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Silanols as Building Blocks for Nanomaterials

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1.1 Introduction

Silanols have been recognized as reactive intermediates and easily condense to form siloxanes. Therefore, most of the early research on the synthesis and isolation of organosilanols utilized an introduction of bulky substituents. The condensation of silanols is accelerated by an existence of acid or base; therefore preparation from chlorosilanes or alkoxysilanes often encountered further condensation reactions. However, when several important factors (acid, base, concentration, temperature) were carefully considered in the reactions, isolation of organosilanols even with smaller substituents was possible, and many isolated silanols have been shown to be stable in the air. Recently accumulating results have been recorded on the isolation of silanols [1, 2].

Silanols are silicon analogue of alcohols; however, in addition to the monosilanols (R₃SiOH), silanediols and silanetriols (R₂Si(OH)₂ and RSi(OH)₃) are also isolable. Because hydroxyl groups play an important role in interactions of molecules or biological species, silanols with multiple hydroxyl groups (often quoted as polysilanols) were expected to serve as useful components of hydrogen-bonded supramolecular aggregates [3, 4] or host molecules [5]. In addition, polysilanols are also potential precursors of siloxanes or silsesquioxanes with well-defined structures [6–10] because various bonding schemes are possible. Detailed chemistry of polysilanols can be found in reviews [11–13].

Most of silicone materials have been produced by controlled hydrolysis/condensation from monosilanes like halosilanes or alkoxysilanes. However, this method affords only kinetically or thermodynamically most stable compounds,
and usually well-defined nanomaterials could not be obtained. In order to construct defined structure of siloxanes, coupling reactions from two different compounds (cross-coupling reaction) are necessary. The reaction from chlorosilanes and silanols in the existence of organic base to form siloxane [8, 9] has been mostly utilized. More recently catalytic siloxane formation from hydrosilanes and silanols/alkoxysilanes was developed [14, 15] and has been widely employed for nanomaterial synthesis. As clearly seen in these examples, silanols are most potential precursors of well-defined siloxanes.

In this chapter, our results in the last two decades regarding synthesis and structure identification of silanols and their application to the precursors of nanomaterials are summarized.

1.2 Synthesis and Applications of Silanols

1.2.1 Silanetriols and Disiloxanetetraols

Our first encounter with polysilanols was in the process of synthesis of cage silsesquioxanes [6]. Although cage octasilsequioxanes have been prepared easily from trichlorosilanes or trialkoxysilanes, small cages, for example, hexasilsequioxanes, were hard to obtain [16]. In order to obtain smaller cages, we introduced bulky groups to stabilize strained cage framework. According to the typical synthetic method for cage silsesquioxane, we examined the hydrolytic condensation from \(t\)-BuSiCl\(_3\) or ThexSiCl\(_3\) (Thex = 1,1,2-trimethylpropyl) to obtain cage hexasilsesquioxanes. Against expectation, obtained white solid was not the targeted hexasilsesquioxanes but silanetriols (\(t\)-BuSi(OH)\(_3\) and ThexSi(OH)\(_3\)). Interestingly, both compounds are air-stable white solid and can be stored without problems. We then traced back the literatures and optimized the reaction condition (Scheme 1.1). Synthesis of \(t\)-BuSi(OH)\(_3\) was effected by following the method by Roesky’s group [17]; thus \(t\)-BuSiCl\(_3\)

\[
\text{RSiCl}_3 \xrightarrow{\text{aniline, H}_2\text{O}} \text{RSi(OH)}_3
\]

\(R = t\)-Bu, 1,1,2-trimethylpropyl (Thex)

\[
\text{RSiCl}_3 \xrightarrow{\text{KOH, SiO}_2, \text{H}_2\text{O}} \text{RSi(OH)}_3
\]

\(R = t\)-Bu, 1,1,2-trimethylpropyl (Thex)

Scheme 1.1 Preparation of silanetriols and disiloxanetetraols.
was treated with aniline/water in ether, and target compound was obtained. For ThexSi(OH)₃, we applied Takiguchi’s method [18] and silanetriols were obtained in 64% yield from ThexSiCl₃.

Similarly, disiloxanetetraols were also obtained from trichlorosilanes. By following the Sommer and Tyler’s method [19], reaction of ThexSiCl₃ with KOH, silica gel, and water in ethanol afforded 1,3-bis(1,1,2-trimethylpropyl)-1,1,3,3-tetrahydroxydisiloxane in 47% yield. Disiloxanetetraol with tert-butyl groups was obtained from t-BuSiCl₃ by the reported method by Lickiss et al. [20].

