Research Article

Characterization and Some Insights into the Reaction Chemistry of Polymethylsilsesquioxane or Methyl Silicone Resins

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Structural characterization of a polymethylsilsesquioxane (PMSQ) and a DT-type methyl silicone resin (MeDT) has been carried out by various instrumental analyses including GPC, NMR, gas chromatography, and gas chromatography-mass spectrometry. Although the PMSQ had a Mw around 5000, the resin contained a significant amount of low molecular weight species consisting of T^2 [MeSi(OH)$O_{2/2}$] and T^3 [MeSiO$_{3/2}$] units, ranging from $T^3_4 T^2_3$ to $T^3_8 T^2_2$ including many isomers. One isomer of $T^3_6 T^2_2$ was isolated of which structure was determined as a cage structure. The species are supposed to consist mainly of cyclotetra- and cyclopentasiloxanes, but presence of strained rings such as cyclotrisiloxane rings also was suggested. In MeDT, species in which the T^2 units in the molecules from PMSQ is replaced with D^2 [Me$_2$SiO$_{2/2}$] were found, for example, $T^3_6 D^2_2$, suggesting that general silicone resins consist of similar structures as silsesquioxanes. The Mark-Houwink exponent for these methyl resins was ~0.3, indicating the molecular shape to be compact. Investigation on the formation chemistry of the cubic octamers indicates that siloxane bond rearrangement is an important mechanism in the molecule build-up process.

1. Introduction

Silicone resins are a class of polysiloxane material primarily built from T (RSiO$_{3/2}$) and Q (SiO$_{4/2}$) units, thus have much higher crosslink density than elastomers that mainly consist of D unit (R$_2$SiO$_{2/2}$) [1, 2]. The M (R$_3$SiO$_{1/2}$) and D units are also used as components in silicone resins but usually at much lower concentrations. In silicone industry, silicone resins are defined as solvent-soluble materials that are stable at room temperature and have functionalities for further crosslinking to give insoluble materials in the final application forms like coatings. In this sense, silicone resins can be differentiated from sol-gel materials in which the final insoluble materials are formed in many cases directly from monomers, although the synthetic chemistry is essentially the same. One of the forms of silicone resins that consists exclusively from T units is called silsesquioxanes or polysilsesquioxanes [2–6]. Silicone resins or silsesquioxanes are known since the beginning of silicone industry in the 1930s

[7], but traditionally these materials have been captured via simple parameters including the molar ratio of substituents to the silicon atom, R/Si ratio (1.0–1.7), molar ratio of phenyl substituent to methyl, and molecular weight. However, little has been known on what structural features are responsible for which property as well as what reaction mechanism results in what structure.

Polyphenylsilsesquioxane (PPSQ) has been often referred to as a ladder polymer since Brown Jr. et al. reported the polymer to have *cis*-syndiotactic conformation [8, 9]. They assigned the structure by X-ray diffractometry (XRD), IR, UV, bond angle calculation, and the exponent *a* value in the Mark-Houwink equation. However, these data do not appear to be sufficient to claim such a defined structure. The XRD pattern is reported by Andrianov et al., which is questionable for a *cis*-syndiotactic structure [10, 11]. Some papers refer to the material as ladder polymers if there are no silanols left or simply by the IR spectra showing two bands at ~1150 and ~1050 cm^{-1} [2], but these data cannot always be
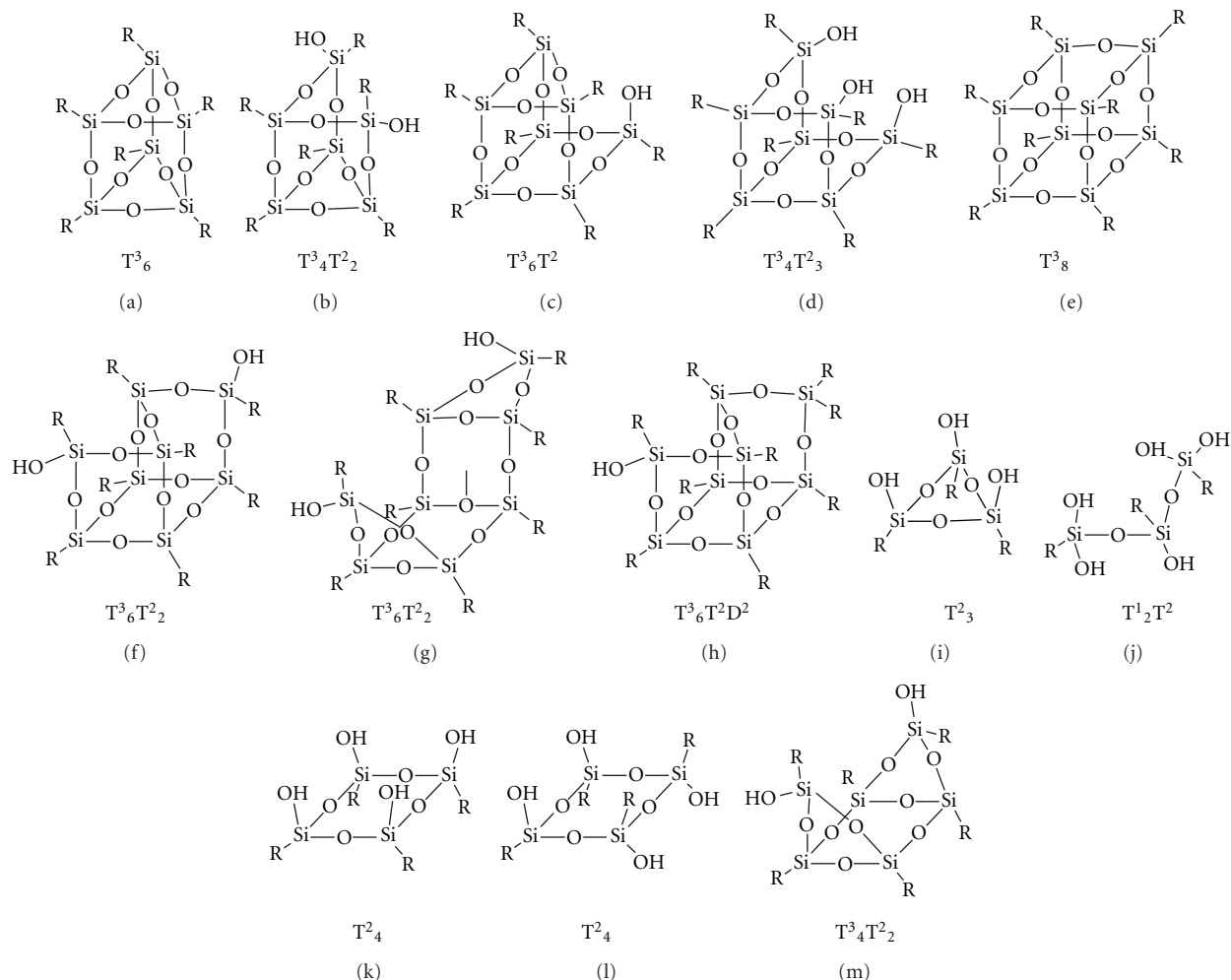
FIGURE 1: Possible structures of silsesquioxanes or silicone resins. Structure (f) was identified in the present study; (a), (e), and (i) have most probably no choice other than these structures; (b), (d), and (j) are identified with other substituents (see the text below); the presence of (h), (k), and (h) are likely; (c), (g), and (l) is possible structures from the chemical formulae.

evidence for a ladder structure. Park and coworkers indicated by calculation that the IR band around 1150 cm^{-1} is derived from the parallel asymmetric Si–O–Si stretch vibration mode while the lower-frequency band around 1050 cm^{-1} is the asymmetric Si–O–Si stretch; thus incompletely condensed cages or T^3_6 cage shown in Figure 1(a) can show these two bands [12]. Among these characterization techniques, the a value in the Mark-Houwink equation is repeatedly reported to give values around 1 [13–15], implying that PPSQ has random coil to rod-like shapes. In their dilute solution study, Helminiak and Berry concluded that the conformation of PPSQ can be represented with a worm-like chain model with a persistence length of 75 Å [16]. Frye and Klosowski strongly opposed the ladder structure and suggested a more or less randomly linked array of polycyclic cages [17]. Real ladder structures can be found only for low molecular weight oligomers, up to heptacyclic ladder structures with isopropyl substituent as prepared by a

stepwise synthesis [18–21] or by oxidation of ladder oligosilanes [22]. Preparation of ladder-like polymethylsilsesquioxanes (PMSQs) by spontaneous condensation of *cis-trans-cis*-tetrabromotetramethylcyclotetrasiloxane is suggested by Chang and coworkers [21]. It does not appear that the material is ultimately proven to have a ladder structure or it may not be known how one can prove a resin having a ladder structure, but an interesting observation in this work is that the IR spectrum of this PMSQ exhibits two absorption bands at 1130 and 1030 cm^{-1}, while tri- or pentacyclic ladder oligomers or a T^3_6 cage (all isopropyl substituted) does not show such clear pair of the two bands. Seki et al. reported the preparation of ladder-like PMSQs by the hydrolytic polycondensation of an isocyanate-functional cyclic tetramer of methyl T^2 having the structure of Figure 1(l) [23]. The triple-detector GPC gave a Mw of 285,000 and a Mn of 110,000 with the Mark-Houwink a value of 0.53. This a value is much lower than what can be claimed as a rigid rod

molecule, but is higher than common PMSQ (*vide infra*), suggesting that this PMSQ may have somewhat extended molecular shape. Another PMSQ with a Mw of 214,000 and a Mn of 71,000 prepared from a hydridofunctional cyclic tetramer showed the a value of 0.38. Both these two PMSQs showed the distinct two bands at 1150 and $1130\,cm^{-1}$ in the IR spectra, indicating that the two IR bands are not directly associated with a ladder structure.

