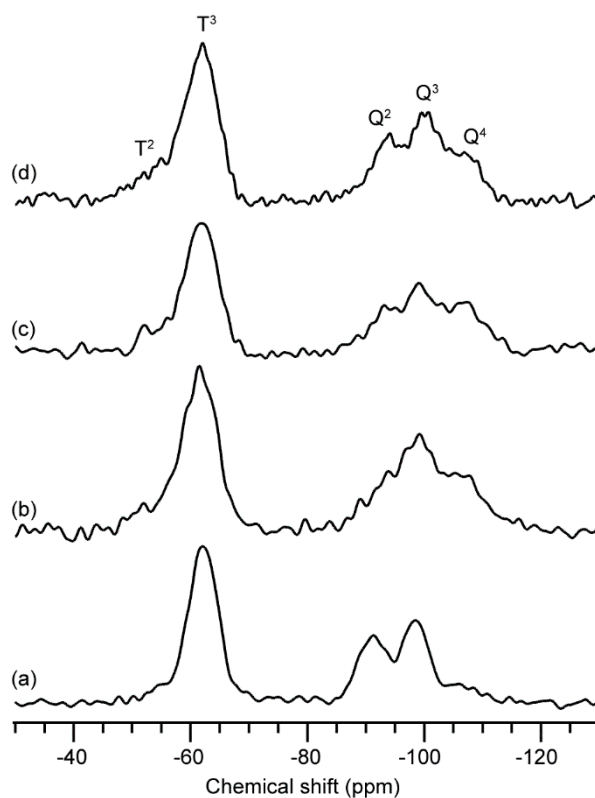


Figure 4.6. ^{29}Si MAS NMR spectra of **Cyclo12-Me-TES**-derived gel. (a) **Cyclo12-gel-as**, (b) **Cyclo12-gel-heat100**, (c) **Cyclo12-gel-heat200**, and (d) **Cyclo12-gel-heat300**.

The signals assigned to ethoxy groups are observed in the ^{13}C cross-polarization (CP)/MAS NMR spectrum (Figure 4.7a), which indicates that the hydrolysis of **Cyclo12-Me-TES** had not completed. As described in the previous section, the hydrolysis reaction

was completed under the conditions for the investigation of hydrolysis and polycondensation process of **Cyclo12-Me-TES**. Such a difference in the degree of hydrolysis can be explained by the difference in the concentrations of the HCl catalyst. The concentration of HCl in the reaction mixture for the preparation of the **Cyclo12-Me-TES**-derived gel ($\text{HCl}/(\text{EtOH}+\text{H}_2\text{O}) = 6.3 \times 10^{-5}$) is much lower than that for the investigation of hydrolysis process of **Cyclo12-Me-TES** ($\text{HCl}/(\text{EtOH}+\text{H}_2\text{O}) = 3.0 \times 10^{-3}$). Even the reaction time was increased from 1 d to 2 d, the ethoxy groups remained (^{13}C CP/MAS NMR: Figure 4.8), and the partial cleavage of the cyclododecasiloxane occurred (^{29}Si MAS NMR: Figure 4.9). To avoid this cleavage, it is important to induce gelation after 1 d by evaporating the solvent.

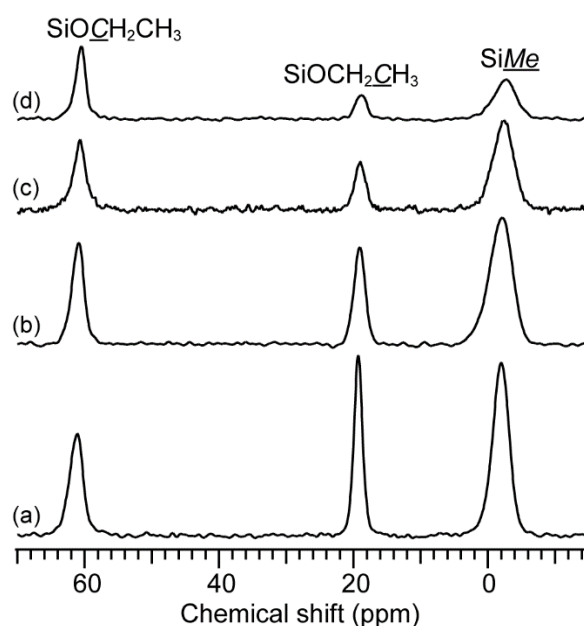


Figure 4.7. ^{13}C CP/MAS NMR spectra of **Cyclo12-Me-TES**-derived gel. (a) **Cyclo12-gel-as**, (b) **Cyclo12-gel-heat100**, (c) **Cyclo12-gel-heat200**, and (d) **Cyclo12-gel-heat300**.

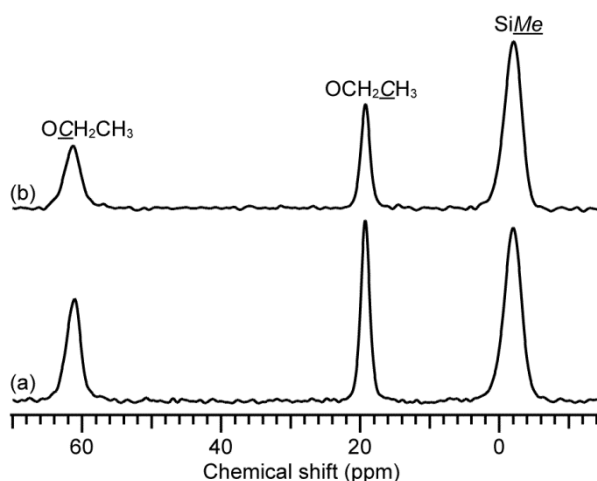


Figure 4.8. ^{13}C CP/MAS NMR spectra of **Cyclo12-gel-as** prepared with different hydrolysis time. (a) 1 d and (b) 2 d.

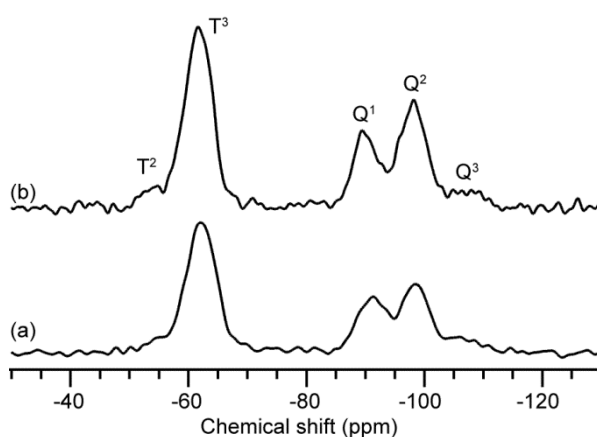


Figure 4.9. ^{29}Si MAS NMR spectra of **Cyclo12-gel-as** with different hydrolysis time. (a) 1 d and (b) 2 d.

After the heat treatment of **Cyclo12-gel-as** under an argon atmosphere, the polycondensation progress was confirmed by ^{29}Si MAS NMR and Fourier-transform infrared (FT-IR) spectroscopies, which demonstrates the reduction in the number of SiOH groups (Figures 4.6b–d and 4.10, respectively), although some ethoxy groups remained (Figures 4.7b–d). In the case of **Cyclo12-gel-heat100**, only the T^3 signal was observed, in common with **Cyclo12-gel-as** (Figure 4.6b), indicating that the cyclododecasiloxane structure of **Cyclo12-gel-as** did not deteriorate at 100 °C. On the other hand, at higher

temperatures, small T² signals appeared in the ²⁹Si MAS NMR spectra of both **Cyclo12-gel-heat200** and **Cyclo12-gel-heat300** (Figures 4.6c and d, respectively). It is likely that the cyclododecasiloxanes were cleaved by increasing strain arising from the progress of polycondensation with heating.

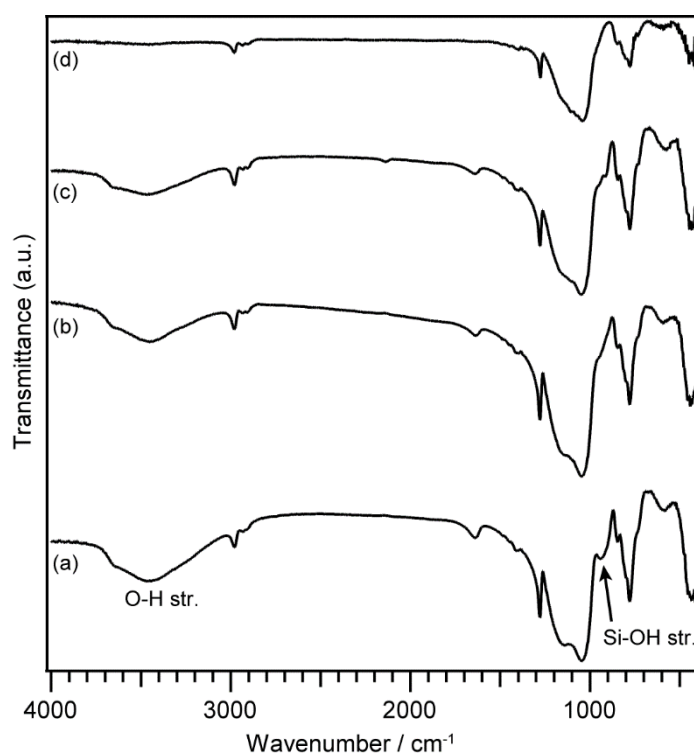


Figure 4.10. FT-IR spectra of **Cyclo12-Me-TEOS**-derived gel. (a) **Cyclo12-gel-as**, (b) **Cyclo12-gel-heat100**, (c) **Cyclo12-gel-heat200**, and (d) **Cyclo12-gel-heat300**.

For comparison, equimolar amounts of tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) were co-hydrolyzed and polycondensed to obtain a xerogel. The ²⁹Si MAS NMR analysis confirmed that the signal intensity of the T² silicon atom of TEOS–MTES-derived gel (Figure 4.11) is higher than that of **Cyclo12-Me-TEOS**-derived gel (Figure 4.6). The lack of T² silicon atoms in the **Cyclo12-Me-TEOS**-derived gel can be attributed to the usage of Cyclo12-Me-TEOS having only T³ silicon atoms as a

precursor under controlled conditions. These results indicate that the cyclic oligosiloxanes, which are composed of silicon atoms with controlled condensation degree, are useful precursors to control the siloxane networks.