With four silanols in hand, we then tried the synthesis of silsesquioxanes from silanols. At that time, many silanols were isolated and structures were determined; however, reactions starting from silanols were not known. In order to stabilize silanols against dehydration, most of isolated silanols possess bulky substituents, and their reactivity was low. We determined to use dicyclohexylcarbodiimide (DCC) as dehydrating reagent, and after several examinations of reaction conditions, we found that reactions at higher temperature in polar solvent afforded the target compounds. Thus treating silanetriols or disiloxanetetraols with DCC in dimethyl sulfoxide (DMSO) or DMF at 120°C, cage hexasilsesquioxanes were obtained in 25–41% yields (Scheme 1.2). We carefully examined the reaction mixture, but no other cage silsesquioxanes (T₈ or T₁₀) were not obtained. The structure of hexasilsesquioxane was established unequivocally by X-ray crystallographic analysis. Prior to our work, synthesis of cyclohexyl-substituted hexasilsesquioxane was reported by the reaction from cyclohexyltrichlorosilane in acetone/water for 4 months [21, 22]. Our method offered more facile access to hexasilsesquioxanes.

Later we applied this reaction to other silanols and obtained several cage silsesquioxanes (Scheme 1.3). Cage hexasilsesquioxanes with bulky mesityl...
(Unno, M., Imai, Y., Matsumoto, H., unpublished result) or Tip (triisopropylphenyl) groups [10] were obtained from respecting silanols by the reactions with DCC. In the case of mesityl-substituted silanols, both hexasilsesquioxane (6%) and octasilsesquioxane (20%) were obtained (Unno, M., Imai, Y., Matsumoto, H., unpublished result). Similar reaction starting from dicyclopentadienyltetraol afforded octasilsesquioxane in 13% yield [7].

It should be noted that hexasilsesquioxane with the most bulky Tip group showed interesting structure [10]. With bulky triisopropylphenyl groups, six Tip groups can only rotate with gear-like motion. In the single crystal, a pair of enantiomer exists and Tip groups are twisted like three blades of a propeller (Figure 1.1). In solution, gear-like rotation could be observed by $^1$H NMR; two different singlet peaks are observed for aryl protons at low temperature ($\text{exo}$-proton: outer of the cage; $\text{endo}$-proton: inner of the cage (see Figure 1.1)), and Tip groups start rotating by elevating temperature. The coalescence temperature was 38°C, and above this temperature, Tip groups freely rotate to show only single acrylic proton. The activation free energy ($\Delta G^*$) was calculated to be 14.8 kcal mol$^{-1}$.

Scheme 1.3 Synthesis of hexasilsesquioxanes from silanols.
As shown in these results, hexsilsesquioxanes with relatively smaller substituents were hard to be obtained because octasilsesquioxanes generate preferably. We applied a reaction from cyclic silanols (details are described in the following section), and reaction with tetrachlorodisiloxane afforded isopropyl-substituted hexasilsesquioxane [8]. This is the hexasilsesquioxane ever known with the smallest substituents (Scheme 1.4). Cage octasilsesquioxane was also obtained from cyclic silanols [8].

Octasilsesquioxanes could also be prepared from disiloxanetetraol. From cyclohexyl disiloxanetetraol, reaction with DCC in DMSO at 120°C afforded octasilsesquioxane in 13% yield (Scheme 1.5) [7]. When cyclohexyltrichlorosilane was hydrolyzed and condensed in acetone/water, hexasilsesquioxane was obtained as reported [21]. More recently Bassindale and Taylor’s group reported the synthesis of cage silsesquioxanes by nonaqueous hydrolysis of trichlorosilanes with DMSO [23]. In our case starting from silanol, high reaction temperature favored the generation of more thermodynamically stable T₈ cage.

1.2.2 Cyclotetrasiloxanetetraol (Cyclic Silanols, All-cis Isomer)

At the same time we investigated cage silsesquioxanes, we were also interested in ladder silsesquioxanes. Although the structure was proposed in 1960 [24]
and various superior properties were expected, obtaining well-defined ladder silsesquioxanes is still challenging. Our first trial to obtain ladder silsesquioxanes was targeting bicyclic ones, and we treated tetrachlorodisiloxane with disiloxanetetraol. The reaction is simple dehydrochlorination reaction, and we succeed to obtain a mixture of stereoisomers with expected molecular weight. We isolated all isomers by recycle-type HPLC, and the structures were determined by X-ray crystallographic analysis. To our surprise, obtained compound was not bicyclic ladder silsesquioxanes but a stereoisomer containing two six-membered rings (Scheme 1.6) (Unno, M.; Suto, A.; Matsumoto, H., unpublished result).