In contrast to more uncertain ladder structures, cage structures are identified in many reports. For instance, completely condensed cages around the cubic octamers with various substituents including methyl, n-hexyl, and phenyl are reported in old and new papers [3–6, 24, 25]. For a hydrogen silsesquioxane (HSQ) synthesized by the toluene-sulfuric acid method [26], Agaskar and Klemperer carefully fractionated cages [27]. They identified completely condensed $^{H}T^{3}_{8}$, $^{H}T^{3}_{10}$, $^{H}T^{3}_{12}$, $^{H}T^{3}_{14}$, and $^{H}T^{3}_{16}$ cage molecules using gas chromatography, ^{1}H and ^{29}Si NMR, elemental analysis, and mass spectrometry. Synthesis and identification of compounds with the structures of Figures 1(a), 1(c), 1(d), and 1(f) having cyclohexyl group as the substituent are presented by Feher and coworkers [28]. Most of these molecules consist of cycloterta- and cyclopentasiloxane rings, but the presence of strained cyclotrisiloxane rings in the structures of Figures 1(a) and 1(c) is also reported.

Methyltrichlorosilane is the most abundant low cost starting material in silicone industry as compared to phenyltrichlorosilane or trichlorosilane. Thus PMSQ or methyl silicone resins are one of the most important materials among silicone resins. In this work, structural characterization of a PMSQ will be described with some insight into the reaction chemistry. The materials were prepared by a simple hydrolytic polycondensation with excess water, which is not a very specific synthetic procedure to form characteristic structures. The interpretation of the ^{29}Si NMR spectra was revisited by trimethylsilyl-($Me_{3}Si$-) capping of the silanol. The presence of low molecular weight compounds was then studied by gas chromatograph (GC) and GC-mass spectrometry (MS) analyses for $Me_{3}Si$-capped species. Isolation of a compound was tried to identify the structure by X-ray crystallography. The understanding of the chemistry for the formation of such molecules was explored by analyzing the reaction species at earlier stage of the hydrolytic polycondensation and by reacting the isolated molecule of known structure in a similar reaction condition trying to uncover the development of the structures during the course of the reaction.

In addition to the PMSQ, a DT-type methyl silicone resin, denoted as MeDT, having a small amount of D unit in addition to the T unit, was studied to compare with the PMSQ. This will show the structural characteristics of a more typical industrial silicone resin and will help verifying the generality of the findings for the PMSQ.

As usually practiced in silicone industry, the term "T" in this paper denotes species derived from $RSiX_{3}$ (X denotes Cl or OR) by hydrolytic condensation. Consequently, structures in the resin denoted as a T unit could contain $RSi(OH)_{3}$,

$RSi(OH)_{2}O_{1/2}$, $RSi(OH)O_{2/2}$, and $RSiO_{3/2}$. These four structures are described as T^{0}, T^{1}, T^{2}, and T^{3}, respectively (the numbers in superscript denote the number of siloxane bonding). Likewise, a D unit represents those species derived from $R_{2}SiCl_{2}$ containing $R_{2}Si(OH)_{2}$, $R_{2}Si(OH)O_{1/2}$, and $R_{2}SiO_{2/2}$, abbreviated as D^{0}, D^{1}, and D^{2}, respectively.

2. Experimental

2.1. Materials. Methyltrichlorosilane (Kanto Chemical), dimethyldichlorosilane, octamethylcyclotetrasiloxane (D_{4}) (Shin-Etsu Chemical), N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA), methyl isobutyl ketone (MIBK, 4-methyl-2-pentanone), dichloromethane, 2-methylpentane, chloroform, distilled water, magnesium sulfate (Wako Pure Chemical), deuterated chloroform ($CDCl_{3}$), and tetrahydrofuran (THF) (Aldrich) were used without further purification.

2.2. Analytical Techniques. GPC curves were obtained using a Tosoh HLC-8020 gel permeation chromatograph equipped with a refractive index detector and two Tosoh TSKgel GMH_{XL}-L columns eluted by chloroform at the flow rate of 1.0 mL/min. The molecular weight was determined relative to polystyrene standards. The calibration curve was corrected for each run from the difference in the retention time of cyclohexane as the internal standard assuming that the retention times of the polystyrene standards and the resin molecules are proportional to the shift of the retention time of the internal standard.

The chromatographic equipment for the GPC with triple detector (light scattering, viscometric, and refractive index detectors) using THF was equipped with a Viscotek T60A light scattering/viscometric detector, a Waters 2410 refractive index detector, and two Polymer Laboratories Mixed E columns, programmed to run at 1.0 mL/min. Instrument calibration was based on polystyrene standard and the sample concentration was 0.5–1 wt%. The sample was prepared four times to verify reproducibility.

^{29}Si NMR spectra were recorded on a Bruker ACP-300 spectrometer in $CDCl_{3}$. The sample concentration was ∼ 600 mg in 2.4 mL of the solvent for a 10 mm tube. Chromium acetylacetonate was used as a relaxation agent in ∼32 mg quantity. A gated decoupling in which protons were irradiated only during the acquisition of FID (free induction decay) was employed with the pulse angle of 45° and the pulse delay of 7 s. The number of scans was >1000 and the line broadening of 2.0 Hz was employed on plotting. The chemical shift was adjusted using tetramethylsilane as either an internal or an external standard.

Gas chromatography-mass spectrometry (GC-MS) study was conducted using a Shimadzu gas chromatograph-quadrupole mass spectrometer, model QP-5050A, utilizing an electron impact ionization source with an ionizing electron energy of 70 eV. The interfacial temperature was 300°C and the ion source temperature was 250°C. The GC was a Shimadzu GC-17A gas chromatograph equipped with a capillary column (J&W Scientific, 30 m × 0.250 mm, coated with DB-5 in 0.10 mm thickness). The GC temperature
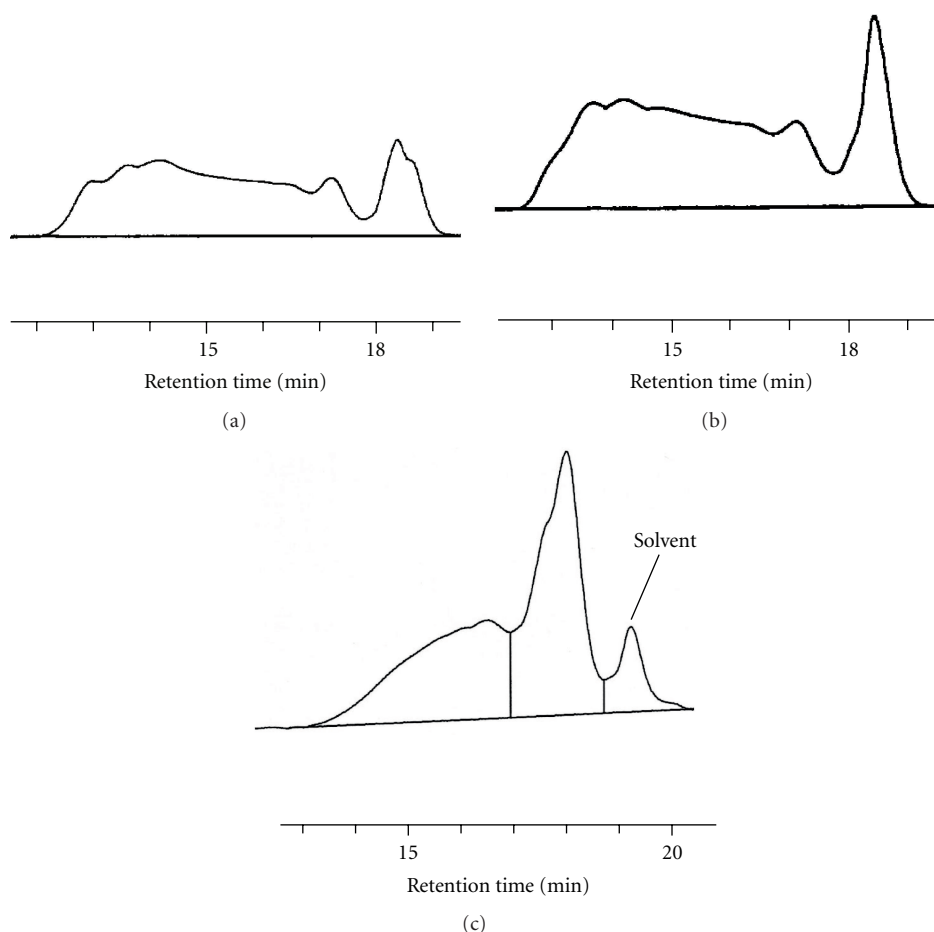
(a)

(b)

(c)

FIGURE 2: GPC curves for (a) PMSQ-1, (b) MeDT-1, and (c) PMSQ-NA.

program used was: initial temperature, 60°C; initial time, 2.00 minutes; program rate, 40°C/min; final temperature, 280°C; injection temperature, 280°C; detector temperature, 300°C. Helium was used as a carrier gas with its pressure of 150 kPa. A sample of ~25 wt% solution containing D_4 as an internal standard was injected in 0.1 μL amount. A Shimadzu GC-14A gas chromatograph equipped with the same capillary column as installed in the GC-MS and a flame ionization detector (FID) was used. The same carrier gas pressure, temperature program, and injection amount as in the GC-MS studies were employed for exactly the same sample. For PMSQ at earlier reaction stage, the following temperature program was used both for GC and GC-MS analyses: initial temperature, 60°C; initial time, 2.00 minutes; program rate, 10°C/min; final temperature, 280°C; He pressure of 100 kPa.

XRD study was performed with a JEOL JDX-3530 diffractometer using Ni-filtered Cu-K$_\alpha$ radiation. The intensity distribution ($2° < 2\theta < 35°$) was observed in the reflecting mode using a goniometer equipped with a monochromator. The crystallinity was determined by the known method from the crystalline peaks and amorphous halo.

X-ray single crystal analysis was performed on a SIEMENS SMART diffractometer at a temperature of about −120°C. The structure was determined by direct methods using program SHELXS.