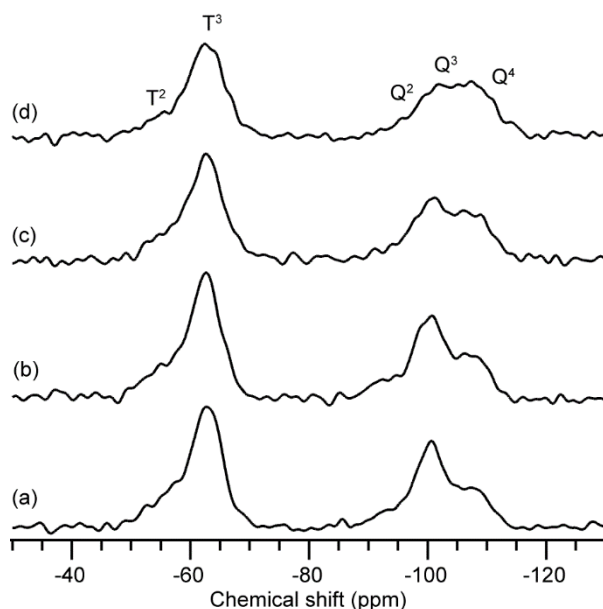


Figure 4.11. ^{29}Si MAS NMR spectra of TEOS-MTES-derived gel. (a) TEOS-MTES-gel-as, (b) TEOS-MTES-gel-heat100, (c) TEOS-MTES-gel-heat200, and (d) TEOS-MTES-gel-heat300.

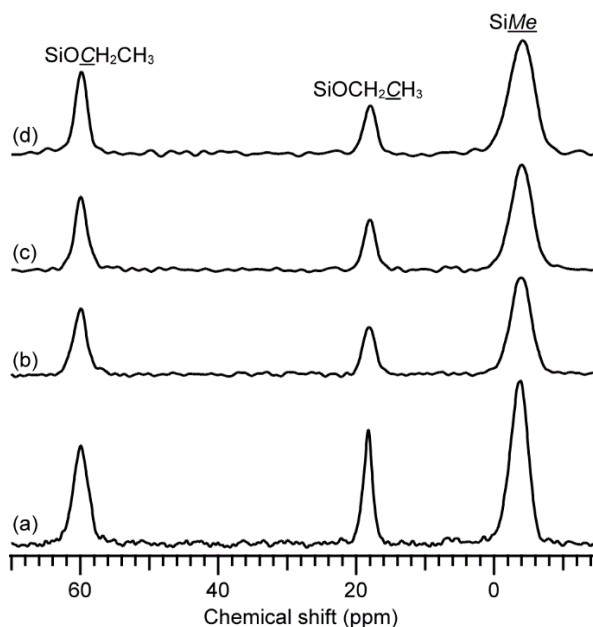


Figure 4.12. ^{13}C CP/MAS NMR spectra of TEOS-MTES-derived gel. (a) TEOS-MTES-gel-as, (b) TEOS-MTES-gel-heat100, (c) TEOS-MTES-gel-heat200, and (d) TEOS-MTES-gel-heat300.

4.3.4 Gas permeation properties of Cyclo12-Me-TEOS-derived membranes and TEOS-MTES-derived membranes

The gas permeance of the **Cyclo12-Me-TEOS**-derived membranes was evaluated at 100 °C, and the influence of the heat treatment of the membranes was investigated. Figure 4.13 shows the gas permeances of the **Cyclo12-Me-TEOS**-derived membranes heated at 100 °C, 200 °C, and 300 °C as a function of kinetic diameter. There are no significant changes in both the shape of these curves and the selectivity with heating temperature (*e.g.*, H₂/SF₆: 550, 700, and 650 for the membranes heated at 100 °C, 200 °C, and 300 °C, respectively). The selectivity for H₂/SF₆ shows higher values than the expected value for Knudsen diffusion (H₂/SF₆ Knudsen selectivity: 6²⁹), indicating that the **Cyclo12-Me-TEOS**-derived membranes show a molecular sieving effect.

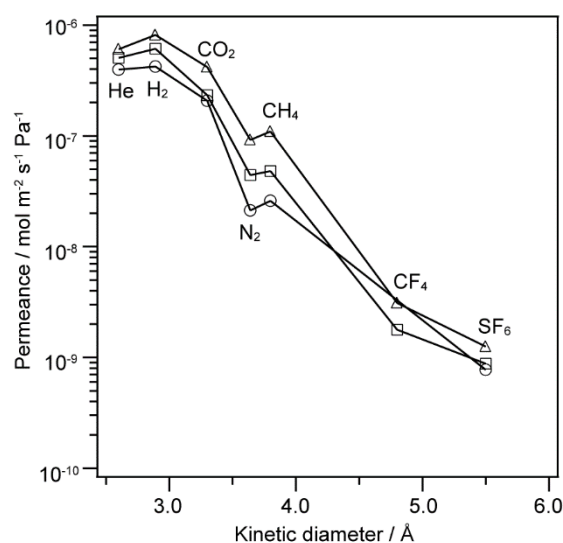


Figure 4.13. Gas permeance at 100 °C for **Cyclo12-Me-TEOS**-derived membranes as a function of molecular size. The membranes are heated at 100 °C (circle), 200 °C (square), and 300 °C (triangle).

The slopes of the gas permeances against the kinetic diameter were almost the

same, and the gas permeances were increased with increasing heat treatment temperature (Figure 4.13). The former result indicates that the average pore diameter of the membrane does not depend on the heating temperature. Assuming that gas molecules pass through the inner space of cyclododecasiloxanes, the slope of gas permeances against kinetic diameter would decrease with the cleavage of the cyclododecasiloxanes. Actually, the cyclododecasiloxanes are slightly cleaved by heat treatments at 200 °C and 300 °C, as shown in Figure 4.6; however, the slopes were almost the same (Figure 4.13). This could indicate that the relative positions of the Si atoms in the cyclododecasiloxane of **Cyclo12-Me-TEs** were not changed significantly by the cleavage of the cyclic siloxanes with heat treatment. The increase in the permeance with increasing heating temperature is probably due to the desorption of adsorbed water with heat treatment, which is often observed for sol-gel derived membranes.³⁰

The physical adsorption of gas molecules affects the gas permeation measured at 100 °C (Figure 4.13), but the effect can be ignored at 200 °C and higher. The gas permeance experiments at 100 °C show that the permeance of **Cyclo12-Me-TEs**-derived membranes does not depend on their heating temperature; therefore, the gas permeance of the **Cyclo12-Me-TEs**-derived membranes was evaluated at 200 °C.

TEOS-MTES-derived membrane was fabricated by hydrolysis and co-condensation of TEOS and MTES, and its gas permeance was also evaluated for comparison. Figure 4.14a shows the gas permeances of the **Cyclo12-Me-TEs**-derived membrane and TEOS-MTES-derived membrane as a function of kinetic diameter. Both membranes were heated at 300 °C after the coating of sols onto porous alumina tubes. Figure 4.14b shows the dimensionless permeances based on the He permeance at 200 °C for these membranes. Compared with dimensionless permeance under the Knudsen mechanism, both membranes showed low dimensionless permeance between N₂ and SF₆,

which indicates that both membranes showed a molecular sieving effect. The **Cyclo12-Me-TES** membrane showed approximately the same level of gas permeance and pore size distribution with that of TEOS–MTES membrane. There are two possible reasons for the similar permeances. (i) The flexibility of siloxane or (ii) the formation of smaller cyclic structure than the cyclododecasiloxane among **Cyclo12-Me-TES** during the condensation of **Cyclo12-Me-TES**. (i) The shape of such a large cyclic siloxane easily changes; in fact, the precursor of the **Cyclo12-Me-TES**-derived membrane ($\text{Cu}_4\text{Na}_4(\text{MeSiO}_2)_{12} \cdot x(n\text{BuOH}) \cdot y\text{H}_2\text{O}$) contains a bending cyclododecasiloxane. So, the inner space of the cyclododecasiloxane may be narrowed and/or distorted by the bending of the ring structure during the sol–gel reaction. (ii) When cyclic siloxanes smaller than the cyclododecasiloxane are formed between the intermolecular spaces of **Cyclo12-Me-TES**, the gas permeance is underestimated by the averaging of the cyclododecasiloxanes and the small intermolecular ring structures. The inclusion of some guest species into the ring before polymerization will be effective for the polymerization of extended cyclododecasiloxane structures, which is now under investigation. In addition, intermolecular spacing among cyclic oligomers is quite important and should be further studied, although the present study suggests that there are no large spaces among the cyclic oligomers, as judged from the permeance data, which is promising for future research on the molecular design of nanobuilding block approach based on ring-type oligosiloxanes.

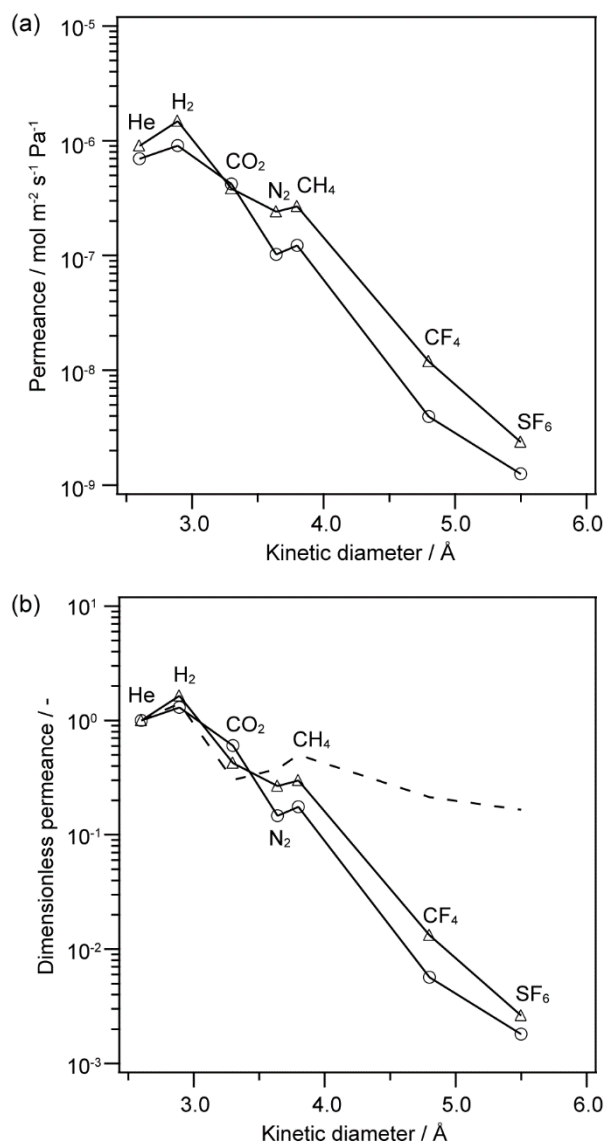


Figure 4.14. (a) Gas permeance and (b) dimensionless permeance based on He permeance at 200 °C as a function of molecular size. (circle) **Cyclo12-Me-TES**-derived membrane heated at 300 °C, (triangle) TEOS–MTES-derived membrane, and (broken line) calculated dimensionless permeance under Knudsen mechanism based on He (The calculation is based on ref. 29).