With this result, we realized that fused eight-membered ring ladder silsesquioxanes could only be obtained from the precursors containing cyclotetrasiloxane rings. Then we set the target compound to be the cyclotetrasiloxanes
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with reactive substituents. As we already knew that silanols were stabilized with even relatively smaller substituents, we chose isopropyl groups as substituents. As shown in Scheme 1.7, we first applied the stepwise synthesis [4]. After obtaining the target compound, we also succeeded to prepare the compound directly from isopropyltrichlorosilane [8].

The key step of laddersiloxane synthesis is substitution reaction of phenyl groups into chlorine atoms. Aluminum chloride has been known to cleave Si–O bonds [25], so this dephenylchlorination was not applied to siloxanes.
However, if substituent on silicon atom is larger than methyl, replacement reaction occurs in quantitative yield. This reaction is also an important step to obtain well-defined laddersiloxanes [9].

Cyclic silanols with the similar structure were previously reported, and substituents were phenyl [26] and cyclohexyl [21] groups. However, there was no evidence for the all-\textit{cis} conformation. Out of four possible stereoisomers (Scheme 1.8), \textit{cis,cis,trans}-isomer can be identified with NMR spectra because three independent silicon atoms and substituents exist. On the other hand, identification of other three isomers is impossible from spectroscopic analysis. In order to construct ladder structures, stereostructure of the starting compound is very important; therefore we tried to obtain a single crystal to determine the structure. Unfortunately, crystallinity of obtained isopropyl cyclic silanol was not good, and no suitable crystals were obtained after several months of trials. Finally a single crystal generated from the solvent containing water, and the result clearly indicated the structure was all-\textit{cis} [4]. Almost at the same time, Feher’s group succeeded to determine the structure of phenyl-substituted cyclic silanol [27]. We also reported the crystallographic analysis of supramolecular aggregates of this cyclic silanol with \textit{i}-Pr$_2$Si(OH)$_2$ [3].

As expected, obtained cyclic silanol served as a quite potential starting material for well-defined siloxanes. For example, perfect ladder silsesquioxanes (we termed “laddersiloxane” for those whose structure was unequivocally determined) up to nonacyclic could be obtained starting from cyclic silanols. As an example, synthesis of pentacyclic laddersiloxane is shown in Scheme 1.9 [9].

This synthesis was based on the coupling reaction of silanols with chlorosilanes. We investigated several combinations of base and solvent and found out that using pyridine as solvent afforded highest yield. As mentioned in the previous section, exchange reaction of phenyl groups into chlorine atoms is also a key step of this synthesis. Obtained laddersiloxanes were mixture of isomers because of the orientation of terminal isopropyl and phenyl groups; however, the stereostructure of starting cyclic silanol (all-\textit{cis}) was perfectly maintained throughout the synthesis, and no stereoisomerization of siloxane framework was observed. The structure of pentacyclic laddersiloxane was determined by X-ray crystallography [9].
Syntheses of well-defined siloxanes starting from all-cis cyclic silanol are summarized in Scheme 1.10. Not only laddersiloxanes, cage silsesquioxanes, or metallasiloxanes [28] (obtained from cyclic silanols and (CpTiCl2)2O) could also be accessed from this single starting compound, showing its versatility.

In the synthesis of longer laddersiloxane, we developed a stereocontrolled approach by use of single diastereomer [29]. Chemistry of laddersiloxanes is summarized in a recent review [30].

Even though the stepwise synthesis afforded the highly ordered laddersiloxanes, preparation of ladder polysilsesquioxanes is still a challenging topic. Condensation of cyclic silanols seems to offer an effective pathway to ladder polysilsesquioxanes; however, cyclic silanols are basically stable and no condensation is observed in neutral condition. Kawakami’s group reported that phenyl cyclic silanols showed stereoisomerization by an action of acid [31]. In the existence of base, siloxane bond cleavage may occur and random structure is possibly obtained. We developed the neutral dehydration reaction using DCC, but only cage silsesquioxanes were obtained from all-cis cyclic silanols (Scheme 1.4). Therefore, currently possible pathway to perfect ladder polysilsesquioxane can be (a) cross-coupling reactions of cyclic silanols with other substituted cyclotetrasiloxanes in a condition to avoid stereoisomerization or (b) self-condensation of cyclic silanols other than...
Scheme 1.10 Well-defined siloxanes prepared from cyclic silanols.
all-cis structure (e.g., cis,trans,cis-isomer). In Scheme 1.11, our approach to ladder polysilsesquioxanes using cis,trans,cis-tetrabromocyclotetrasiloxane is depicted. Starting from readily available methylphenyldichlorosilane, dehydration/condensation in THF/water afforded a mixture of 6-, 8-, and 10-membered cyclic siloxanes with various stereostructures. Surprisingly, targeted cis,trans,cis-cyclotetrasiloxane could be obtained as white solid by direct recrystallization of the mixture. Treatment of cyclotetrasiloxane with bromine afforded tetrabromide, and the stereostructure was confirmed by transfer to tricyclic ladder siloxane. This tetrabromide was moisture sensitive, and when the compound was in the air, spontaneous hydrolysis and following condensation occurred to give white solid. Although X-ray structure analysis was not possible, the product indicated the highly ordered structure from NMR and IR spectra and from high thermal stability [32]. Unfortunately obtained white solid was insoluble to organic solvents. Then we are now investigating the synthesis of soluble ladder polysilsesquioxanes with different substituents.