2.3. Preparation of PMSQ. Using the method described in a previous paper [29], the PMSQ was synthesized from 1196 g (8.00 mol) of methyltrichlorosilane in 3.20 L each of MIBK and water and heat aging at 50°C for 2 h 50 min. The PMSQ (PMSQ-1) was obtained as a white solid in 528 g quantity. Another batch, PMSQ-2, was synthesized in a 9 mol scale heat aging at 50°C for 4 h, providing 562 g of the material. To obtain a PMSQ without the heat aging, 74.7 g (0.500 mol) of methyltrichlorosilane was reacted by the same method using 200 mL each of MIBK and water, and the product was recovered immediately after the completion of the dropwise addition of methyltrichlorosilane to the mixture of MIBL and water with the maximum temperature during the addition over 26 min of 20.0°C (PMSQ-NA).

2.4. Preparation of MeDT. The MeDT resin was prepared in a similar manner using a mixture of 1155 g (7.7 mol) of methyltrichlorosilane and 165 g (1.3 mol) of dimethyldichlorosilane, and 4.00 L of MIBK and 3.42 L water. The heat aging after the hydrolysis was performed at 60°C for 2 h, giving a solid MeDT in 580 g yield. Another lot, MeDT-2, was
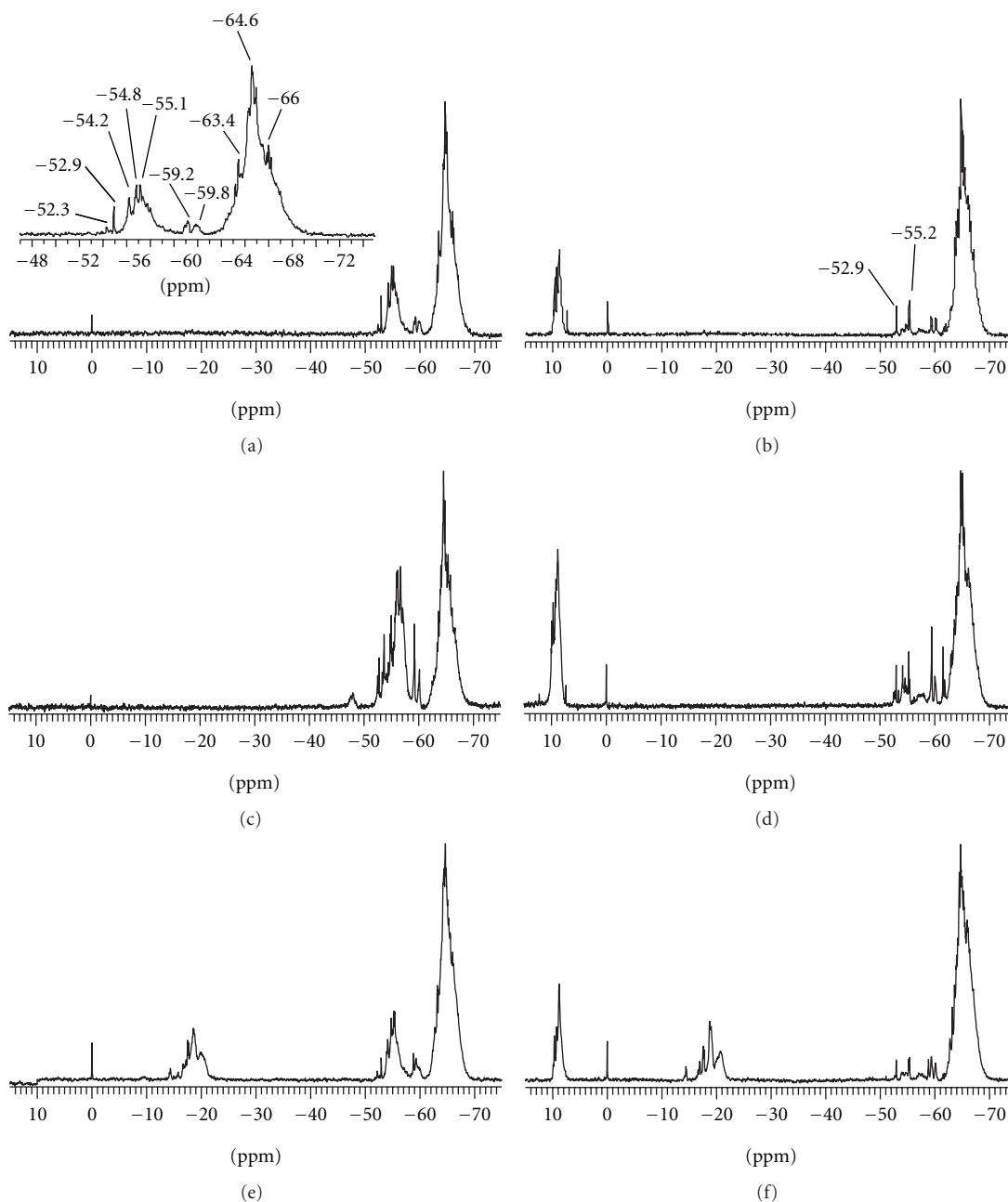
Figure 3: ^{29}Si NMR spectra of (a) PMSQ-1, (b) Me$_3$Si-capped PMSQ-1, (c) PPMSQ-NA, (d) Me$_3$Si-capped PMSQ-NA, (e) MeDT-1, and (f) Me$_3$Si-capped MeDT-1.

synthesized in the same scale with the heat aging at 60°C for 3 h.

2.5. Isolation of a Molecule. To 100 g of PMSQ-1, a mixture of 1400 mL of hexane and 600 mL of chloroform, was added. After stirring for 30 min, the mixture was allowed to stand for 20 min, followed by decanting the supernatant solution. By stripping the solvent, Fraction 1, the lower molecular weight fraction, was obtained in 31% yield. Fraction 1 (19.99 g) was dissolved in 204 mL of acetone (0.098 g/mL). While stirring, 54 mL of distilled water was added to the solution, and the

mixture was allowed to stand overnight, giving two separated layers. The top layer was separated by decantation, and 14 mL of water was added, which again gave two layers. The solvent in the top layer was stripped off, followed by redissolving in 77 mL of acetone (resin/acetone ratio of 0.098 g/mL). Removing the solvent from the supernatant solution gave the lowest molecular weight fraction, Fraction 4, as a solid (5.204 g). To 2.00 g of Fraction 4, 11.4 g of chloroform was added (15 wt%) and the solution was allowed to stand overnight at room temperature. Insoluble material remained in the solution, the amount of which increased by

standing overnight. A crude cage material, Fraction 4-P1, was obtained by collecting the precipitates by filtration (0.068 g). By concentrating the filtrate followed by standing overnight, 0.067 g of a crude product (Fraction 4-P2) was isolated by filtration. Further concentration of the filtrate afforded a crude product, Fraction 4-P3, in a very small amount (0.008 g). Similarly, 0.10 g of a crude material (Fraction 4-P4 and 5) was obtained from 1.74 g of Fraction 4 and 0.48 g of a crude product (Fraction 4-P6 and 7) was obtained from 9.58 g of another Fraction 4. Recrystallization of 0.64 g of the crude products (**1**: mixture of Fraction 4-P1, 4, 5, 6, and 7) from an acetone/chloroform mixture gave crystals (**X1**, 0.43 g). Needle crystals, **X2**, were obtained from **X1** by slow evaporation of the solution (acetone/chloroform = 3/1) covered with a heptane layer.

2.6. Trimethylsilyl-(Me_3Si-) Capping of Silanol in the Methyl Silicone Resins.

A 25 mL three-neck flask with a septum, a three-way stopcock, a glass stopper, and a magnetic stir bar was charged with 3.01 g of PMSQ-1, followed by purging with nitrogen through the stopcock. After dissolving in 9.0 mL of dichloromethane, 1.7 mL of BSTFA was added using a syringe through the septum over 2 min while cooling on an ice-water bath. The amount of BSTFA was set at ~1.2 times of the SiOH present in the resin simply calculated from the T^2 region (-50 to -58 ppm) in the ^{29}Si NMR spectrum and the theoretical amount of water in the dichloromethane as calculated by the solubility of water of 0.198 wt%. After stirring at room temperature for ~10 minutes, ~10 mL of water was added, followed by washing the slightly basic organic phase with water to neutral. The organic phase was dried over magnesium sulfate and the solvent was stripped off under vacuum. Me_3Si-capping of the OH in MeDT was carried out in the same way.

2.7. Quantification Method of GC Peaks.

The quantification procedure for the Me_3Si-capped PMSQ-1 is described below. Me_3Si-capped PMSQ-1 (73.8 mg) was dissolved in 0.17 mL of chloroform. A stock solution of D_4 was prepared by dissolving 31.7 mg of D_4 in 157.7 mg of chloroform. The stock solution (23.8 mg, 30 μL) was added to the solution of Me_3Si-capped PMSQ as an internal standard, which made the amount of D_4 in the PMSQ solution 3.98 mg (0.0134 mmol). The PMSQ solution was subjected to both the GC-MS and the GC analyses. After assigning the GC peaks from the GC-MS assignment, quantification was made assuming that the GC peak area with a FID detector was proportional to the number of methyl groups. The following shows an example taking peak **x** in Figure 4 for $T^3_6T^2_2$: Dividing the GC area for D_4 by the number of methyl group, 8, gives mole equivalent area for the D_4. In the present case, the D_4 GC peak at 3.372 min had an area of 7217; thus the mole equivalent area was 902.1. Since the amount of D_4 was 0.0134 mmole, the GC peak area for 1 mmol of D_4 is 67320 (902.1/0.0134). The peak **x** at 6.826 min for $T^3_6T^2_2$ had the peak area of 1478. Since the number of methyl group for a *trimethylsilyl-capped* $T^3_6T^2_2$ is 14, the mole equivalent area for this molecule was 105.6 (1478/14). From this value and the molar equivalent
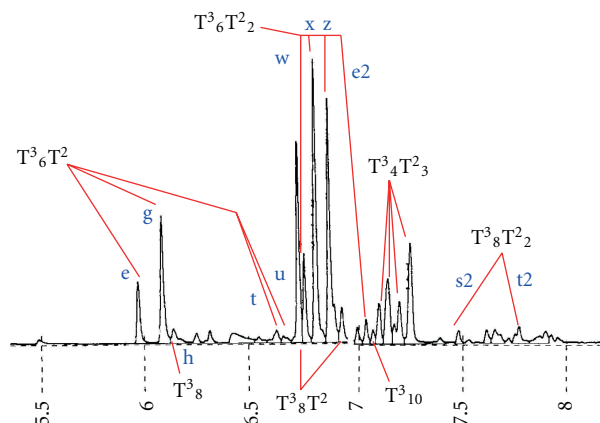