4.4 Conclusions

An alkoxy-silylated cyclododecasiloxane was successfully synthesized as a nanobuilding block for siloxane-based materials. The cyclic structure of the molecule can be retained during the sol–gel reaction and membrane preparation processes, which

indicates that the cyclic siloxane is a useful precursor for siloxane-based materials with controlled structures. A membrane composed of the cyclic siloxane was fabricated, and the membrane showed molecular sieving effect for H₂/SF₆. These results demonstrate that oligomeric siloxanes with relatively large ring structures are useful nanobuilding blocks for nanomaterials. Further studies on the control of extended ring structure with precisely controlled arrangements are underway for the creation of functional siloxane-based nanomaterials.

4.5 Notes and References

‡ The cyclododecasiloxane of complex shows a saddle conformation before silylation because of the interaction among SiO⁻ groups and metal cations. After silylation, the cyclic structure can take an extended and planar state because such strong interactions to regulate the configuration does not work. The inside diameter of cyclododecasiloxane is calculated by using Chem3D.

§ Two TES groups located in the end of the continuous three TES groups (Q unit), facing to the same direction against cyclododecasiloxane plane, are set in the *cis* and *trans* positions against both of the adjacent TES groups. The center TES groups are in the *cis* position against both of the adjacent TES groups. Hence, the signals due to TES groups are observed at -88.95 ppm and -89.04 ppm, and signal intensity ratio of these signals is 1 : 2. In addition, magnification of the signal due to the Si atoms (T unit) of cyclododecasiloxane exhibits the presence of the shoulder signal probably due to the conformation.

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Chapter 5

Polymerization of Cyclododeca-siloxanes with Si–H and Si–OEt Side Groups by Piers-Rubinsztajn Reaction

Adapted with permission from M. Yoshikawa, H. Shiba, H. Wada, A. Shimojima, K. Kuroda, “Polymerization of Cyclododeca-siloxanes with Si–H and Si–OEt Side Groups by Piers-Rubinsztajn Reaction”, *Bull. Chem. Soc. Jpn.* **2018**, DOI: 10.1246/bcsj.20170410. Copyright 2018 The Chemical Society of Japan.

5.1 Introduction

Controlled construction of siloxane networks is an important requirement in siloxane-based materials chemistry because the properties of the final materials rely on the structure of the networks. Precise structural control of siloxane networks can be achieved by using oligosiloxanes that have regulated structures and polymerizable functional groups as precursors (building blocks).¹⁻⁴

Cyclic siloxanes have been focused as building blocks recently.⁵⁻⁸ In particular, large cyclic siloxanes, such as cyclododecasiloxane, are attractive hosts that can accommodate metal cations⁹ within the internal ring-shaped void space.¹⁰⁻¹² Therefore, the polymerization of cyclic siloxanes with retaining their cyclic structures can provide functional materials based on the inner spaces. Zheng *et al.* reported the polymerization of cyclododecasiloxanes with both hydrosilyl and vinyl groups by hydrosilylation.¹³ Thiol-ene polymerization of cyclododecasiloxanes having both thiol and vinyl groups was also reported.¹⁴ Compared to these systems where cyclic siloxanes are connected with organic linkers, cross-linking by siloxane bonds is more desirable for the preparation of siloxane-based materials with higher stability. Shchegolikhina *et al.* reported a solid-phase condensation of cyclododecasiloxane possessing silanol groups to produce nanostructured siloxane-based materials.^{15, 16} However, this study did not evaluate the retention of the cyclic siloxane structures after the siloxane formation. Recently, we reported the sol-gel reactions (hydrolysis and polycondensation) of cyclododecasiloxanes possessing triethoxysilyl groups,¹⁷ and found that the partial cleavage of the original cyclic structure occurred during the reactions depending on the conditions.

When using cyclic oligosiloxanes as precursors for siloxane-based materials, selection of siloxane bond formation reactions is important for the construction of siloxane networks while retaining the original structure. Although the sol-gel reaction of

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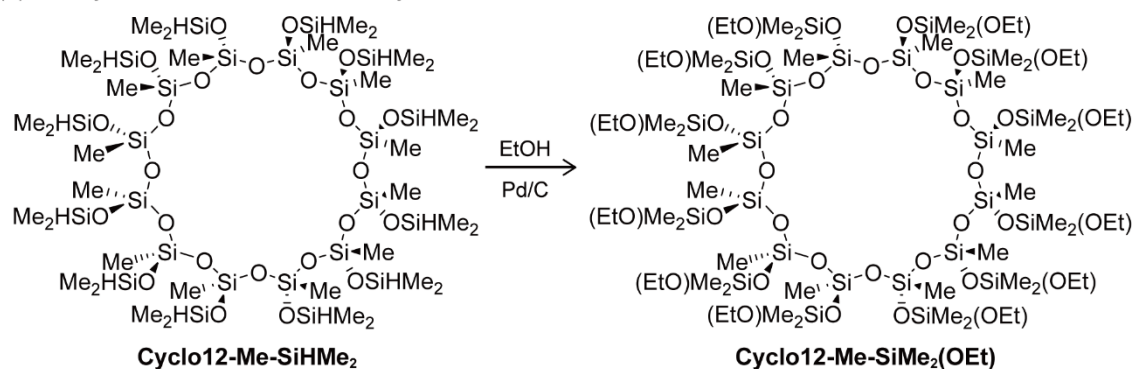
alkoxysilanes and chlorosilanes is a common method for the construction of siloxane networks, uncontrolled networks are often formed because several reactions (hydrolysis, dehydration condensation, and de-alcohol condensation) compete with one another.¹⁸ In addition, the formed siloxane bonds can be hydrolyzed under the required hydrolytic conditions¹⁹. Therefore, the original siloxane structure of oligosiloxanes may decompose depending on the reaction conditions. To control the siloxane networks during the polymerization of oligosiloxanes, the use of non-hydrolytic siloxane bond formation reactions is preferable due to the absence of water in the reaction systems.²⁰

The Piers-Rubinsztajn (P-R) reaction is a de-hydrocarbon condensation reaction between alkoxy silanes and hydrosilanes that forms siloxane bonds and is catalyzed by tris(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$) ($\text{SiOR} + \text{HSi}' \rightarrow \text{SiOSi}' + \text{RH}$, R: alkyl).²¹⁻²³ The P-R reaction has been used for synthesizing silicones as well as oligosiloxanes for several reasons:²⁴ (i) high reaction rates; (ii) facile removal of gaseous hydrocarbon byproducts; and (iii) prevention of deactivation of the catalyst by water contamination. Recently, Laine *et al.* reported polymerization of a cubic oligosiloxane with a tetraalkoxy silane or a bridged organoalkoxy silane by the P-R reaction.²⁰ In their work, the effectiveness of the P-R reaction for the preparation of 3-D siloxane networks was shown. However, the retention of oligosiloxane structures was not investigated unfortunately. Also, to the best of our knowledge, application of the P-R reaction for the direct cross-linking of oligosiloxanes without any linker molecules has not been reported.

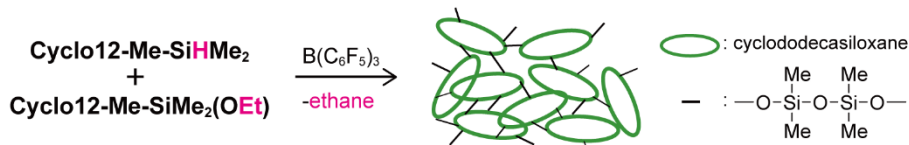
In this study, two differently functionalized cyclododecasiloxanes were polymerized by the P-R reaction. A cyclododecasiloxane, possessing both methyl and ethoxydimethylsilyl groups as side groups (**Cyclo12-Me-SiMe₂(OEt)**), was synthesized by the ethoxylation of a cyclododecasiloxane with hydrosilyl groups (**Cyclo12-Me-**

SiHMe₂) as a macromonomer (Scheme 5.1a). The two cyclic compounds were polymerized in the presence of B(C₆F₅)₃ (Scheme 5.1b). The detailed structural characterizations confirmed that the cyclic structure of the cyclododecasiloxane precursors was retained after the polymerization.

(a) Ethoxylation of -SiHMe₂ modified cyclododecasiloxane



(b) Polymerization of cyclododecasiloxanes by the Piers-Rubinsztajn reaction



Scheme 5.1. Synthesis of **Cyclo12-Me-SiMe₂(OEt)** from **Cyclo12-Me-SiHMe₂** and polymerization of cyclododecasiloxanes by the P-R reaction.

5.2 Experimental

5.2.1 Materials

Activated alumina (Al₂O₃, *ca.* 45 μm in particle size), 1-butanol (> 99.0%), ethanol (dehydrated > 99.5%), hexane (> 95.0%), sodium hydroxide (NaOH > 97.0%), toluene (dehydrated > 99.5%), palladium-activated carbon (Pd/C, 5 wt% as Pd), and pyridine (dehydrated > 99.5%) were purchased from Wako Pure Chemical Industries, Ltd. Chlorodimethylsilane (Me₂SiHCl, > 95.0%), methyltriethoxysilane (> 98.0%), and tris(pentafluorophenyl)borane (B(C₆F₅)₃, > 97.0%) were purchased from Tokyo Chemical

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Industry Co., Ltd. Copper(II) chloride (CuCl_2 , > 97%) was purchased from Sigma-Aldrich Co., LLC. Anhydrous magnesium sulfate (Mg_2SO_4 , > 99.5%) was purchased from Junsei Chemical Co., Ltd. Silver nitrate aqueous solution (0.01 M) was purchased from Kanto Chemical Co., Inc. All reagents were used as received.

5.2.2 Synthesis of $\text{Cu}_4\text{Na}_4(\text{MeSiO}_2)_{12} \cdot (n\text{BuOH})_x \cdot (\text{H}_2\text{O})_y$

The blue $\text{Cu}_4\text{Na}_4(\text{MeSiO}_2)_{12} \cdot (n\text{BuOH})_x \cdot (\text{H}_2\text{O})_y$ compound was synthesized according to a previous report²⁰ and the method was modified as described in section 4.2.2.