Our synthesis of cyclic silanols was accomplished by treatment of chlorosilanes with water in an appropriate solvent. Then various products were possible and the yields were not satisfactory. Following our report, Shchegolikhina’s group developed a high-yield synthesis of cyclic silanols by isolating sodium or potassium silanolate [33–35]. Metal salts of organosilanols or organosilanolates were isolated and identified by Feher et al. [36], Roesky et al. [37], or Corriu’s group [38], and the Russian group showed the first result of cyclotetrasiloxane silanolates. As shown in Scheme 1.12, phenyltrialkoxysilane was treated with
aqueous NaOH in butanol. After the reaction, generated white needles were collected and then treated with hydrochloric acid. The target tetraphenylcyclotetrasiloxanetetraol was obtained in 80% yield. The structure (all-cis) was determined by X-ray crystallography.

By this method, cyclic silanols with various substituents were obtained in relatively good yield with simple procedure. We applied this synthesis to various alkoxysilanes and obtained silanlates in good yields. For example, isobutyl-substituted cyclic silanol was obtained in 74% yield from commercially available alkoxysilane. By optimizing the condition, we improved the yield from the reported one (34%) (Scheme 1.13).

Both sodium silanolate and silanol possessed all-cis configuration, indicating no stereoisomerization occurred. It should be noted that stereoisomerization of cyclic silanols easily occurred by an action of HCl. As shown in Scheme 1.14, all-cis phenylcyclotetrasiloxanetetraol afforded all four isomers after treatment of 1 M HCl in acetone for 10 min at room temperature. In order to avoid stereoisomerization, reaction with aqueous HCl must be maintained at low temperature and keep the reaction time short.
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We then investigated the preparation of silanolates in detail in order to obtain the optimized condition. We treated commercially available phenyltrimethoxysilane with aqueous NaOH in 2-propanol. By adjusting the concentration to 2 mol l\(^{-1}\), highest yield 99% was recorded after 17 h of reaction at room temperature. Obtained solid indicated single peak in \(^{29}\text{Si} \text{NMR in D}_2\text{O} (−54.8 \text{ ppm}), and all-cis structure was determined by treatment with dimethylchlorosilane to give all-cis siloxycyclotetrasiloxane, whose structure was established by X-ray crystallography (Scheme 1.15) [39].

Similar transformation could be applied to isobutyl- and vinyl-substituted silanolates. As shown in Scheme 1.16, substitute dimethylsiloxycyclotetrasiloxanes were obtained by facile single-step reaction from trimethoxysilanes. In these reactions, no purification of sodium or potassium silanolates was necessary; silylation after filtration and drying of the crude product afforded good results [39]. In the case of vinyl-substituted compound, potassium hydroxide gave better yield. In addition, treatment of dimethylchlorosilane resulted in the
stereoisomerization in the case of vinyl compounds. Therefore, triethylamine was added to the reaction mixture to avoid isomerization. In each reaction, selection of the solvents is important because solubility of these salts is different by substituents.

It is noteworthy that these extended cyclic siloxanes contain reactive vinyl or hydrosilyl groups. Therefore these compounds are potential precursors for highly ordered siloxanes or siloxane-containing organic polymers.

In addition, oxidation of these hydrosilanes with $m$-chloroperbenzoic acid ($m$CPBA) afforded silanols (Scheme 1.17). These silanols are also interesting in view of precursors of siloxanes as well as host molecule for anions with extended silanol arms [39]. The structures of both compounds were established by X-ray crystallographic analysis. In the crystal, the molecules form hydrogen-bonded dimer.