Figure 4: Gas chromatograph of Me_3Si-capped PMSQ with the peak assignment by the GC-MS. The molecular compositions are described as uncapped PMSQ.

peak area for D_4, the amount of this molecule is calculated as 0.00157 mmole (105.6/67320). By multiplying the molecular weight of *uncapped* $T^3_6T^2_2$, 554, the amount of this molecule is calculated as 0.872 mg. Since the amount of the entire resin, 73.8 mg, was based on the Me_3Si-capped PMSQ, the weight of the uncapped resin was calculated by the ^{29}Si NMR data. The average molecular formula of PMSQ-1 was determined as $T^{2(OH)}_{0.045}T^{3(OSiMe3)}_{0.150}T^3_{0.805}$ by simply assigning the resonances around 10 ppm as the M unit, those between -51 and -58 ppm as the T^2 unit, and those at -58 to -71 ppm as the T^3 unit. This gives the average formula weight of 79.70, from which that for the uncapped resin was calculated as 68.88. From these values, the amount of the resin used for the GC quantification on uncapped basis was calculated as 63.8 mg ($73.8 \times 68.88/79.70$). Thus the amount of the molecule of peak **x** is 1.37 wt% of the entire PMSQ. (The residual resonances in the T^2 region after the capping was assigned to T^3 in strained rings as shown below, but in this calculation, the integration in the T^2 region was simply used as T^2 silicon, which will not cause major impact on the calculation.)

2.8. Quench Capping of Early Reaction Intermediates (PMSQ-QC).

A D_4 stock solution was prepared by dissolving 30.2 mg of D_4 in 294.5 mg of MIBK. In a 20 mL vial was placed 2.2 mL of 2-methylpentane and 0.8 mL (~0.78 g, ~3.0 mmol) of BSTFA, and the vial was placed in a dry ice-acetone bath of $-70°$C. In a 10 mL vial with a magnetic stir bar and a digital thermocouple thermometer, 0.7 mL of water, 0.35 mL of MIBK, and 30 μL (23.7 mg) of the D_4 stock solution (2.20 mg of D_4) were stirred vigorously in an ice-water bath. After the temperature of the mixture in the 10 mL vial reached 1.2°C, 0.1 mL (0.178 g, 1.19 mmol) of methyltrichlorosilane was added dropwise using a 1.0 mL syringe in 140 s (the maximum reaction temperature during the addition was 9.2°C), and the mixture was stirred another 35 s. The relative amount of MIBK to methyltrichlorosilane was the same as the above PMSQ synthesis, but the amount of water was twice the standard condition. The content of

Material	Mw	Mn	18 min peak area
PMSQ-1	6370	1140	19.0%
PMSQ-NA	790	500	53.0%
MeDT-1	4220	1040	22.9%

the reaction vial was then dumped into the 20 mL vial. The organic phase was separated from the frozen water phase and was washed with 3-4 mL of water 4 times to neutral. The 2-methylpentane was stripped off to obtain a solid product which was subjected to GC and GC-MS analyses in the same way as the Me₃Si-capped PMSQ. However, one difference was that the amount of the entire resin is not known. Thus, firstly the amount of a molecule was determined in mmol relative to the amount of D_4 (0.00742 mmol), which was multiplied by the number of silicon atoms in that molecule. This amount was expressed as percent of the feed methyltrichlorosilane (1.19 mmol) as Si mol% in Table 4.

2.9. Quantification of $T^3{}_8$ Cubic Octamer.

To a mixture of 45 mL of MIBK and 60 mL of water on an ice bath, 22.4 g (0.15 mol) of methyltrichlorosilane dissolved in 15 mL of MIBK was added dropwise. The reaction temperature was kept at 5–9°C during the addition over 1 h. After the completion of the addition, the reaction mixture was heated on an oil bath. It took 23 min for the reaction temperature to increase to 50°C, after which the heating was continued at 50°C for 3 h. After the MIBK phase was washed to neutral, the insoluble materials were collected from the MIBK phase by centrifugation (6000 rpm, 15 min). The precipitate was washed by dispersing in MIBK followed by centrifugation. The MIBK used for washing was combined with the MIBK phase. The precipitate was further washed with acetone and dried under vacuum for 3 h (284.4 mg). The water phase and the water used for this washing were combined and subjected to centrifugation. The precipitate was washed with acetone twice and dried. All the precipitates obtained were combined. The solvent was removed from the MIBK phase after removing the precipitate, giving a resin as a solid (10.2 g). The resin was Me₃Si-capped by the method described above and subjected to GC analysis using D_4 as an internal standard. In other two runs, the products were recovered immediately after the completion of the addition of the chlorosilane (0 h aging) and after 17 h aging at 50°C.

2.10. Reaction of the Isolated $T^3{}_6 T^2{}_2$.

The crude isolated $T^3{}_6 T^2{}_2$ cage, **1**, (50.0 mg, 0.0901 mmol) was dissolved in 0.864 mL of MIBK (the amount of MIBK relative to Si was three time of the PMSQ synthesis due to the solubility of $T^3{}_6 T^2{}_2$). After adding 0.30 mL of 24 wt% hydrochloric acid, the mixture was heated at 50°C for 3 h. The MIBK phase was washed with water to neutral before recovering the precipitate by centrifugation. The amount of the precipitates was 9.7 mg (19 wt% of the starting material). From the MIBK phase, 37.5 mg of a resin was obtained by removing the solvent (**1-R**, 75 wt% of the starting material). The content

of the $T^3{}_8$ cage in the precipitated was determined by XRD crystallinity and that in the resin was determined by the aforementioned GC/GC-MS method after Me₃Si-capping.

3. Results and Discussion

3.1. GPC Analysis.

Figure 2 represents the GPC curves for PMSQ-1 and MeDT-1 with the molecular weight data listed in Table 1. Both materials showed multimodal curves. The weight average molecular weight, Mw, were 6370 for PMSQ-1 and 4370 for MeDT-1. Both materials contained low molecular weight species, the peak at 17.9 min for PMSQ-1, 19.0% peak area with the Mw of 390, and the peak at 18.5 min for MeDT-1, 22.9% peak area with the Mw of 410. For PMSQ-2 and MeDT-2, GPC using coupled refractive index, viscosity, and light scattering detectors was conducted. Because the light scattering signal was too weak for realistic measurement, the universal calibration method was used as an alternative and the results are summarized in Table 2. The relationship between molecular weight M and intrinsic viscosity $[\eta]$ is typically represented by the Mark-Houwink equation:

$$[\eta] = KM^a, \tag{1}$$

where the coefficient K and the exponent a depend on the solute-solvent pair and temperature. The Mark-Houwink exponent can provide information with respect to molecular shape, where the limits are 0 for spheres and 2 for rod-like molecules. The a values around 0.3 mean that the molecule is far from rigid-rod shapes.

3.2. NMR Spectroscopy.

Figure 3(a) shows the ²⁹Si NMR spectrum of PMSQ-1 together with the T unit region magnified. The integration data are summarized in Table 3. The spectrum consists of three major envelopes: (i) −51 to −58 ppm, (ii) −58 to −60.5 ppm, and (iii) −60.5 to −70 ppm. Region (i) will be assigned to T^2 silicon and (ii) and (iii) to T^3 silicon [30–32]. These broad resonances suggest the presence of a variety of environments. At the same time, sharp peaks are observed at −52.3, −52.9, −54.2, −54.8, −55.1, −63.2, −63.4, −64.3, −64.6, −64.9, −66.0 ppm, and so forth, indicating that specific environments are heavily populated or preferred. Figure 3(b) illustrates the ²⁹Si NMR spectrum of Me₃Si-capped PMSQ-1. The resonances in the T^2 region decreased and a new resonance appeared around 9 ppm for the vinyl dimethyl-M unit. The NMR integration for the M region, the decrease in the T^2 region, and the increase in the T^3 region indicated that no condensation essentially took place during the capping reaction. However, the resonances including the two sharp peaks at −52.9 and −55.2 ppm remained in the −51 to −58 ppm region. A deuteration technique in IR spectroscopy by Lipp to detect trace silanol in PDMS revealed that the silanol content of the Me₃Si-capped PMSQ was 0.12 wt%, implying that the capping efficiency was around 95% [33]. Feher and coworkers reported that an incompletely condensed cyclohexylsilsesquioxane of the structure (b) in Figure 1 showed the ²⁹Si NMR peaks at

TABLE 2: Universal GPC data.

	Mn	Mw	$[\eta]_n$	$[\eta]_w$	Rg_n	Rg_w	M-H a	M-H $\text{Log}\,K$
PMSQ-2	3640	17400	0.025	0.028	1.66	2.33	0.329	−2.845
MeDT-2	3700	24600	0.024	0.028	1.68	2.46	0.293	−2.752

TABLE 3: ^{29}Si NMR data for PMSQ-1 and MeDT-1.

Materials	M	D^1 $(-12/-15)$	D^2-a $(-15/-19.2)$	D^2-b $(-19.2/-23)$	T^1 $(-46/-49)$	T^2 $(-50/-58)$	T^3-a $(-58/-60.5)$	T^3-b $(-60.5/-70)$
PMSQ-1	—	—	—	—	—	0.194	0.034	0.772
—cap[a]	0.150	—	—	—	—	0.045	0.024	0.931
PMSQ-NA	—	—	—	—	0.015	0.378	0.039	0.568
—cap[a]	0.292	—	—	0	—	0.102	0.045	0.854
MeDT-1	—	0.004	0.093	0.047	—	0.142	0.027	0.688
—cap[a]	0.111	0.005	0.088	0.053	—	0.035	0.023	0.797

[a]The sum of the D and the T region integration is standardized as unity excluding the M unit.