5.2.3 Synthesis of cyclododecasiloxane possessing dimethylsilyl groups (Cyclo12-Me-SiHMe₂)

Cyclododecasiloxane possessing dimethylsilyl groups (Cyclo12-Me-SiHMe₂) was synthesized according to the method reported by Zheng *et al.*¹⁵ but with minor modifications. $\text{Cu}_4\text{Na}_4(\text{MeSiO}_2)_{12} \cdot (n\text{BuOH})_x \cdot (\text{H}_2\text{O})_y$ (2.00 g) was dispersed in dehydrated toluene (40 mL) in a Schlenk flask under a N_2 atmosphere. Dehydrated pyridine (7 mL, 86.7 mmol) was then added to the flask and the blue powders were dissolved. Me_2SiHCl (9.8 mL, 90 mmol) was added to the solution to produce a blue-green colored precipitate. The mixture was stirred at room temperature for 24 h under a N_2 atmosphere. Toluene, pyridine, and unreacted Me_2SiHCl were removed *in vacuo*, and hexane was added to the remaining solid. The suspension was filtered to remove the solid residue and washed with deionized water until no white precipitates were generated with an aqueous solution of AgNO_3 . The hexane layer was filtered after drying over MgSO_4 , and the filtrate was evaporated using a rotary evaporator. Finally, a colorless clear liquid was obtained (1.41 g, yield 89%).

The ^{29}Si , ^{13}C , ^1H NMR, and FT-IR data (Figures 5.1-5.4) as well as MS data for the compound were consistent with the reported results,¹⁵ confirming the formation of **Cyclo12-Me-SiHMe₂**.

Cyclo12-Me-SiHMe₂. ^1H NMR (500.13 MHz, CDCl_3 , 25 °C, TMS): δ = 4.74 (sept, J = 3.0 Hz, 12H; SiH), 0.203 (d, J = 3.0 Hz, 48H; $\text{OSiH}(\text{CH}_3)_2$), 0.200 (d, J = 3.0 Hz, 24H; $\text{OSiH}(\text{CH}_3)_2$), 0.11 ppm (s, 36H; O_3SiCH_3); ^{13}C NMR (125.76 MHz, CDCl_3 , 25 °C, TMS): δ = 0.56 ($\text{OSiH}(\text{CH}_3)_2$), -2.57 (O_3SiCH_3), -2.60 ppm (O_3SiCH_3); ^{29}Si (99.36 MHz, CDCl_3 , 25 °C, TMS): δ = -6.27 (M^1 , 4Si; OSiHMe_2), -6.30, (M^1 , 8Si; OSiHMe_2), -66.1 (T^3 , 8Si; O_3SiMe), -66.4 ppm (T^3 , 4Si; O_3SiMe); HRMS (ESI, 2 kV): calcd. for $\text{C}_{36}\text{H}_{120}\text{O}_{24}\text{Si}_{24}\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 1631.2524; found: 1631.2498; IR (liquid film, KBr plate): 2965, 2905, 2133, 1809, 1419, 1269, 1255, 1126, 1047, 907, 837, 796, 787, 771, 628, 432 cm^{-1} .

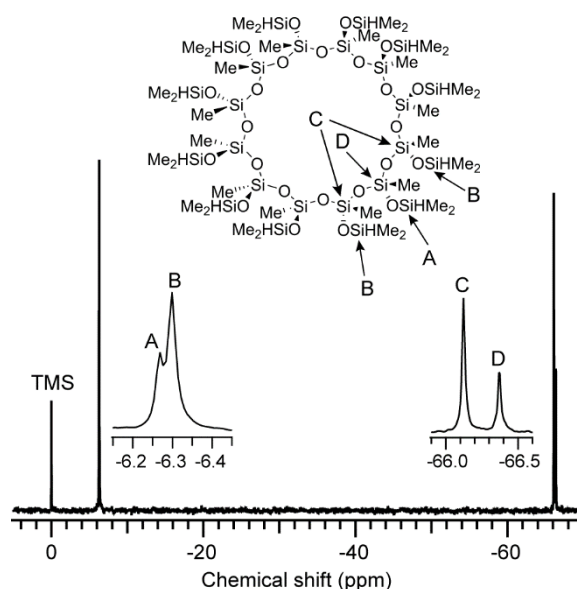


Figure 5.1. ^{29}Si NMR spectrum of **Cyclo12-Me-SiHMe₂**.

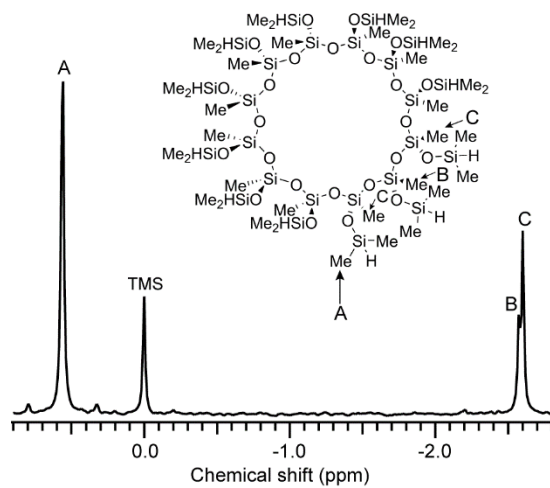


Figure 5.2. ^{13}C NMR spectrum of Cyclo12-Me-SiHMe₂.

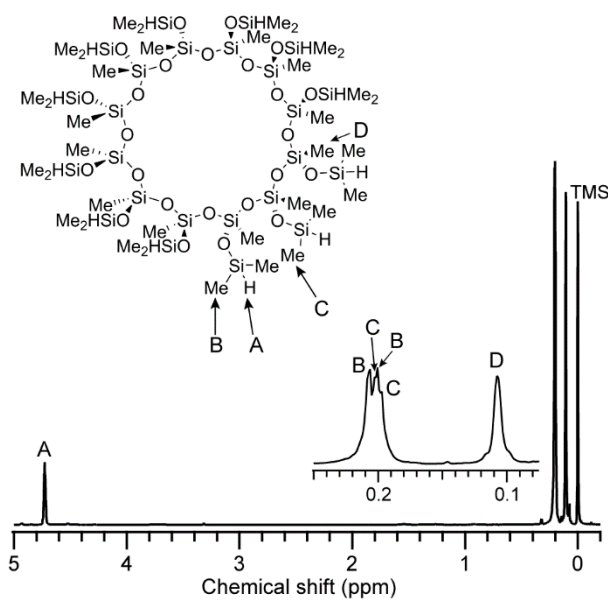


Figure 5.3. ^1H NMR spectrum of Cyclo12-Me-SiHMe₂.

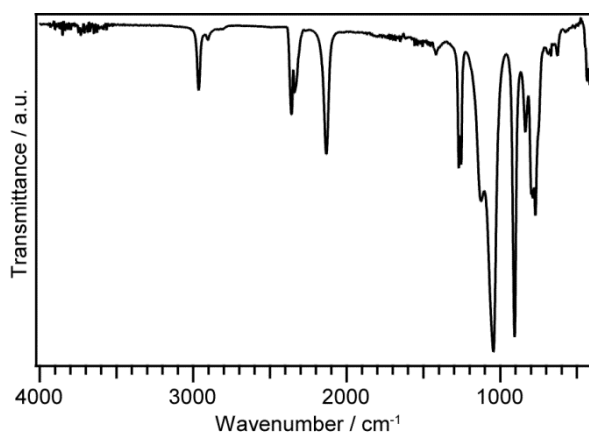


Figure 5.4. FT-IR spectrum of Cyclo12-Me-SiHMe₂.

5.2.4 Synthesis of cyclododecasiloxane possessing ethoxydimethylsilyl groups (Cyclo12-Me-SiMe₂(OEt))

Pd/C (*ca.* 0.05 g) was dispersed in dehydrated ethanol (30 mL) in a Schlenk flask under a N₂ atmosphere. Cyclo12-Me-SiHMe₂ (2.24 g) was then added to the flask, and the mixture was stirred at 50 °C for 24 h. After cooling the mixture to room temperature, the suspension was filtered to remove Pd/C. The filtrate was evaporated on a rotary evaporator to obtain a colorless clear viscous liquid (2.81 g, yield 94%).

Cyclo12-Me-SiMe₂(OEt). ¹H NMR (500.13 MHz, CDCl₃, 25 °C, TMS): δ = 3.74 (q, J = 7.0 Hz, 24H; OCH₂CH₃), 1.19 (t, 36H; OCH₂CH₃), 0.16 to 0.17 (s, 12H; O₃SiCH₃), 0.12 to 0.13 ppm (s, 24H; OSi(CH₃)₂(OEt)), ¹³C NMR (125.76 MHz, CDCl₃, 25 °C, TMS): δ = 57.8 (OCH₂CH₃), 18.4 (OCH₂CH₃), -0.98 to -1.01 (OSi(CH₃)₂(OEt)), -2.24 to -2.28 ppm (O₃SiCH₃); ²⁹Si (99.36 MHz, CDCl₃, 25 °C, TMS): δ = -12.6 (D¹, 12Si; OSiMe₂(OEt)), -67.7 (T³, 8Si; O₃SiMe), -67.9 ppm (T³, 4Si; O₃SiMe); HRMS (Electrospray ionization, 2 kV): calcd. for C₆₀H₁₆₈O₃₆Si₂₄Na⁺ [M+Na]⁺: 2159.5670; found: 2159.5740; IR (liquid film, KBr plate): 2971, 2927, 2904, 2879, 2360, 2341, 2331, 1260, 1169, 1114, 1082, 1040, 953, 844, 795, 748 cm⁻¹.

5.2.5 Polymerization between Cyclo12-Me-SiHMe₂ and Cyclo12-Me-SiMe₂(OEt) by the P-R reaction

Cyclo12-Me-SiHMe₂ (0.25 g, 0.16 mmol) and Cyclo12-Me-SiMe₂(OEt) (0.34 g, 0.16 mmol) were dissolved in dehydrated toluene (6.5 mL) in a Schlenk flask under a N₂ atmosphere. A toluene solution of B(C₆F₅)₃ (0.02 M, 1.7 mL) was then added to the flask. After the addition of B(C₆F₅)₃, gas generation was observed for a few minutes. The mixture was stirred at room temperature for 24 h, prior to the removal of B(C₆F₅)₃ with two different methods. **Method 1:** The solvent was evaporated under vacuum, and the colorless transparent solid on the wall surface of the Schlenk flask was collected. The solid was washed with hexane to remove the catalyst. **Method 2:** Activated Al₂O₃ was added to the solution and the mixture was stirred for 1 h to adsorb the catalyst. The suspension was then filtered to remove Al₂O₃. The filtrate was evaporated *in vacuo* and a colorless viscous liquid was obtained.