**Scheme 1.17** Synthesis of cyclotetrasiloxanes with extended silanol arms.

1.2.3 Cyclotetrasiloxanetetraol (Cyclic Silanols, Other Isomers)

As shown in Scheme 1.10 and following schemes, all-$cis$ cyclic silanol showed its capacity as the precursors of various well-defined siloxanes. This fact also indicates the potential of other three stereoisomers. For example, as shown in scheme 1.11, $cis,trans,cis$-isomer is the most promising starting compound for ladder polysilsesquioxanes, because only this isomer is capable of generating straight-chain polymers with unlimited molecular weight. With this point of view, we investigated the synthesis of other three isomers. When we started this project, there was a report of the isomerization of all-$cis$-[PhSiO(OH)]$_4$ with catalytic amount of organochlorosilane (Me$_3$SiCl, Me$_2$SiCl$_2$, HCl, or
acetic acid [40]. However, in this case no results for isolation and identification of each isomer were shown. Even though the isomerization from all-\textit{cis} isomer is most desirable because all-\textit{cis} isomer can be obtained in high yields, separation of stereoisomer of silanols seems to be difficult. Therefore, we devised a method: (i) separation of stereoisomers of phenyl-substituted cyclotetrasiloxane (D₄), (ii) replacement of phenyl groups of each compound with chlorine atom by dearylchlorination reaction, and (iii) hydrolysis of tetrachloride to afford silanols. The key step of this synthesis is dearylchlorination step, and we have to maintain the stereostructure during this reaction. Fortunately, all reactions including hydrolysis proceeded in a stereospecific manner, and targeted isomers of cyclic silanols were all isolated. The structures were unequivocally established by X-ray crystallography (Scheme 1.18) [41].

Interestingly melting points of these isomers were quite different from each other (\textit{cis,trans,cis}: 186–187°C, \textit{cis,cis,trans}: 157–158°C, all-\textit{trans}: 160–161°C, and all-\textit{cis}: 165–169°C), reflecting the different hydrogen bonding schemes.

Although this procedure allows us to access each isomer for the first time, separation of stereoisomers with HPLC (first step) prohibited obtaining target compounds in gram quantities. More recently, the Japanese group [31] and Russian group [42] independently reported the acid-catalyzed isomerization of phenyl-substituted cyclic silanols. In 2014, Yagihashi and Shimada’s group reported the synthesis and isolation of stereoisomers of phenyl-substituted cyclotrisiloxanetriols [43]. Their method could be applied to cyclotetrasiloxanetetraols to isolate stereoisomers. With these results, obtaining isomers of phenyl-substituted cyclic silanols in larger amount is now possible; however those with alkyl or vinyl groups could not be acquired yet.

1.2.4 Cyclotrisiloxanetriol

For cyclic silanols, there is another example other than cyclotetrasiloxanetetraol, that is, cyclotrisiloxanetriols with smaller ring size (Scheme 1.19). Because six-membered siloxane rings are more strained than eight-membered ones, ring-opening reactions were known. Therefore, isolation of cyclotrisiloxanetriol was limited to those with large substituents or inclusion in the inorganic cage in the early stage.

There were several synthetic reports for [RSiO(OH)]₃ (R = Ar(Me₃Si)N (Ar = 2,6-dimethylphenyl) [44], (Me₃Si)₂CH [45], Ph [43, 46], \textit{m}-tolyl [47], 2-naphthyl [48], Tip (2,4,6-triisopropylphenyl) [49], and 3,5-xylyl [46]. Among these examples, some cyclotrisiloxanetriols were stabilized by bulky substituents: \textit{cis,trans}-[Ar(Me₃Si)NSiO(OH)]₃ (Ar = 2,6-dimethylphenyl) [44] and all-\textit{cis}-[(Me₃Si)₂CHSiO(OH)]₃ reported by Roesky et al., and \textit{cis,trans}-[TipSiO(OH)]₃ by our group [49]. As another approach, all-\textit{cis}+[RSiO(OH)]₃ (R = Ph, \textit{m}-tolyl,
Scheme 1.18  Synthesis of all isomers of cyclic silanols.
2-naphthyl, 3,5-xylyl) were isolated by stabilization in self-assembled coordination cages. In many cases, cyclotrisiloxanetriols have been synthesized by multistep reaction. In all aforementioned cases, cyclic silanols were protected by bulky substituents or included in a cage system. Therefore reactions starting from those silanols were not known. We thought, as in the case of cyclotetrasiloxanetetraols, that these cyclotrisiloxanetriols could serve as useful precursors of highly ordered siloxanes. For this point of view, we investigated the synthesis of cyclotrisiloxanetriols with relatively smaller substituents.