−55.57, −56.94, −57.11, and −66.40 ppm in the intensity ratio of $1:2:2:1$ [34]. Since there are only two T^2 silicon atoms among the six, this clearly indicates that the T^3 silicon in the strained cyclotrisiloxane ring gives resonances around −56 ppm for this silsesquioxane structure with an aliphatic substituent. Unno and coworkers reported the chemical shift for hexasilsesquioxane (Figure 1(a)) with substituents of 1,1,2-trimethylpropyl and t-butyl giving peaks at −55.1 and −54.3 ppm, respectively [35]. All these pieces of information imply that an aliphatic substituted T^3 silicon in a cyclotrisiloxane ring gives ∼10 ppm downfield shift. Therefore it is highly likely that the major part of the residual resonances in the −51 to −58 ppm region for the Me$_3$Si-capped PMSQ represent silicon atoms of T^3 in strained rings. It is safe to say that only 75–80 mol% of the silicon in the −51 to −58 ppm region can be assigned to T^2. In other words, the T^2/T^3 molar ratio of the PMSQ from traditional ^{29}Si NMR assignment is 0.19/0.81, but the actual composition is roughly $T^2_{0.15}T^3_{0.85}$.

Table 3 and Figures 3(e) and 3(f) show the data and spectra for the ^{29}Si NMR spectrum of MeDT-1. Essentially the same phenomenon that there are residual resonances in the −51 to −58 ppm region after Me$_3$Si-capping was seen. However, the integration of the D silicon region around −20 ppm is not affected by the capping, indicating that there is no D^1 silicon in MeDT-1. Usually D^2 silicon, represented by those in polydimethylsiloxane, appears around −22 ppm [36]. Those in −15 to −19 ppm region denoted as D^2-a in Table 3 will be D^2 silicon next to a T unit. The sharp peak at −14.4 ppm which was not affected by the capping could be a D^2 silicon in strained ring structures. In a similar manner to the PMSQ, the composition of MeDT-1 could be described as $D^2_{0.15}T^2_{0.10}T^3_{0.75}$.

3.3. GC-MS and GC Analysis. PMSQ-1 was subjected to GC and GC-MS analyses using the Me$_3$Si-capped material to avoid silanol condensation in the high-temperature GC injection port and the detector. Figure 4 shows the GC chart using an FID detector. GC-MS analysis was carried out using the same capillary column as the GC in which molecular weights of 18 peaks were identified. The molecular weights are assigned based upon the common knowledge that a methyl radical (molecular mass of 15) is readily cleaved from neutral species [37] which are subjected to 70 eV electron ionization. As a reference data, T^3_8 was directly placed in the ionization chamber of the GC-MS instrument, which gave the expected [M-Me]$^+$ ion at 521 daltons, arising from the loss of a CH$_3$ radical from the odd electron molecular ion of the neutral (nominal mass = 536 Daltons). As can be seen in Figure 4, seven species with their isomers were detected. Mass spectrometry of PMSQ materials is reported for matrix-assisted laser desorption/ionization time-of-flight (MALDI) MS [38], graphite plate laser desorption/ionization time-of-flight (GPLDI-TOF) MS [39, 40], and electro-spray ionization Fourier transform ion cyclotron resonance (ESI-FTICR) MS [38]. These mass spectroscopic methods can directly analyze silanol-functional PMSQs without the Me$_3$Si-capping, but the GC-MS method can identify the presence of isomers and quantify the identified material in combination with a GC. As described in the experimental section, the peaks in Figure 4 were quantified using D$_4$ as an internal standard as listed in Table 4. The molecular weight observed in the GC-MS is for the capped species. For instance, $[MeSiO_{3/2}]_6[MeSi(OSiMe_3)_{2/2}]_2$ was actually observed instead of the original $T^3_6T^2_2$, but the amount of each species shown in Table 4 was calculated on the uncapped molecules as described in the experimental section. The sum of the seven types of species, 18 compounds all together including isomers, was 7.9 wt% of the entire PMSQ, in which the most abundant compound was $T^3_6T^2_2$.

The GC-MS and GC study of MeDT-1 was carried out by the same method. For the PMSQ, one molecular weight detected by the GC-MS corresponded to one combination of T^3 and T^2. For MeDT, however, there were multiple compositions which corresponded to a given molecular weight for the capped resin. The molecular weight of 550 could

Table 4: QR-ES-Metflex GC quantification summary.

Composition	Number	FW w/o cap	FW w/cap	PMSQ-1 wt% w/o cap	PMSQ-NA wt% w/o cap	PMSQ-QC Si mol% w/o cap
T^0	a	94	310	—	—	0.02
T^3_6	b	402	402	—	0.18	0
T^2_3	c	228	444	—	—	0.01
T^1_2	d	170	454	—	—	0.03
$T^3_6 T^2$	e	478	550	0.37	1.12	0.32
$T^3_6 T^2$	f	478	550	—	0.09	0.07
$T^3_6 T^2$	g	478	550	0.81	2.13	0.48
$T^3_4 T^2_2$	h	420	564	—	1.64	0.55
$T^3_4 T^2_2$	j	420	564	—	1.92	1.80
T^3_8	k	536	536	0.11	—	—
$T^3_2 T^2_3$	l	362	578	—	—	0.28
$T^3_4 T^2$	m	344	416	—	—	0.33
$T^3_2 T^2_3$	n	362	578	—	—	0.25
T^2_4	o	304	592	—	—	0.41
$T^3_2 T^2_3$	p	362	578	—	—	0.30
T^2_4	q	304	592	—	—	0.36
$T^3_2 T^2_3$	r	362	578	—	0.31	0.87
$T^3_2 T^2_3$	s	362	578	—	—	0.20
$T^3_6 T^2$	t	478	550	0.13	trace?	—
$T^3_6 T^2$	u	478	550	0.07	trace?	—
$T^3_8 T^2$	v	612	684	1.20	0.47	0.12
$T^3_6 T^2_2$	w	554	698	0.41	0.38	0.32
$T^3_6 T^2_2$	x	554	698	1.37	1.28	0.35
$T^3_6 T^2_2$	y	554	698	—	0.35	0.20
$T^3_6 T^2_2$	z	554	698	1.33	1.19	0.31
$T^3_8 T^2$	a2	612	684	0.26	0.22	0.13
$T^3_6 T^2_2$	b2	554	698	—	—	0.11
$T^3_8 T^2$	c2	612	684	—	0.22	0.13
$T^3_8 T^2$	d2	612	684	—	0.21	0.11
$T^3_6 T^2_2$	e2	554	698	0.12	0.65	0.31
T^3_{10}	f2	670	670	0.12	—	—
$T^3_4 T^2_3$	g2	496	712	0.17	0.79	0.60
$T^3_4 T^2_3$	h2	496	712	0.37	1.19	0.75
$T^3_4 T^2_3$	i2	496	712	—	0.25	0.23
$T^3_4 T^2_3$	j2	496	712	0.26	0.94	0.44
$T^3_4 T^2_3$	k2	496	712	—	—	0.20
$T^3_4 T^2_3$	l2	496	712	0.52	2.22	1.11
$T^3_2 T^2_4$	m2	438	726	—	0.82	1.67
$T^3_2 T^2_4$	n2	438	726	—	0.51	1.24
$T^3_2 T^2_4$	o2	438	726	—	0.29	0.66
$T^3_2 T^2_4$	p2	438	726	—	0.17	0.44
T^2_5	q2	380	740	—	—	0.29
T^2_5	r2	380	740	—	—	0.20
$T^3_8 T^2_2$	s2	688	832	0.08	—	—
$T^3_8 T^2_2$	t2	688	832	0.18	—	—
Total				7.87	19.57	16.36

TABLE 5: GC quantification of assignable low molecular weight species in MeDT-1.

GC time	Structure[a]	FE w/cap	FW w/o cap	wt% w/o cap
4.896	$T^3_4T^2_2$	416	416	0.16
5.474	$T^3_4T^2_2$	490	490	0.13
5.513	$T^3_6D^2$	476	476	0.84
5.606	$T^3_4D^2_3$	490	490	0.16
5.749	$T^3_6D^2_2$ [a]	550	550	0.62
5.832	$T^3_6D^2_2$ [a]	550	550	0.30
6.011	$T^3_6D^2_2$ [a]	550	550	0.11
6.075-1	$T^3_4T^2D^2_2$ [b]	564	492	0.15
6.075-2	$T^3_6\,D^2_2$ [a]	550	550	0.31
6.118-1	$T^3_4T^2D^2_2$ [b]	564	492	0.32
6.118-2	$T^3_4T^2D^2_2$ [b]	564	492	0.46
6.149	$T^3_4T^2D^2_2$ [b]	564	492	0.15
6.189	$T^3_4T^2D^2_2$ [b]	564	492	0.45
6.278	$T^3_6T^2D^2$	624	552	0.63
6.338-1	$T^3_8D^2$	610	610	0.286
6.338-2	$T^3_6T^2D^2$	624	552	1.30
6.446	$T^3_8D^2$	610	610	0.10
6.566	$T^3_6T^2D^2$	624	552	0.28
6.647	$T^3_8T^2$	684	612	1.41
6.748-2	$T^3_8T^2$	684	612	0.37
	Total	—	—	8.53

[a]This molecule is most possibly $T^3_6D^2_2$ but could be $T^3_6T^2$.
[b]This molecule is most possibly $T^3_4T^2D^2_2$ but could be $T^3_4T^2_2$.

be interpreted as a capped $T^3_6T^2$ or a $T^3_6D^2_2$ (not capped being completely condensed), and the molecular weight of 564 could be a capped $T^3_4T^2_2$ or a capped $T^3_4T^2D^2_2$. To help determine which composition was the correct assignment to the GC-MS molecular weight, an uncapped resin was subjected to GC-MS, which gave the same peaks of molecular weight of 550 (m/e of 535) as the capped material. Thus the molecular weight of 550 for the capped species was assigned as $T^3_6D^2_2$, not $T^3_6T^2$. Based upon the appearance in electrospray mass spectrometry, the capped molecular weight of 564 could be $T^3_4T^2D^2_2$ [41]. Based on these considerations, the assignment and quantification were made as summarized in Table 5. Eight species ranging from $T^3_4D^2_2$ to $T^3_8T^2$ (20 compounds all together including isomers) were detected with their sum of 8.5 wt% on an uncapped resin basis.