5.2.6 Characterization

Solution ¹H, ¹³C, and ²⁹Si NMR spectra were measured by a JNM-ECZ 500 (JEOL) spectrometer with resonance frequencies of 500.13 MHz, 125.76 MHz, and 99.36 MHz, respectively, at room temperature, using 5 mm glass tubes.²⁷ Tetramethylsilane (TMS) was used as an internal reference at 0 ppm and CDCl₃ was used to obtain lock signals. ²⁹Si NMR spectra were measured with a 45° pulse and a recycle delay of 10 s with the addition of a small amount of Cr(acac)₃ (acac: acetylacetonate) as a relaxation agent. Solid-state ²⁹Si magic-angle-spinning (MAS) NMR spectra were recorded on a JNM-ECX 400 (JEOL) spectrometer with a resonance frequency of 78.7 MHz at room temperature with a 45° pulse and a recycle delay of 200 s. The recycle delay was set at five times longer than the longitudinal relaxation time (T₁) to ensure complete relaxation

of all nuclear spins. The samples were placed in 4 mm zirconia tubes and spun at 6 kHz. The chemical shifts were externally referenced to poly(dimethylsilane) at -33.8 ppm. Solid-state ^{13}C cross-polarization (CP)/MAS NMR spectra were also recorded on a JNM-ECX 400 (JEOL) spectrometer with a resonance frequency of 99.5 MHz at room temperature with a recycle delay of 10 s and a contact time of 5 ms. The samples were placed in 4 mm silicon nitride tubes and spun at 10 kHz. The chemical shifts were externally referenced to methyl groups of hexamethylbenzene at 17.4 ppm. High-resolution electrospray ionization mass (HRMS) analysis was conducted by using an Exactive Plus (Thermo Fisher Scientific) instrument. Samples were dissolved in ethanol. Fourier transform infrared (FT-IR) spectra were recorded with the FT/IR-6100 (JASCO) spectrometer at ambient temperature. The FT-IR spectra of powder samples were measured using a KBr disk under vacuum conditions. The liquid samples were measured as liquid films between KBr plates at ambient pressure.

5.3 Results and Discussion

5.3.1 Characterization of Cyclo12-Me-SiMe₂(OEt)

The ^{29}Si NMR spectrum of Cyclo12-Me-SiMe₂(OEt) (Figure 5.5a) shows three signals at -12.6 ppm (D^1), -67.9 ppm (T^3), and -67.7 ppm (T^3). The two T^3 signals can be assigned to the Si atoms constituting the cyclododecasiloxanes. The D^1 signal can be assigned to the dimethyl(ethoxy)silyl groups. The integrated intensity ratio of the signals (A:B:C = 12:8:4) is consistent with the structure shown in Figure 1a. The presence of two T^3 signals is due to the different conformations of the side groups of cyclododecasiloxane. The three consecutive Si atoms in cyclododecasiloxane contain three side groups that are orientated in the same direction. Therefore, the chemical shifts of the centered and two terminal Si atoms differ. The integrated intensity ratio of the signals (1:2) indicates that

the first signal at -67.9 ppm is produced by the central Si and the latter signal (-67.7 ppm) is due to the terminal Si atoms. This ratio supports the conformation of the cyclododecasiloxane.

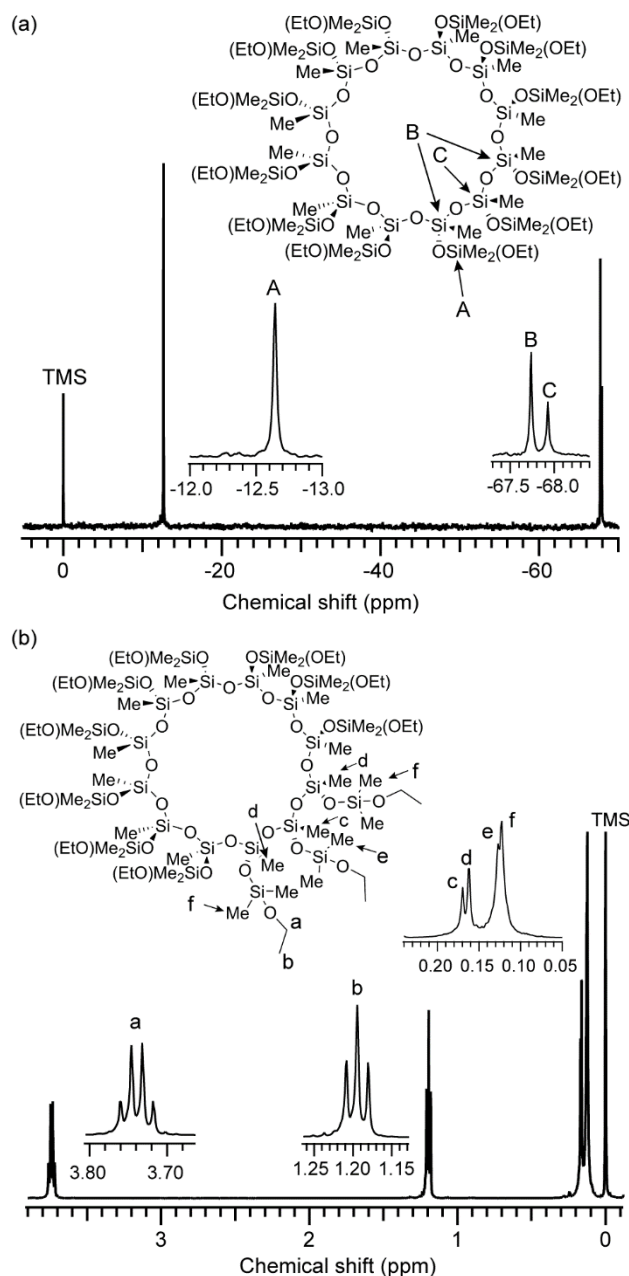


Figure 5.5. (a) ²⁹Si and (b) ¹H NMR spectra of Cyclo12-Me-SiMe₂(OEt).

The ^1H NMR spectrum of **Cyclo12-Me-SiMe₂(OEt)** (Figure 5.5b) shows six signals assigned to the methyl groups (0.16 to 0.17 ppm for O_3SiCH_3) and dimethyl(ethoxy)silyl groups (3.72 to 3.76 ppm for $-\text{OCH}_2\text{CH}_3$, 1.18 to 1.21 ppm for $-\text{OCH}_2\text{CH}_3$, and 0.12 to 0.13 ppm for $-\text{Si}(\text{CH}_3)_2(\text{OEt})$). The disappearance of a $-\text{SiH}$ group signal indicates that the $-\text{SiH}$ groups of **Cyclo12-Me-SiHMe₂** are completely converted following ethoxylation. These results were also supported by the measured ^{13}C NMR and FT-IR spectra (Figures 5.6 and 5.7, respectively). The measured intensity ratio of the ^{29}Si and ^1H NMR signals was consistent with the calculated value of the chemical formula. The appearance of two signals for O_3SiCH_3 is also due to the conformation of the ring. The quartet and triplet signals assigned to the ethoxy groups were not further resolved into two sets, which may be caused by too close chemical shifts between the ethoxy groups linked to the central and terminal Si atoms. The high-resolution ESI-MS data of **Cyclo12-Me-SiMe₂(OEt)** showed a peak at $m/z = 2159.5740$ attributed to a Na^+ adduct of **Cyclo12-Me-SiMe₂(OEt)** (calcd. for 2159.5670), which indicated complete ethoxylation of **Cyclo12-Me-SiHMe₂**.

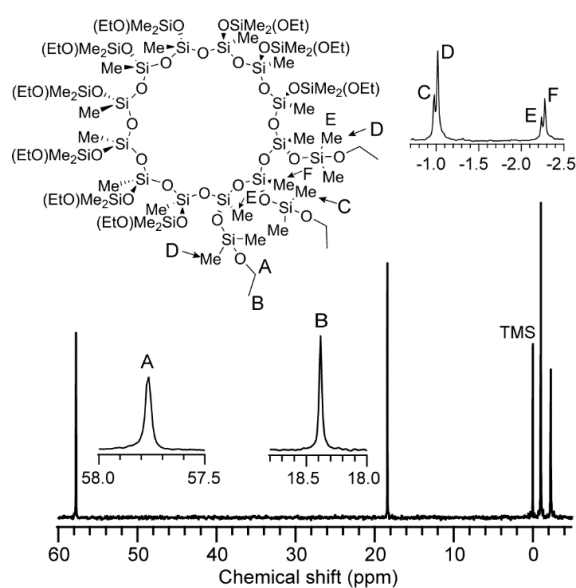


Figure 5.6. ^{13}C NMR spectrum of **Cyclo12-Me-SiMe₂(OEt)**.

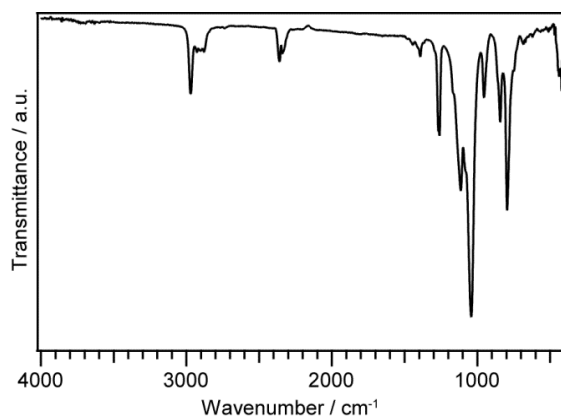


Figure 5.7. FT-IR spectrum of Cyclo12-Me-SiMe₂(OEt).

5.3.2 Polymerization of cyclododecasiloxanes

As described in the experimental section, B(C₆F₅)₃ was removed by the following two methods after polymerization by the P-R reaction, resulting in products with different morphologies.

Method 1: evaporation and washing

A white solid was obtained when the solvent was evaporated first, which implied that the remaining catalyst promoted the reaction to yield a solid that was insoluble in organic solvents. Then, the solid residue was treated with hexane to remove the catalyst, and hexane was evaporated to form a white solid (Figure 5.8a).

Method 2: adsorption with activated alumina

A transparent sticky viscous liquid, which was soluble in organic solvents, was obtained after the removal of the catalyst by Al₂O₃, and subsequently, the solvent was evaporated (Figure 5.8b). This morphological difference is probably due to the different degrees of polymerization.

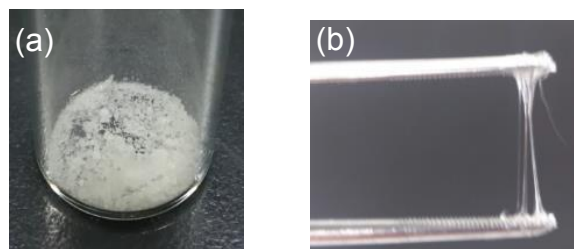


Figure 5.8. Appearances of the products prepared by the P-R reaction. (a) White solid obtained by **method 1** and (b) viscous liquid obtained by **method 2**.