If hydrolytic condensation is applied to substituted trichlorosilanes or trialkoxysilanes, larger cyclotetrasiloxane rings generated with small substituents. Then we devised a new approach: dearylchlorination followed by hydrolysis.
yield. Then we applied the reaction with ZnO. This reaction favors the generation of kinetic products (smaller rings), and target compound was obtained with several by-products. When o-tolyl group was introduced in order to increase the steric hindrance, hydrolytic condensation then worked well and cyclotrisiloxanes were obtained in satisfactory yields [50].

As in the case of cyclotetrasiloxanes, dearylchlorination proceeded and chlorosiloxanes were obtained. Because generated chlorosilanes were unstable toward moisture, we subsequently treated the crude product with water to generate the corresponding silanols. After work-up, recrystallization of crude mixture afforded targeted cyclic silanols. However, not like the case of cyclotetrasiloxanes, this reaction did not proceed in stereospecific manner, and only cis,trans-isomer was obtained selectively (Scheme 1.21) [50]. The mechanism of this selectivity is not clear yet, but stereoisomerization presumably occurred at the stage of hydrolysis by generating HCl in water, like in the case of isomerization of cyclotetrasiloxanetetraol by acid.

Similarly, tri(tert-butyl)cyclotrisiloxanetriol was obtained from cyclotrisiloxanes. Also in this case, only cis,trans-isomer was obtained selectively (Scheme 1.22). The structures of all compounds were determined by X-ray crystallography. It is noteworthy that triisopropylcyclotrisiloxanetriols have the smallest substituents of the known cyclotrisiloxanetriols at that time, but it is stable toward air and moisture and could be handled under ambient conditions without problems. Cyclotrisiloxanetriols with relatively smaller substituents can be potential precursors of well-defined silsesquioxanes in the different structures from cyclotetrasiloxanes.

As mentioned in the previous section, facile synthesis of phenylcyclotrisiloxanetriol was reported in 2014 [43]. They traced the condensation reaction from PhSi(OH)₃ and found that cyclotrisiloxanetriol was generated in certain amount in the early stage of the reaction. They isolated cis,trans-isomers by column chromatography (Scheme 1.23). Another isomer (cis,cis) was also observed by the HPLC analysis, but isolation was not possible because the

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**Scheme 1.21** Synthesis of triisopropylcyclotrisiloxanetriol.
amount was not enough. Interestingly obtained cis,trans-phenylcyclotrisiloxanetriol was stable in a crystalline form or in THF or CH3CN.

Almost at the same time, we also traced the condensation reaction previously in order to find a facile synthesis of cyclotrisiloxanetriols. As shown previously, we and another group reported the synthesis of cyclotrisiloxanetriols; however multistep reactions were necessary, or yields still need improvement. If we can offer a facile method to obtain cyclotrisiloxanetriols, application of this compound could be much easier.

In the reaction of hydrolysis/condensation from ethyl-substituted trichlorosilanes in acetone/water solution, we found that cyclotrisiloxanetriol generated in the early stage of the reaction. Then we performed the reaction at 0°C, and after 1 h, the solution was extracted by ether. The organic layer was washed with saturated aqueous NaHCO3 and brine, dried, and concentrated to afford crude solid. When we washed the crude solid with CHCl3, we could obtain the target compound as white solid (Scheme 1.24).

Although the yield was not satisfactory (4%), this method is very simple, and target compound was easily obtained in 1 h from commercially available trichlorosilane. Because cyclotrisiloxanetriols with small substituents may serve as potential precursors, this method is meaningful.

We examined this procedure in various chlorosilanes and found that cyclopentyltrichlorosilane also afforded cyclotrisiloxanetriol. Because of increasing bulkiness, we needed longer reaction time and higher temperature. In this case, after stirring
for 14 h at 20°C, white precipitate generated. This solid was collected and recrystallized from THF, and hexane afforded \textit{cis,trans}-tricyclopentylcyclotrisiloxanetriol in pure form (4%). The solution was worked up similarly, and disiloxanetetraol was obtained in 23% yield (Scheme 1.25).

1.3 Structures and Properties of Nanomaterials Obtained from Silanols

1.3.1 Structure of Laddersiloxanes

The structures of laddersiloxanes up to pentacyclic could be determined by X-ray crystallography. To obtain high-functional materials, it is valuable to determine the structure precisely and investigate structure–property relationship, because this approach makes it possible to devise the structure that is expected to show superior properties. In addition to the laddersiloxanes described previously, we also synthesized laddersiloxanes by oxidation of ladder polysilanes (Scheme 1.26) \cite{51}. With this synthesis, we could access to the \textit{anti}-type laddersiloxanes. Our stepwise synthesis started from all-\textit{cis} cyclic silanols, and stereostructure was maintained throughout the elongation steps. Then all the products contained \textit{syn}-type structure (e.g., Scheme 1.27).