Comparing the PMSQ and the MeDT resin, the number of the species detected by GC and GC-MS and their sum were similar. But it is noted that many of the T^2 units [$CH_3Si(OH)O_{2/2}$] in the PMSQ are replaced with D^2 unit [$(CH_3)_2SiO_{2/2}$], the units with two siloxane bonds and two substituents. While $T^3_6T^2_2$ was the most abundant species in the PMSQ, $T^3_6T^2D^2$ (exemplified in Figure 1(h)) was the most abundant in the methyl-DT resin. Most of the molecules in the PMSQ were incompletely condensed silsesquioxanes, but 35% of the molecules were completely condensed in the MeDT. It should be noted that these
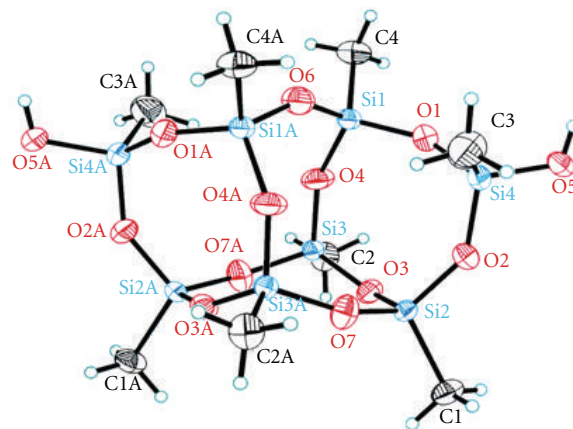

FIGURE 5: The structure of X2.

structures are not specific to silsesquioxanes, but common to silicone resins.

3.4. Isolation of a Compound and Consideration for the Structures. One compound 1 was able to be isolated from PMSQ-1 by solvent fractionation and recrystallization as described in the experimental section. GC analysis of the Me_3Si-capped material showed that crude crystal of 1 mainly consisted of peak z in Figure 4 with the relative GC peak area of 90%. The GC purity increased to 98% after recrystallization (X1). Figure 5 shows the X-ray single crystal structure of X2 which proves that the molecule is $T^3_6T^2_2$. The molecule consisted of two identical parts related by a crystallographic twofold axis passing through atom O6. Schematically, this compound is described as shown in Figure 1(f). Tables 6 and 7 show the bond distances and the bond angles, respectively. The Si–O bond lengths range from 1.601(3) to 1.630(3) Å, which are comparable to values found in the other Si–O ring systems [28, 42]. Figure 6 shows the unit cell structure of X2. The molecules showed no short intramolecular contact distances and were connected by intermolecular hydrogen bonding between the hydroxyl groups. Four neighboring hydroxyl groups were arranged about a crystallographic fourfold axis. There were no other significant intermolecular interactions, but a chloroform molecule was statically distributed over four symmetry equivalent positions.

Figure 7(a) shows the ^{29}Si NMR spectrum of crude 1 mainly consisting of four sharp resonances at −55.7, −63.6, −64.5, and −65.1 ppm with the integration ratio of 1:1:1:1. The peak at −55.7 ppm is of the T^2 silicon and the other three peaks are of the T^3 silicon atoms. The pattern was similar to that of the cyclohexylsilsesquioxane of the same structure (pyridine/C_6D_6, −58.46, −65.66, −67.51, −68.58 ppm, 1:1:1:1) [28]. The spectrum verifies that T^3 silicon atoms in a cyclotetrasiloxane or a cyclopentasiloxane ring, not in a strained cyclotrisiloxane, appear in the −65 ppm region, not in the −55 ppm region. The ^{29}Si NMR peak assignment was further verified by Me_3Si-capping as shown in Figure 7(b). The spectrum shows four resonances at −64.0, −64.1, −64.8, and −65.4 ppm with the integration ratio of 1:1:1:1,

TABLE 6: Bond distances for **1**, **X2**.

Atom 1	Atom 2	Distance (Å)
Si1	O1	1.609 (3)
Si1	O4	1.626 (3)
Si1	O6	1.615 (2)
Si1	C4	1.828 (5)
Si2	O2	1.614 (3)
Si2	O3	1.630 (3)
Si2	O7	1.620 (3)
Si2	C1	1.840 (4)
Si3	O3	1.621 (3)
Si3	O4	1.601 (3)
Si3	O7	1.608 (3)
Si4	O1	1.612 (3)
Si4	O2	1.620 (3)
Si4	O5	1.611 (3)
Si4	C3	1.848 (5)
Si3	C2	1.819 (4)

TABLE 7: Bond angles for **1**, **X2**.

Atom 1	Atom 2	Atom 3	Angle (deg)
O1	Si1	O4	109.0 (2)
O1	Si1	O6	108.6 (1)
O1	Si1	C4	110.5 (2)
O4	Si1	O6	108.7 (2)
O4	Si1	C4	110.9 (2)
O6	Si1	C4	109.1 (2)
O2	Si2	O3	108.9 (2)
O2	Si2	O7	109.1 (2)
O2	Si2	C1	109.7 (2)
O3	Si2	O7	108.6 (1)
O3	Si2	C1	110.0 (2)
O7	Si2	C1	110.4 (2)
O3	Si3	O4	109.2 (1)
O3	Si3	O7	109.4 (1)
O3	Si3	C2	110.0 (2)
O4	Si3	O7	107.9 (2)
O4	Si3	C2	111.2 (2)
O7	Si3	C2	109.2 (2)
O1	Si4	O2	109.0 (2)
O1	Si4	O5	109.0 (2)
O1	Si4	C3	109.8 (2)
O2	Si4	O5	105.3 (2)
O2	Si4	C3	112.1 (2)
O5	Si4	C3	111.4 (2)
Si1	O1	Si4	151.5 (2)
Si2	O2	Si4	144.1 (2)
Si2	O3	Si3	145.5 (2)
Si1	O4	Si3	153.9 (2)
Si1	O6	Si1	146.8 (3)
Si2	O7	Si3	153.3 (2)

FIGURE 6: The unit cell structure of **X2**.

reflecting the conversion of the T^2 silicon to T^3 by the capping. The M/T ratio was 1/4 as expected.

The isolation of this molecule and the identification of the structure clarify the presence of cage molecules in the
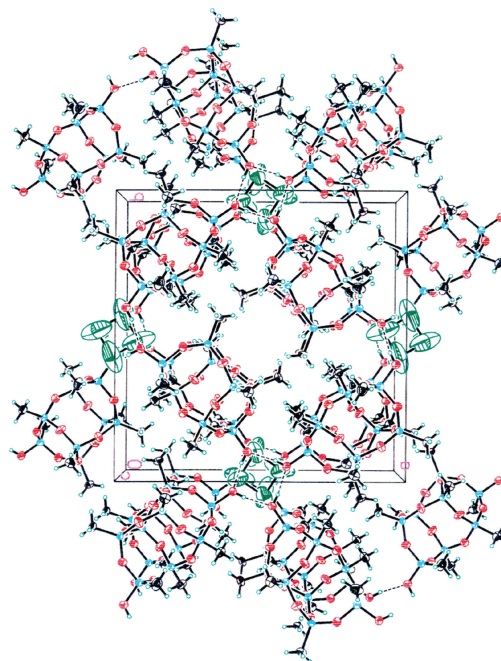
PMSQ. As shown in Figure 4 and Table 4, there are three other isomers for the composition of $T^3_6 T^2_2$, peaks w, x, and e2. Since the structure of these species is unknown, it is possible to draw a ladder-like structure shown in Figure 1(g). For the chemical formulae like $T^3_6 T^2$ or $T^3_8 T^2$, however, one cannot draw such ladder-like structures. T^3_8 and T^3_{10} are surely cage structures. Thus it is safe to say that the presence of cage molecules in the PMSQ is evident. Since Feher and coworkers reported spontaneous formation of structures (a), (d), and (f) for cyclohexyl substituent [28], the major structure of $T^3_4 T^2_3$ could be (d) in Figure 1. The presence of cage molecules may be in line with the low Mark-Houwink exponent values. Another observation is that the structure of $T^3_6 T^2$ cannot be drawn without including at least one cyclotrisiloxane ring as shown in Figure 1(c) as an example. This structure was reported by Feher and coworkers as the dehydration product from the material having the structure of Figure 1(d) for a cyclohexylsilsesquioxane. If a ladder structure as in Figure 1(g) exists, that also contains cyclotrisiloxane rings. The presence of $T^3_6 T^2$ and the residual resonance in the −55 ppm region after Me₃Si-capping in the ²⁹Si NMR spectrum verifies the presence of strained cyclotrisiloxane rings.