5.3.3 Characterization of the white solids obtained by method 1

Figure 5.9a shows the ^{13}C CP/MAS NMR spectrum of the white solid obtained by **Method 1**. The signals at 1.4 ppm and -2.0 ppm were assignable to $-\text{Si}(\text{CH}_3)_2\text{O}-$ and O_3SiCH_3 , respectively. The signals of the SiOEt groups (58 ppm for $-\text{OCH}_2\text{CH}_3$ and 18 ppm for $-\text{OCH}_2\text{CH}_3$) of **Cyclo12-Me-SiMe₂(OEt)** were not observed, indicating the complete conversion of the precursor. The FT-IR spectrum (Figure 5.10) also supported the completion of the P-R reaction, as signals from the $\text{Si}-\text{H}$ groups and $-\text{CH}_2-$ of OEt groups were not observed after the reaction.

The formation of the siloxane network was confirmed by ^{29}Si MAS NMR spectroscopy (Figure 5.9b). The signal due to the $-\text{OSi}(\text{OEt})$ groups in **Cyclo12-Me-SiMe₂(OEt)** (-12.6 ppm) disappeared after the reaction. The chemical shift of the signal at -6.0 ppm was close to that of the $-\text{OSiHMe}_2$ groups of **Cyclo12-Me-SiHMe₂** (-6.3 ppm). However, the disappearance of $-\text{OSiHMe}_2$ groups was confirmed by FT-IR spectroscopy (Figure 5.10c). Therefore, all the reaction sites of two precursors were used for condensation. Five new peaks were observed at -6.0 ppm, -17.5 ppm, -19.9 ppm, -56.1 ppm, and -65.6 ppm. The signal at -65.6 ppm was assigned to the T^3 Si atoms in the cyclododecasiloxanes because the chemical shift of the signal is very close to those of the precursors. The D^2 signal at -19.9 ppm was assignable to the Si atoms bridging the cyclododecasiloxanes formed by the cross-linking between $-\text{OSiHMe}_2$ and $-\text{OSi}(\text{OEt})$.

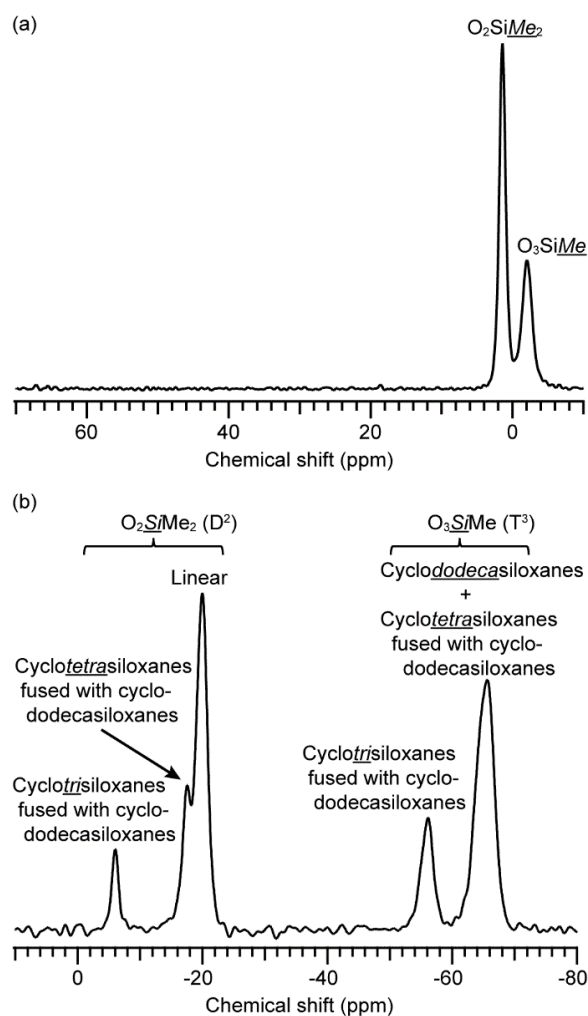


Figure 5.9. (a) ^{13}C CP/MAS and (b) ^{29}Si MAS NMR spectra of the white solid obtained by method 1.

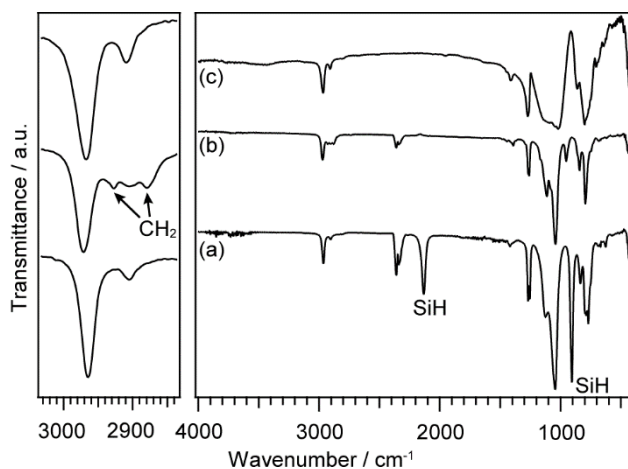
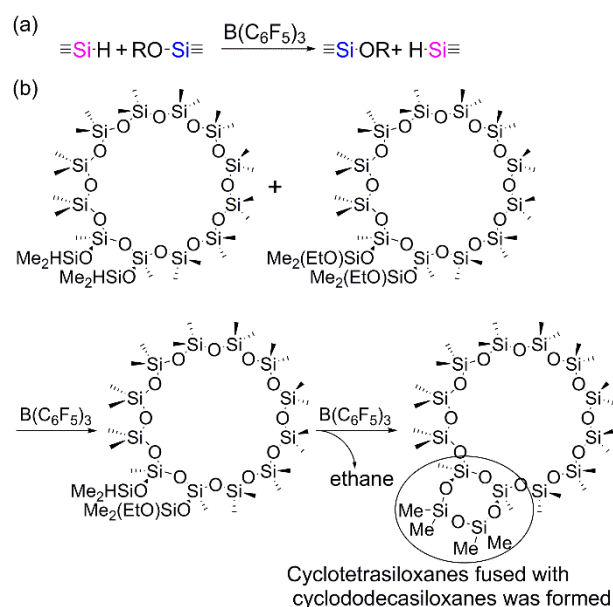


Figure 5.10. FT-IR spectra of (a) Cyclo12-Me-SiHMe₂, (b) Cyclo12-Me-SiMe₂(OEt), and (c) the white solid.

The signal observed at -17.5 ppm could be assigned to the cyclotetrasiloxanes fused with the cyclododecasiloxanes, because the difference in chemical shift between the peaks at -17.5 ppm and -19.9 ppm (2.4 ppm) was similar to the difference measured between cyclic tetrasiloxane and linear polysiloxane (2.7 ppm²⁸⁻³⁰), as shown in Figure 5.11a. It is therefore considered that the peak at -17.5 ppm is the D^2 signal of cyclotetrasiloxanes formed by the group exchange reaction³¹ (Scheme 5.2a) and the following P-R reaction, as shown in Scheme 5.2b. Regarding the signals that have been assigned to the T^3 silicon atoms, the difference in the measured chemical shifts between cyclic tetrasiloxane and linear polysiloxane is too small to be observed by solid-state NMR spectroscopy (0.5 ppm^{32, 33}, Figure 5.11b). The T^3 signal of cyclotetrasiloxanes overlapped with the signal due to the cyclododecasiloxanes at -65.6 ppm. The ^{29}Si MAS NMR data showed that 20% of the side-groups of **Cyclo12-Me-SiHMe₂** and **Cyclo12-Me-SiMe₂(OEt)** were used for the formation of cyclotetrasiloxanes (Figure 5.9b).



Scheme 5.2. The formation mechanism of cyclotetrasiloxane fused with cyclododecasiloxane by exchange reaction and the following P-R reaction (extra side groups are omitted for clarity): (a) Reaction scheme of exchange reaction and (b) the formation mechanism of the cyclotetrasiloxane.

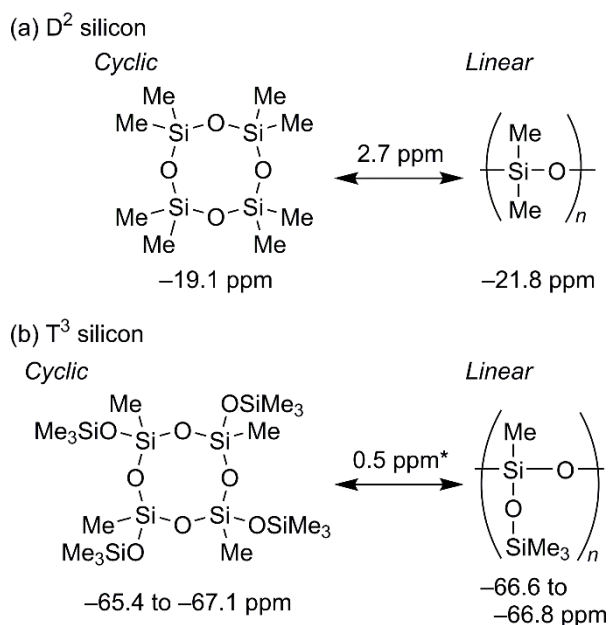
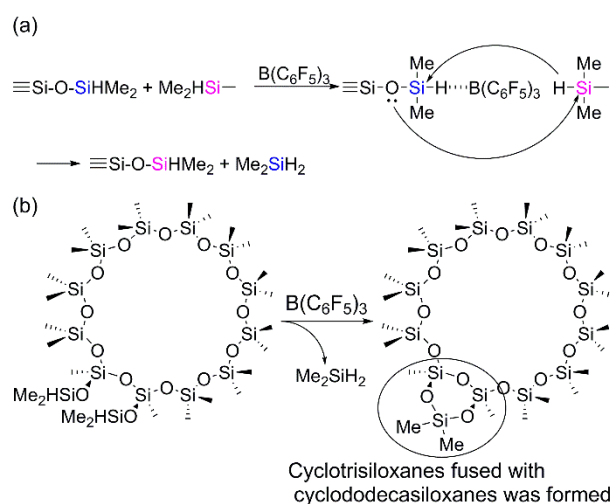


Figure 5.11. The difference in chemical shifts of cyclic tetrasiloxane and linear polysiloxane containing (a) D² and (b) T³ silicon atoms.^{22-24, 26,27} *The difference was calculated by using the average chemical shift of cyclic- and linear siloxanes.