All laddersiloxanes possess basically double-helix structure; however helicity is different one by one. In Scheme 1.28, structures of tricyclic laddersiloxanes
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These stereoisomers were synthesized following the procedure in Scheme 1.27 [9] and separated by recycle-type HPLC. In order to clarify the helicity, torsion angles between two terminal Si–O–Si parts are indicated. If this number is large, the structure is more helical.

For stereoisomers, helicity was basically similar because only the orientation of isopropyl and phenyl groups is different from each other. However, the melting point of each isomer was quite different. This is explained by the packing scheme or π–π interaction of phenyl groups significantly varied by the position of phenyl groups.

How about the structures of different size laddersiloxanes? The results are summarized in Scheme 1.29. For anti-laddersiloxanes with isopropyl...
Scheme 1.27 Synthesis of tricyclic laddersiloxanes. Only phenyl groups are shown in the structure, and Si–O–Si bond is shown as a line for clarity.

Scheme 1.28 Torsion angles and melting point of tricyclic laddersiloxanes. Only phenyl groups are shown in the structure, and Si–O–Si bond is shown as a line.

Scheme 1.29 Torsion angles of anti-laddersiloxanes. Substituents (isopropyl) are omitted, and Si–O–Si bond is shown as a line.
substituents, torsion angles increased by the number of rings from mono- to tricyclic, but pentacyclic laddersiloxanes showed smallest torsion angle because the symmetry center exists in the molecule.

However, *anti*-pentacyclic laddersiloxanes with four phenyl groups on the terminal silicon showed the largest torsion angle ($68.8^\circ$; Scheme 1.30). These results indicated that helical structures of laddersiloxanes significantly vary with slight difference of substituents. It should be mentioned that these helical structures are only observed in the crystal and molecular twists fast in solution and no helical enantiomers ($P$ and $M$) were observed.

### 1.3.2 Thermal Property of Laddersiloxanes

Thermal property of different laddersiloxanes offers us many insights regarding the real structures. All tricyclic laddersiloxanes and several pentacyclic laddersiloxanes form a good crystal, and X-ray structure analysis revealed that each molecule aligns in parallel. On the other hand, laddersiloxanes larger than heptacyclic afforded no crystals because of the flexibility of the framework. Therefore structures of longer laddersiloxanes are expected to be different from shorter ones. In Figure 1.2, the result of thermogravimetry (TG) and differential thermal analysis (DTA) of a single isomer of pentacyclic laddersiloxane is shown as an example. As this compound is a molecule, sublimation
was observed and most of the weight was lost at 423°C. This tendency was observed for other crystalline laddersiloxanes (tricyclic laddersiloxanes) [9].

However, laddersiloxanes longer than heptacyclic are not solid but viscous oils. The result of TG analysis of heptacyclic laddersiloxane (isomeric mixture) is shown in Figure 1.3. Because several structures are included, shoulder peak was observed, but the mixture lost its weight at 567°C [29].

In both cases, no weight loss other than sublimation was observed. As these laddersiloxanes possess isopropyl groups, thermal retro-hydro-silylation was expected to lose propene. However, such a degradation reaction was not observed for laddersiloxanes at least below the sublimation points, and they are stable up to 287°C (pentacyclic) and 326°C (heptacyclic). In Table 1.1, results of the thermogravimetric analysis of various laddersiloxanes are summarized.

Figure 1.2 TG result of a pentacyclic laddersiloxane in N\textsubscript{2}.
All laddersiloxanes excluding polycyclic ones contain isopropyl groups, and phenyl groups also exist in the terminals. Polycyclic laddersiloxane contains only methyl groups and is synthesized by the procedure shown in Scheme 1.11. The TG result of polycyclic laddersiloxane is shown in Figure 1.4. Because of its polymeric form, no sublimation was observed for this compound. Instead, weight loss was observed from 464°C and 12.4% decrease was observed at 817°C. Above this temperature, no additional weight loss was observed up to 1000°C. When all methyl groups were eliminated as methyl radicals, weight
loss was calculated to be 16%. Therefore, the skeleton of polymeric ladder structure is stable up to 1000°C. In addition, $T_d^5$ (5% weight loss temperature) for this polycyclic ladder-siloxane was 641°C. This value is significantly higher than other ladderlike silsesquioxanes that indicated $T_d^5$ between 400 and 520°C [52]. This result clearly indicates that this polymer contains flawless ladder structure.