3.5. Early Stage of the Reaction. To obtain insight into the formation of these low molecular weight species in PMSQ-1, reaction intermediates at much earlier reaction stage were captured. PMSQ-1 was prepared by adding 8.00 mol (~1200 g) of methyltrichlorosilane to a mixture of water and MIBK over 3 h 4 min allowing the reaction temperature to increase to 23°C, followed by heating up to 50°C taking
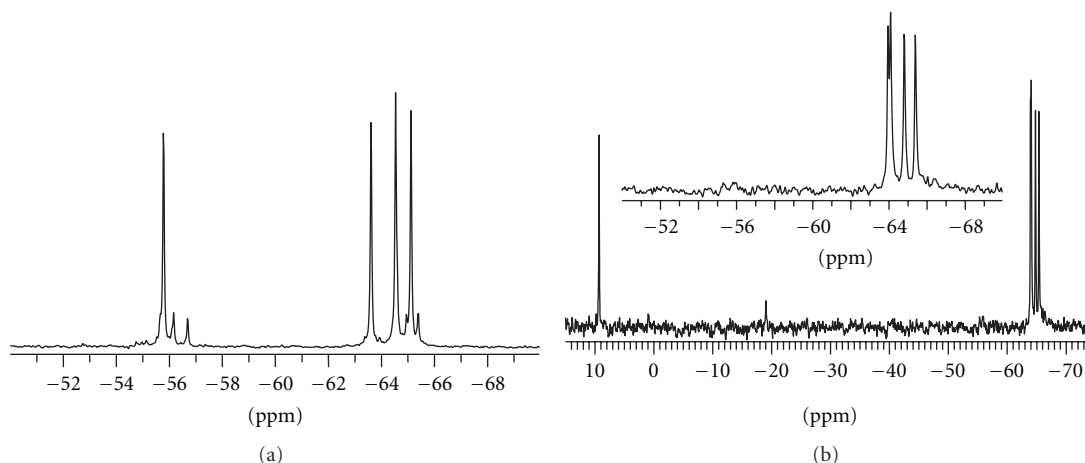
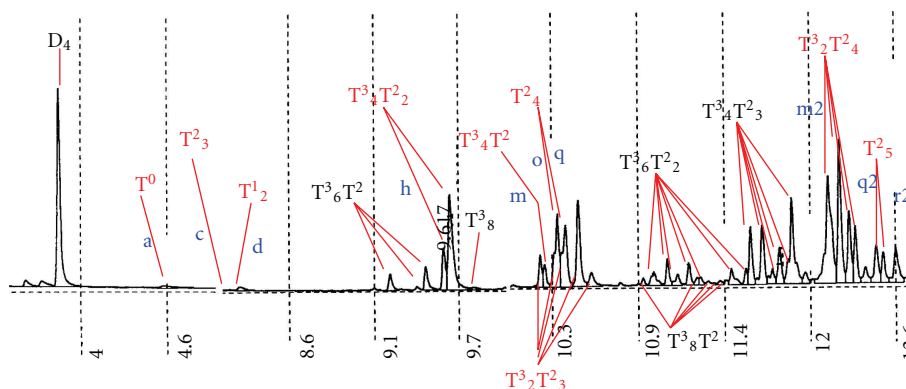FIGURE 7: ^{29}Si NMR spectrum of (a) crude **1** and (b) Me$_3$Si-capped **X1**.

FIGURE 8: Gas chromatograph of PMSQ-QC with the peak assignment by the GC-MS. The molecular compositions are described as uncapped PMSQ.

53 min and aging at 50°C for ~3 h. In contrast, to capture the reaction intermediates at earlier stage, firstly a quench capping approach was carried out. Methyltrichlorosilane (0.2 g) was added to a stirred mixture of water and MIBK over 140 s suppressing the reaction temperature only up to 9°C. After stirring for 35 s, the reaction mixture was poured into 2-methylpentane containing BSTFA in a dry ice-acetone bath to freeze the acid-water phase and cap the silanol by trimethylsilyl group. The reaction product, PMSQ-QC, was subjected to GC and GC-MS analyses in a similar way to the analysis of the Me$_3$Si-capped PMSQ-1.

Figure 8 shows the FID-GC chart with the peak assignment from GC-MS for PMSQ-QC. The GC quantitative analysis data are summarized in Table 4. Since the amount of the entire resin is not known for PMSQ-QC, the amount of each species relative to the entire resin on the uncapped basis was calculated as silicon mol% (see the Experimental section), which is close to weight percent. Many species that were not present in PMSQ-1 were observed: T^0 [CH$_3$Si(OH)$_3$], T^1_2 [HO(CH$_3$)$_2$Si-O-Si(CH$_3$)$_2$OH], T^2_3 [cyclic trimer of CH$_3$Si(OH)O$_{2/2}$], T^2_4 [cyclic tetramer, two isomers], T^2_5 [cyclic pentamer, two isomers], $T^2_4T^2$ [one isomer], $T^2_2T^2_3$ [five isomers], $T^2_2T^2_4$ [four isomers], and

$T^2_4T^2_2$ [three isomers]. Including those common with the PMSQ, which are $T^2_6T^2$, $T^2_6T^2_2$, and $T^2_4T^2_3$, the sum of the identified species was 16.4%, indicating that more than 80% of the silicon is already in higher molecular weight species. Most of the cage structures found in PMSQ-1 or in the literature [3–6, 27, 28] consist of cyclotetra- or cyclopentasiloxanes. The abundance of T^2_4 and T^2_5 in PMSQ-QC may be in line with this. The amount of the cyclic trimer, T^2_3 exemplified in Figure 1(i), was very small but clearly identified, while a linear trimer, $T^1_2T^2$ illustrated in Figure 1(j), was not detected. Thus the formation of strained cyclic trimer was evidenced. In a computer simulation of condensation of HSi(OH)$_3$ and trisilanol with other substituents under excess water condition [43, 44], Kudo and Gordon suggested that the energy for the formation of cyclic trimer is not very much higher than that for cyclic tetramer. For the formation mechanism of cyclic tetramer, they indicated that insertion of T^0 to cyclic trimer is even more favored than the condensation of two T^1_2 molecules or T^0 and a linear trimer. Kelts and Armstrong observed the formation of cyclic trimers of Q^2, [Si(OH)$_2$O$_{2/2}$], by ^{29}Si NMR spectroscopy for the hydrolytic polycondensation of tetraethyl orthosilicate [45]. Brunet reported the formation

of cyclic trimers by the acidic sol-gel reaction of methyltri-ethoxysilane as observed by DEPT ^{29}Si NMR spectroscopy [46]. Among the detected species in the present study, the structures of $T^2_2T^2_3$ and $T^2_4T^2_2$ also cannot be drawn without including cyclotrisiloxane rings as exemplified in Figure 1(m) (the structures represent one possible isomer but it is not verified that these exact structures are real). All these observations imply that the condensation favors the formation of such strained rings at this stage of the reaction. For cyclic tetramer, T^2_4, all *cis* isomer shown in Figure 1(k) is reported for phenyl [47] and isopropyl [18] substituents. Kudo and Gordon simulated that the formation of the all *cis* isomer is most favored due to hydrogen bonding among the silanols in the transition state [43]. They calculated that the next stable isomer is the structure of Figure 1(l).

As the reaction stage in between PMSQ-1 and PMSQ-QC, a PMSQ was recovered immediately after the completion of the addition of methyltrichlorosilane (0.500 mol) to a mixture of water and MIBK without heat aging, PMSQ-NA. Figure 2(c) shows the GPC curve. The low molecular weight end overlaps with the solvent peak and the relative area of the peak around 18 min reached 53%. The *Mw* and the *Mn* are much lower than those of PMSQ-1. Figure 3(c) represents the ^{29}Si NMR spectrum. As summarized in Table 3, the resonance in the T^1 region (-46 to -49 ppm) was present and the resonances in the T^1 and the T^2 region were twice of those in the T^2 region in PMSQ-1. By Me$_3$Si-capping as shown in Figure 3(d), the resonances in the T^2 region again remained of which relative area was greater than that for PMSQ-1.

The GC and the GC-MS data for PMSQ-NA by the same method described before are listed in Table 4. The change in PMSQ-QC, PMSQ-NA, and PMSQ-1 can be summarized as follows.

(1) Species present in PMSQ-QC but reduced or extinct in PMSQ-NA and extinct in PMSQ-1 are T^0, T^2_3, T^1_2, T^2_4 (both 2 isomers), T^2_5 (both 2 isomers), $T^3_2T^2_3$ (all the 5 isomers), $T^3_4T^2$, $T^3_2T^2_4$ (all the 4 isomers), $T^3_4T^2_3$ (1 out of the 6 isomers), and $T^3_6T^2_2$ (1 out of the 6 isomers).

(2) Species that increase monotonously (including those not present in PMSQ-QC and PMSQ-NA) are T^3_8, T^3_{10}, $T^3_6T^2$ (2 out of the 5 isomers), $T^3_8T^2$ (2 out of the 4 isomers), and $T^3_6T^2_2$ (3 out of the 6 isomers). The isolated isomer of $T^3_6T^2_2$, *z*, is one of these.

(3) Species that increase from PMSQ-QC to PMSQ-NA, but then decrease or become extinct in PMSQ-1, are $T^3_6T^2$ (3 out of the 5 isomers), $T^3_4T^2_2$ (both 2 isomers), $T^3_6T^2_2$ (2 out of the 6 isomers), $T^3_8T^2$ (2 out of the 4 isomers), and $T^3_4T^2_3$ (5 out of the 6 isomers). Many of the species of which structures cannot be drawn without a cyclotrisiloxane ring are in this category.

It should be noted that the sum of the material detected by the GC-MS analysis increased from 16.4% in PMSQ-QC to 19.6% in PMSQ-NA. This suggests that the buildup of

TABLE 8: The amount of T^3_8 formed during the hydrolytic polycondensation of MeSiCl$_3$.

Aging time (h)	Yield (wt%)		
	In precipitates	In soluble PMSQ	Total
0	1.06	—	(1.06)
3.0	2.92	0.41	3.33
17.0	4.54	0.17	4.71

the molecules during the course of the reaction is not simply proceeding by continued condensation.

3.6. Reaction Chemistry for the Formation of the T^3_8 Cubic Octamer.

In an effort to obtain insights into the chemistry for the structure buildup in silsesquioxanes or silicone resins, formation of T^3_8 cubic octamers was pursued. Three separate runs were carried out: after completing the dropwise addition of methyltrichlorosilane to a mixture of MIBK and water, (i) the product was immediately recovered (0 h aging), (ii) aged at 50°C for 3 h, and (iii) aged at 50°C for 17 h. For each run, precipitates were collected both from the MIBK and the water phases, followed by determining the amount of T^3_8 by X-ray diffraction crystallinity, which was around 80%. The soluble resins were subjected to Me$_3$Si-capping by BSTFA, for which the GC quantification was carried out in the same way as mentioned above. The amounts of T^3_8 by these methods are listed in Table 8. The amount of T^3_8 in the resin at 0 h aging was not able to be determined because the GC peak of T^3_8 overlapped with that of $T^3_4T^2_2$, preventing from the quantitative analysis. However, it is safe to say that the amount of T^3_8 increased with increasing aging time, because the major part of the material is found in the precipitate.