The signals observed at -6.0 ppm and -56.1 ppm in the ^{29}Si MAS NMR spectra were assignable to $-\text{OSiHMe}_2$ groups and T² silicon (MeRSi(OSi)_2 , R: H or OEt) formed by cleavage of the cyclododecasiloxanes, respectively. However, residual $-\text{SiH}$ and $-\text{SiOEt}$ groups were not detected by ^{13}C CP/MAS NMR and FT-IR spectroscopies (Figures 5.9a and 5.10c, respectively). These signals, therefore, could be assigned to the T³ silicon. Due to the high chemical shifts for of T³ silicon and the measured integrated intensity ratio of the signals (-6.0 ppm: -56.1 ppm at 1:2), these signals were assigned to the cyclotrisiloxanes fused with cyclododecasiloxanes. Indeed, the difference in the chemical shift of the D² silicon atom between -6.0 ppm and -19.9 ppm (13.9 ppm) was similar to the observed difference between cyclic trisiloxane and linear polysiloxane (13.6 ppm²⁸⁻³⁰) (Figure 5.12a). Therefore, the D² signal at -6.0 ppm was assigned cyclotrisiloxanes formed by the intramolecular de-dimethylsilane condensation, which is

a known competing reaction of the P-R reaction³⁴ (Scheme 5.3a and b). Similarly, the difference (9.5 ppm) between the T³ signals at -56.1 ppm and -65.6 ppm was consistent with the difference between cyclic trisiloxane and linear polysiloxane (9.5 ppm^{32, 35}, Figure 5.12b). The signal at -65.6 ppm due to cyclododecasiloxanes was regarded to be the same as that of linear siloxanes because the chemical shifts of cyclic siloxanes, which is larger than cyclohexasiloxane, were almost the same as that of the linear polysiloxanes.²⁸ Finally, the signal at -56.1 ppm was assigned to the T³ signal of cyclotrisiloxanes formed by the de-dimethylsilane condensation reaction.



Scheme 5.3. The mechanisms of (a) de-dimethylsilane condensation²⁸ and (b) formation of cyclotrisiloxane fused with cyclododecasiloxane by de-dimethylsilane condensation reaction. Extra side groups were omitted for clarity.

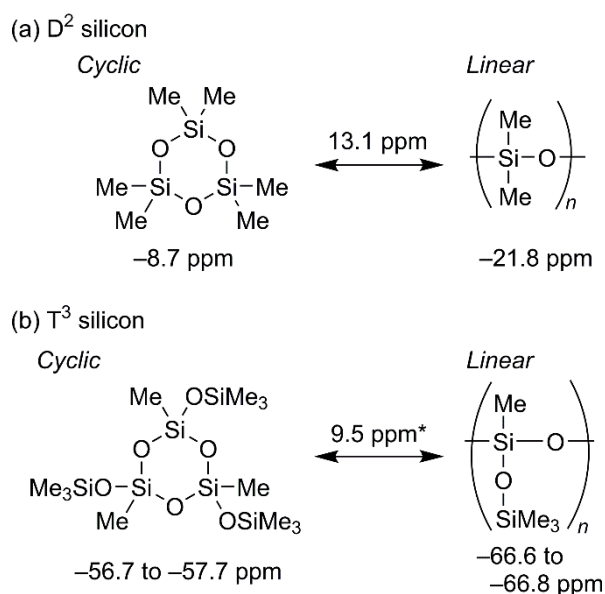


Figure 5.12. The difference in chemical shifts of cyclic trisiloxane and linear polysiloxane containing (a) D² and (b) T³ silicon atoms.^{22-24,26,29} *The difference was calculated by using the average chemical shift of cyclic- and linear siloxanes.

The rate of de-dimethylsilane condensation is lower than that of the P-R reaction by 3–4 orders of magnitude.³⁶ However, the ²⁹Si MAS NMR spectra (Figure 5.9b) show that 10% of dimethylsilyl groups were used for the formation of cyclotrisiloxanes. This high degree of side reaction is due to the structures of cyclododecasiloxane. When the cyclic structure of cyclododecasiloxanes is retained during polymerization, rotation of the side polymerizable groups of cyclododecasiloxane is partially inhibited. Therefore, as the intermolecular condensation reaction progresses, further intermolecular polymerization of unreacted side groups is restricted, thus resulting in the intramolecular de-dimethylsilane condensation between neighboring and unreacted side groups to form cyclotrisiloxanes.

The de-dimethylsilane condensation reactions lead to unpaired and unreacted –SiOEt groups. However, unreacted –SiOEt groups were not detected by ¹³C CP/MAS NMR and FT-IR spectroscopies (Figures 5.9a and 5.10, respectively). A possible reason

for this observation is that the eliminated dimethylsilanes reacted with $-\text{SiOEt}$ groups to form siloxane bonds according to the P-R reaction.

According to the measured spectroscopic results mentioned above, although the cross-linking progresses inhomogeneously because of de-dimethylsilane condensation, the cyclododecasiloxanes are successfully polymerized in a high reaction ratio with retention of their underlying ring structure. This result indicates that the P-R reaction is useful for not only the preparation of silicones but also the polymerization of siloxane-based building blocks to obtain siloxane-based materials with controlled siloxane structures.

5.3.4 Characterization of the viscous liquid obtained by method 2

The ^1H NMR spectrum of the viscous liquid obtained by **method 2** (as previously detailed) is given in Figure 5.13a. The signal of Si-H (4.74 to 4.76 ppm) observed before the reaction (Figure 5.3) was not observed in spectrum recorded after the reaction. The intensity of the signals of Si-OEt (3.75 ppm for $-\text{OCH}_2\text{CH}_3$ and 1.20 ppm for $-\text{OCH}_2\text{CH}_3$) was lower in comparison to that recorded for the precursor before the reaction (Figure 5.5b). The reaction ratio of the ethoxy group was calculated as 95% from the integrated intensity ratio ($-\text{OCH}_2\text{CH}_3/(\text{O}_2\text{SiMe}_2 + \text{O}_3\text{SiMe})$). The ^{13}C NMR spectrum (Figure 5.14) shows the signals assigned to the ethoxysilyl groups (58.7 ppm for $-\text{OCH}_2\text{CH}_3$ and 18.4 ppm for $-\text{OCH}_2\text{CH}_3$). These signals also indicate the presence of unreacted ethoxysilyl groups. The FT-IR spectra of the samples recorded before and after the reaction (Figure 5.15) also confirmed that the bands assigned to Si-H (2133 cm^{-1}) and $-\text{CH}_2-$ (2927 cm^{-1} and 2879 cm^{-1}) were diminished after the reaction. The ^1H NMR and FT-IR results indicated the progress of the P-R reaction and revealed that unreacted side groups were present in the final product.

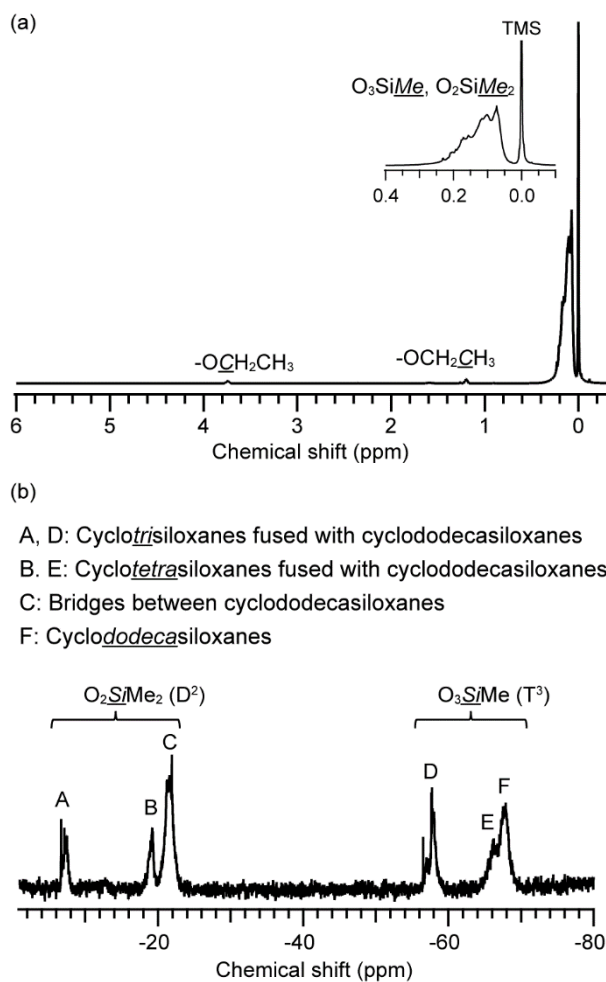


Figure 5.13. (a) ^1H and (b) ^{29}Si NMR spectra of the viscous liquid obtained by **method 2**.

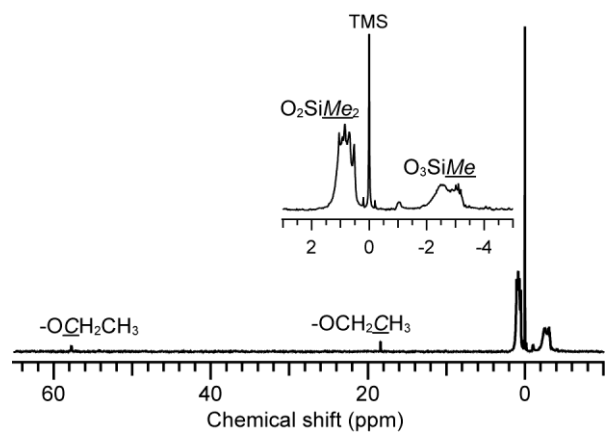


Figure 5.14. ^{13}C NMR spectrum of the viscous liquid obtained by **method 2**.

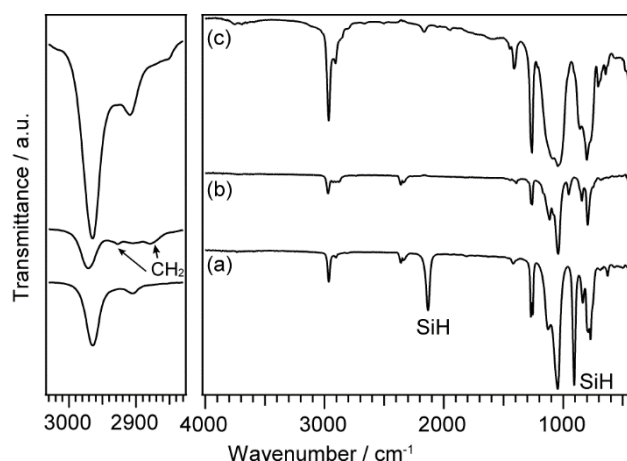


Figure 5.15. FT-IR spectra of (a) **Cyclo12-Me-SiHMe₂**, (b) **Cyclo12-Me-SiMe₂(OEt)**, and (c) the viscous liquid.