### 1.3.3 Thermal Property of Other Silsesquioxanes

In order to construct highly stable materials, obtaining structure–stability relationship is meaningful. In addition to ladder-siloxanes, we synthesized various cyclic, cage, double-decker, and other silsesquioxanes. For the sake of excluding the effect of substituents, the phenyl group was selected in view of easy availability, thermal stability, and high refractive index. In addition to known hexaphenyldisiloxane, hexaphenylcyclotrisiloxane, octaphenylcyclotetrasiloxane, and cage octaphenylsilsesquioxane, we prepared two new ladder-siloxanes and double-decker silsesquioxane following the reactions in Scheme 1.31 [53].

Thermal properties of phenyl-substituted siloxanes and silsesquioxanes are summarized in Table 1.2. The $T_d^5$ temperatures are basically in order of the molecular weights, except that cage silsesquioxane showed slightly higher temperature than that of double-decker. Tricyclic ladder-siloxane with 6,8,6-membered rings and cage silsesquioxane did not sublime, and residue was observed at 1000°C. If all phenyl groups were removed, the remaining weight is 33% for ladder-siloxane and 40% for cage silsesquioxane. Therefore, in the case

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**Figure 1.4** TG result of methyl ladder-polysiloxane in N₂.
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of 6,8,6 laddersiloxane, it was expected that thermal bond fission occurred and part of Si–O atoms were missed as well as phenyl groups. For cage silsesquioxane, silicon carbide-like product is thought to generate.

It is noteworthy that difference of substituents substantially affects the thermal stability. Octaisopropylcyclotetrasiloxane showed Td₅ at 205°C and sublimed at 345°C (Table 1.1), while octaphenylcyclotetrasiloxane is much more stable, showing Td₅ at 343°C and sublimation at 429°C. This result indicates that effect of substituents is larger than the structure of the skeleton.
1.3.4 Refractive Indices of Silsesquioxanes

Although thermal stability of siloxane materials is superior, refractive indices of conventional silicone are relatively low. In order to use siloxane materials for high-performance LED, improvement of refractive indices is necessary. For the aim of the development of silicone materials with high refractive indices, we investigated the relationship of the structures of silsesquioxanes and indices. Because of the availability of various structures, we selected isobutyl-substituted silsesquioxanes (Scheme 1.32). Synthesis of these compounds was reported in the literature [54]. Both laddersiloxanes and cyclic siloxane were prepared from isobutyl-substituted cyclic silanol.

The results of refractive indices and the Abbe number are summarized in Table 1.3. In the case of alkyl-substituted silsesquioxanes, the difference of refractive indices was not large. Nevertheless, 6,8,6-membered laddersiloxane

![Scheme 1.32 Various silsesquioxanes for high RI materials.](image)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$n_0$ (589 nm)</th>
<th>Abbe no: $\nu_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Me}_2\text{SiO})_n$</td>
<td>1.4030</td>
<td>54</td>
</tr>
<tr>
<td>$i$-BuSi(OMe)$_3$</td>
<td>1.3908</td>
<td>62</td>
</tr>
<tr>
<td>Disiloxane</td>
<td>1.4001</td>
<td>56</td>
</tr>
<tr>
<td>Cyclotrisiloxane</td>
<td>1.4179</td>
<td>54</td>
</tr>
<tr>
<td>Cyclotetrasiloxane</td>
<td>1.4181</td>
<td>46</td>
</tr>
<tr>
<td>[6,8,6]-Laddersiloxane</td>
<td>1.4306</td>
<td>64</td>
</tr>
<tr>
<td>[8,8,8]-Laddersiloxane</td>
<td>1.4281</td>
<td>59</td>
</tr>
</tbody>
</table>
showed the highest RI values. Our previous results indicated that density of laddersiloxanes became higher with increasing lengths. This may be the reason of higher RI values. In addition, 6,8,6-membered laddersiloxane also recorded the highest Abbe numbers, indicating low dispersion. There is a tendency that high RI value materials often show lower Abbe numbers; laddersiloxanes may be promising for high RI value with low dispersion materials.

### 1.4 Summary and Outlook

Silanols, formerly regarded as unstable intermediates, have now been revealed to possess a capacity to show diverse chemistry. In addition, silanols are also linkers of organic and inorganic materials. Further development will be expected.

### References

18 Takiguchi, T. J. Am. Chem. Soc. 1959, 81, 2359.