Figure 9 illustrates various potential routes for the formation of T^3_8. The natural thought would be simple condensation of precursor molecules, represented by routes (i)–(iv). The species T^0, T^1_2, T^2_4, and $T^2_2T^2_4$ appearing in routes (i), (ii), and (iv) are present at the very early stage exemplified by PMSQ-QC. However, T^0, T^1_2, and T^2_4 are extinct in PMSQ-NA (0 h aging) and in PMSQ-1 (3 h aging) and $T^2_2T^2_4$ decreased in PMSQ-NA and is extinct in PMSQ-1. Considering the fact that the amount of T^3_8 continues to increase during the 17-hour aging, there appear to be no clear evidence that routes (i), (ii), and (iv) are the major mechanism of T^3_8 formation. Route (iii) does not require such early reaction stage intermediates, but there is no evidence of the presence of this structure among the isomers of $T^3_6T^2_2$.

To investigate if siloxane bond rearrangement was involved in forming T^3_8, aging of the isolated $T^3_6T^2_2$, crude **1**, was conducted at 50°C for 3 h in MIBK with hydrochloric acid of a similar concentration as the PMSQ synthesis. The solution after the reaction was cloudy, for which centrifugation was carried out after washing the MIBK phase with water. WAXD analysis of the precipitates showed that they were T^3_8 with the crystallinity of 82%. The amount of the precipitates was 19 wt% of the starting material; hence the amount of T^3_8 was 16 wt%. From the MIBK phase
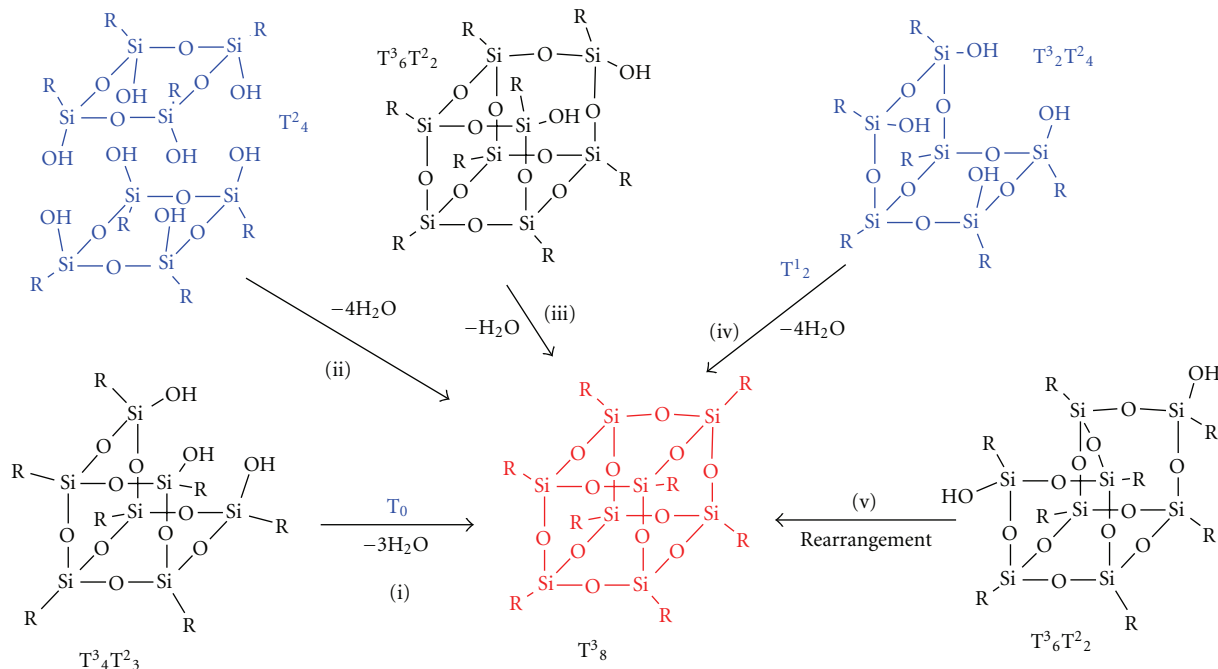
FIGURE 9: Potential routes for the formation of the T^3_8 cubic octamer.

TABLE 9: Formation of T^3_8 from $T^3_6T^2_2$ Cage 1 compound.

Composition	GC time (min)	wt% w/o capping	
		Before aging 1	After aging $1 - R$
$T^3_6T^2_2$	10.8	—	5
$T^3_6T^2_2$	10.9	0.3	20
$T^3_6T^2_2$	11.1	90	17
T^3_8	—	0	16[a]

[a]Determined by WAXD of the precipitate.

after centrifugation, a resin was obtained by removing the solvent (1-R, 75 wt% of the starting material), which was subjected to GC analysis after Me$_3$Si-capping (1-R-cap). As summarized in Table 9, the amount of the starting material decreased to 17 wt%, while two other isomers of $T^3_6T^2_2$ formed in 5 and 20 wt% yields by the reaction. $T^3_6T^2$ and $T^3_4T^2_3$ were also detected but the amounts of these molecules were much smaller compared with that of the $T^3_6T^2_2$ isomers. GPC of 1-R-cap revealed the formation of higher molecular weight species too. These findings prove that siloxane bond rearrangement of low molecular weight molecules is one of the mechanisms for T^3_8 formation, route (v) in Figure 9. We can speculate that such reaction mechanism can be applied to molecules other than T^3_8. In the hydrolytic polycondensation of phenyltrimethoxysilane in alkaline media, Lee and Kawakami reported that the $T^3_4T^2_3$ structure, Figure 1(d), is first formed, which was then consumed to provide the so-called double-decker structure, $T^3_4T^2_4$, that need siloxane bond rearrangement [48].

4. Concluding Remarks

The present study focused on the characterization of a PMSQ and a methyl-DT silicone resin that were synthesized by hydrolytic polycondensation of chlorosilanes without specific control of the reaction. The key findings can be summarized as follows.

Firstly, as opposed to the proposal by Brown and coworkers that PPSQs have ladder structures [8, 9], the PMSQ was found to contain cage molecules. Presence of intense low molecular weight peak in the GPC curve, several sharp peaks on the broad envelope of resonances in the ^{29}Si NMR spectrum, and low Mark-Houwink exponent value are the indirect evidences. More direct proof was obtained by the GC and GC-MS study which revealed the presence of ~20 low molecular weight species with their sum of ~8 wt%. Isolated $T^3_6T^2_2$ molecule, Presence of T^3_8 and T^3_{10} cage molecules, and some species of which structures can be drawn only as cages from the chemical formulae determined by the GC-MS clarified the presence of cage structures. Cyclization plays a critical role in the formation of these materials to deviate from Flory's random branching theory as pointed out by McCormick and coworkers for the sol-gel reaction of tetraethyl orthosilicate [49] and methyltriethoxysilane [50].

Secondly substantial evidences for the presence of strained cyclotrisiloxane rings were found. Among the chemical formulae identified by the GC-MS analysis, the structures of $T^3_6T^2$ cannot be drawn without including at least one cyclotrisiloxane ring (see Figure 1(c)). The ^{29}Si NMR spectrum of the PMSQ of which silanols were capped by trimethylsilyl group suggested the presence of strained T^3

structure by the residual resonances in the classical T^2 region, -50 to -58 ppm. A cyclic trimer of T^2 was directly observed at the very early stage of the reaction (PMSQ-QC). In addition, 2 out of the 5 isomers of $T^3_6T^2$ increased monotonously from PMSQ-QC to the PMSQ, and the other 3 isomers increased from PMSQ-QC to PMSQ-NA, then decreased in the PMSQ. This suggests that the cyclotrisiloxane rings are not always unstable species.

In the study to clarify the formation mechanism of T^3_8 cubic octamer, no clear evidence was identified that T^3_8 was formed by simple condensation of precursor molecules. In contrast, when the isolated $T^3_6T^2_2$ (90% purity) was subjected to the same heat aging condition in acidic media as the synthesis of the PMSQ, the amount of the starting material was reduced to 17%, and T^3_8 and two other isomers of $T^3_6T^2_2$ were found in 16, 20, and 5% amounts, respectively. Thus, siloxane bond rearrangement is an important mechanism in the formation of cage molecules or low molecular weight species. The amount of the species detected by the GC-MS analysis in PMSQ-QC and PMSQ-NA could be in line with this observation. Some species increased from PMSQ-QC to PMSQ-NA then decreased in the PMSQ, and some molecules monotonously increased from PMSQ-QC to the PMSQ. This could be indicating that the reaction is not proceeding only by simple continuation of condensation.

Finally the methyl-DT resin containing 15 mol% of a D^2 unit $[(CH_3)_2SiO_{2/2}]$ showed essentially the same tendency as the PMSQ, showing the presence of cage molecules as analyzed by GPC, ^{29}Si NMR spectroscopy, and GC/GC-MS studies (the reaction chemistry was not pursued). One feature was that many of the T^2 unit $[CH_3Si(OH)O_{2/2}]$ in the PMSQ were replaced with D^2 unit $[(CH_3)_2SiO_{2/2}]$ in the methyl-DT resin. Thus the form of the molecule as an incompletely condensed cage in the PMSQ, for example, $T^3_6T^2_2$, was a completely condensed cage, for example, $T^3_6D^2_2$. The presence of cyclotrisiloxane rings was suggested in a similar manner by the residual resonance in the -50 to -58 ppm region in the ^{29}Si NMR spectrum after trimethylsilyl-capping and the presence of species that one cannot draw a structure without including a cyclotrisiloxane ring, for example, T^3_6D. This has clarified that a methyl-DT resin, which is a more common industrial silicone resin, consists of similar structures as silsesquioxanes and the generality of the trend found in the PMSQ.

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