The formation of siloxane networks was confirmed by ^{29}Si NMR spectroscopy (Figure 5.13b). Six broad peaks (labeled as A to F in Figure 3b) were observed. The signals C and F were assigned to the D^2 silicon atoms bridging the cyclododecasiloxanes and the T^3 silicon atoms constituting the cyclododecasiloxanes, respectively. Signals A and D were assigned as the cyclotrisiloxanes, while signals B and E were assigned to the cyclotetrasiloxanes, in agreement with the spectra of the product obtained by **method 1**.

Depending on the removal method of the catalyst, the reaction sites of cyclododecasiloxanes can be retained after polymerization. The presented results also indicate that the obtained polymers can be functionalized or used as modifiers.

5.4 Conclusions

Polymerization between **Cyclo12-Me-SiMe₂(OEt)** and **Cyclo12-Me-SiHMe₂** by the P-R reaction proceeded with a high degree of polymerization, and the morphology of the obtained polymer was shown to be controlled by the removal method of the catalyst. Furthermore, the condensation reaction progressed with retention of the original

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cyclododecasiloxane structures. Thus, we have demonstrated the effectiveness of the P-R reaction for the preparation of siloxane-based materials with controlled siloxane structures.

5.5 References

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Chapter 6

Conclusion

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This chapter summarizes the findings obtained by this study and also shows some remarks on the applicability of siloxane bond formation for the preparation of oligosiloxane-based compounds. Then the applicability and limit of this concept and future prospects will be mentioned. The contents of this thesis are both the novel synthetic methods of oligosiloxanes possessing alkoxy groups and the polymerization of the synthesized oligosiloxanes. The selection of both siloxane bond formation reactions and the reaction conditions is quite critical to achieve them, which is repeatedly mentioned throughout the thesis. Some principles for the synthesis and polymerization of oligosiloxanes possessing alkoxy groups are shown on the basis of the results obtained in this thesis.

Chapter 2 has clarified that oligosiloxane possessing both alkoxy groups and several organic functional groups can be synthesized by combining two kinds of non-hydrolytic siloxane bond formation reactions. Although only one kind of such an oligosiloxane was synthesized in this study, this synthetic pass can produce various oligosiloxanes by changing the starting materials. In addition, the synthesized oligomer can be polymerized by sol–gel reaction without cleaving the original siloxane bonds. This result indicates that the oligosiloxane synthesized here is a useful building block to control the composition of siloxane-based materials in a molecular level. The synthetic method developed here will contribute to the progress of synthetic chemistry and material chemistry of siloxane-based compounds.

Chapter 3 has described the substitution reaction of trimethylsilyl (TMS) groups linked to siloxane with alkoxysilyl groups, and the reaction is applied to the synthesis of oligosiloxanes possessing alkoxy groups. When the oligosiloxane having both alkoxysilyl and TMS groups was used as a precursor, the alkoxysilyl groups can be retained after substitution of TMS group with another alkoxysilyl group. This result indicates that TMS

groups can be used as a protecting group for the synthesis of oligosiloxanes. The expansion of the applicable region of this reaction will contribute to the development of synthetic chemistry of siloxane-based compounds.

Chapter 4 has described the synthesis of cyclododecasiloxane possessing alkoxy groups as side groups and the polymerization by sol-gel reaction. Although the cyclic structure of the synthesized oligosiloxane was retained after the reaction, the membrane prepared from the cyclic oligosiloxane did not show the gas permeance expected by the cyclic structure. This gas permeance may be caused by the flexibility of the cyclododecasiloxane structure and the random polymerization of the cyclododecasiloxanes. These results indicate that the control of both conformation and orientation of cyclic oligosiloxanes must be developed to use the inner space of large cyclic siloxanes. The detailed future prospects will be shown below.

Chapter 5 has proved the synthesis of cyclododecasiloxane possessing alkoxy groups and the polymerization of cyclododecasiloxanes by the Piers-Rubinsztajn (P-R) reaction. Although the side-reaction competed with the main P-R reaction, the starting oligosiloxanes were polymerized with retaining the original cyclic structures. This result shows the usefulness of the P-R reaction to polymerized oligosiloxanes to control siloxane networks.

The findings obtained by the chapters 2 and 3 have clarified that judicious choice of appropriate starting materials, by focusing the different reactivities among different alkoxy groups for non-hydrolytic SiOSi formation, is important to synthesize oligosiloxanes. It should also be noted that organosiloxane compounds possessing both trimethylsilyl and other alkoxy groups can be used as starting materials by considering the different reactivities of such functional groups. This viewpoint is one of the most basic concepts in synthetic organic chemistry. The results reported in this thesis

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show that so-called “protecting group”, very common in organic synthetic chemistry, is applicable to inorganic synthetic chemistry of siloxane-based compounds. It has been difficult to apply such a basic idea to the formation of oligosiloxane structures, which means the synthetic chemistry of oligosiloxanes is undeveloped compared with organic chemistry. This thesis will contribute to further development of the synthetic chemistry of oligosiloxanes.

In chapters 4 and 5, the polymerization of cyclododecasiloxanes without cleaving the original cyclic structures is discussed. The results shown in those chapters indicate the potential of large cyclic oligosiloxanes possessing alkoxy groups as building blocks for well-regulated siloxane-based materials. To utilize the inner space of cyclic siloxanes for separation, adsorption, and so on, the conformation and orientation of cyclic oligosiloxanes should be controlled. The inclusion of guest molecules to the inner space of cyclic siloxanes seems effective to control their conformations. For example, polymers containing ammonium groups in the main chain are expected to be a guest compound to form rotaxanes. If polyrotaxanes are formed among such polymers and cyclic siloxanes, the orientation control is also achieved after cross-linking of cyclic siloxanes and the following removal of the axis molecules. On the other hand, their chemical modifications with functional groups which show noncovalent interactions (hydrogen bond, π - π interaction, and electrostatic interaction) is effective to control the orientation of cyclic siloxanes. As an alternative approach, solid-liquid or liquid-liquid interfaces should be used to orientate cyclic siloxanes. These approaches for control of the conformation and orientation of cyclic siloxanes will contribute to organosilicon chemistry.

List of Achievements

Original articles related to this thesis

- (1) M. Yoshikawa, H. Shiba, H. Wada, A. Shimojima, K. Kuroda
“Polymerization of Cyclododecasiloxanes with Si–H and Si–OEt Side Groups by the Piers-Rubinsztajn Reaction”
Bull. Chem. Soc. Jpn. **2018**, just accepted, DOI: 10.1246/bcsj.20170410.

- (2) M. Yoshikawa, Y. Tamura, R. Wakabayashi, M. Tamai, A. Shimojima, K. Kuroda
“Protecting and Leaving Functions of Trimethylsilyl Groups in Trimethylsilylated Silicates for the Synthesis of Alkoxysiloxane Oligomers”
Angew. Chem. Int. Ed. **2017**, 56, 13990-13994.

- (3) M. Yoshikawa, H. Shiba, M. Kanezashi, H. Wada, A. Shimojima, T. Tsuru, K. Kuroda
“Synthesis of a 12-Membered Cyclic Siloxane Possessing Alkoxysilyl Groups as a Nanobuilding Block and Its Use for Preparation of Gas Permeable Membranes”
RSC Adv. **2017**, 7, 48683-48691.

- (4) M. Yoshikawa, R. Wakabayashi, M. Tamai, K. Kuroda
“Synthesis of a Multifunctional Alkoxysiloxane Oligomer”
New J. Chem. **2014**, 38, 5362-5368.

Other articles (not related to this thesis)

- (1) S. Sakamoto, M. Yoshikawa, K. Ozawa, Y. Kuroda, A. Shimojima, K. Kuroda
“Formation of Single Nanometer-scale Silica Nanoparticles by Evaporation-induced Self-Assembly”

Langmuir, in press, DOI: 10.1021/acs.langmuir.7b04042.

- (2) Y. Komata, M. Yoshikawa, Y. Tamura, H. Wada, A. Shimojima, K. Kuroda
“Selective Formation of Alkoxychlorosilanes and Organotrialkoxysilane with Four
Different Substituents by Intermolecular Exchange Reaction”
Chem. Asian J. **2016**, *11*, 3225-3233.

Oral and poster presentations

- (1) 井川華子, 吉川昌, 和田宏明, 下嶋敦, 黒田一幸
“長鎖アルキル基を有する 6 員環シロキサンの自己集合によるナノ構造体
の作製”
第 56 回セラミックス基礎科学討論会, 2A09, つくば国際会議場, 茨城, 2018
年 1 月
- (2) 森岡春香, 近藤壮一, 吉川昌, 下嶋敦, 和田宏明, 黒田一幸
“ポリシロキサンの側鎖ビニル基の配列制御に向けたオリゴシロキサンの
重縮合”
第 36 回無機高分子研究討論会, 4, 東京理科大, 東京, 2017 年 11 月
- (3) 杉山朋陽, 司馬寛也, 吉川昌, 和田宏明, 下嶋敦, 黒田一幸
“アルコキシシリル基を有する六員環シロキサンの加水分解・重縮合”
第 7 回 CSJ 化学フェスタ 2017, P3-006, タワーホール船堀, 東京, 2017 年
10 月
- (4) 森岡春香, 近藤壮一, 吉川昌, 下嶋敦, 和田宏明, 黒田一幸

“側鎖ビニル基の配列が制御されたポリオルガノシロキサンの精密合成”

第7回 CSJ 化学フェスタ 2017, P1-120, タワーホール船堀, 東京, 2017 年
10 月

(5) 井上なつみ, 吉川昌, 下嶋敦, 和田宏明, 嶋田豊司, 黒田一幸

“Meerwein 試薬を用いた F 含有チタン酸化物の合成”

日本セラミックス協会 2017 年年会, 日本大学, 東京, 2017 年 3 月

(6) 井川華子, 吉川昌, 和田宏明, 下嶋敦, 黒田一幸

“アルキル基を有する環状シロキサンの自己集合によるナノ構造体の作製”

第6回 CSJ 化学フェスタ 2016, P7-011, タワーホール船堀, 東京, 2016 年
11 月

(7) 司馬寛也, 吉川昌, 任秀秀, 金指正言, 都留稔了, 和田宏明, 下嶋敦, 黒田
一幸

“分離膜応用に向けた大環状シロキサンからなるシロキサン系薄膜の作製
とその気体透過特性”

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“環状シロキサンをビルディングブロックとしたシロキサン系材料の作製”

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11 月

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“分離膜応用に向けた大環状シロキサンからなるゾル-ゲル薄膜の作製とその気体透過特性”

第3回 ZAIKEN フェスタ, 3M03, 各務記念材料技術研究所, 東京, 2016年11月

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