Silsesquioxanes

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Contents

I. Introduction 1409
II. Nonfunctional Silsesquioxanes 1410
A. Phenylsilsesquioxane 1410
1. Preparation 1411
2. Characterization and Properties 1412
3. Applications 1414
B. Methylsilsesquioxane 1415
1. Preparation 1415
2. Characterization and Properties 1416
3. Applications 1416
C. Copolymer of Phenylsilsesquioxane and Methylsilsesquioxane 1417
D. Others 1417
1. Substituted Phenyl- and Benzylsilsesquioxanes 1417
2. Aliphatic Silsesquioxanes 1417
3. Hydridosilsesquioxane 1418
4. Other Silsesquioxanes 1418
III. Organo-Functional Silsesquioxanes 1419
A. Vinyl- and Allyl-Functional Silsesquioxanes 1419
1. Vinyl-Functional Silsesquioxanes 1419
2. Allyl-Functional Silsesquioxanes 1420
B. Methacryl-Functional Silsesquioxanes 1420
C. Amino-Functional Silsesquioxanes 1421
D. Epoxy-Functional Silsesquioxanes 1421
E. Others 1421
IV. Commercial Silicone Resins 1421
A. Classification 1422
B. Structures 1422
1. Type of Organic Radicals 1422
2. R/Si Ratio 1422
3. Phenyl/Methyl Ratio 1423
4. Molecular Weight 1423
C. Preparation 1423
D. Cross-Linking 1423
E. Properties 1424
1. Oxidative Stability 1424
2. Mechanical Properties 1424
3. Weatherability 1424
4. Hydrophobicity 1425
5. Chemical Resistance 1425
6. Electrical Properties 1425
F. Application 1425
V. Materials Science and Emerging Applications of Silsesquioxanes 1426
A. Bridging Silsesquioxanes 1426
B. Ceramic Precursors 1426
1. Inorganic/Organic Hybrids 1426
2. Pyrolysis of Silsesquioxanes to Silicon Oxy Carbide Ceramics 1426
VI. References 1427

I. Introduction

The term silsesquioxanes in this review refers to all structures with the empirical formulas $RSiO_{3/2}$ where R is hydrogen or any alkyl, alkylene, aryl, arylene, or organo-functional derivatives of alkyl, alkylene, aryl, or arylene groups. Bridging alkylene and arylene derivatives are only covered in a cursory way in this review as they are part of a more detailed review covered in this issue by K. J. Shea and D. A. Loy. The structures of silsesquioxanes have been reported as random structure, ladder structure, cage structures, and partial cage structure, as illustrated in Figure 1, and are discussed in more detail elsewhere in this review.

The first commercialization of silicones began with silsesquioxane chemistry. The silicone industry started with commercialization of silicone resins consisting primarily of silsesquioxanes for electrical insulation at high temperatures. Presently, however, polydimethylsiloxane is the predominant material in the industry. Development research was started in 1930s in Corning Glass Works and General Electric Company on the basis of academic work by F. S. Kipping. The research work at Corning Glass Works, led by J. F. Hyde, resulted in formation of Dow Corning Corp. in 1943. General Electric, where W. Patnode and E. G. Rochow were acting as pioneers, started commercial production of silicones in 1946. Early history of silicones and the role of silsesquioxanes can be found in several books.[1-4]

Even though silsesquioxane chemistry spans more than a half century, interest continues to increase as illustrated in Figure 2. A Dow Corning data base which encompasses most of silicon chemistry was searched for the term "silsesquioxane". Figure 2 shows a plot of publications and patents versus the year of publication from 1955 to 1993. An approximate exponential growth is apparent even to the present. (The last year is incomplete due to delays in entries.) One can also observe that most of the commercial activity, based on the number of patents, has occurred in three countries—Japan, United States, and Russia. See Figure 3.

In this review, structures, preparation, and properties of the silsesquioxanes, in general, are critically

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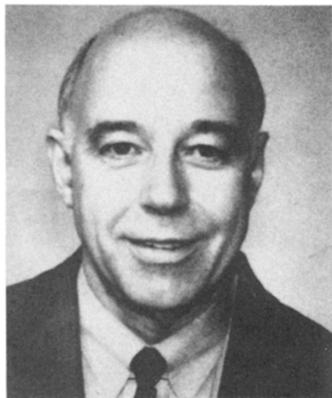
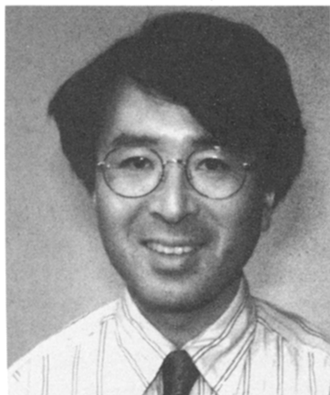


Ronald H. Baney, born in Alma, MI, received his B.S. (1955) in chemistry from Alma College and Ph.D. (1959) in inorganic chemistry from University of Wisconsin under Professor R. West, and joined Dow Corning in 1959 and worked in various positions in the research of organosilicon science to date. He spent a sabbatical leave at Cambridge University with Professor E. Ebsworth in 1965–1966, and at Nagoya University with Professor S. Hirano as an honored visiting industrial scientist in 1985–1986. He is currently a senior research scientist and is assistant research director at the Japan Research Center, Dow Corning Asia, where he has been since 1992. His research interests include chemical bonding phenomena in silicon compounds, cure chemistry of silicone materials, thermal and oxidative degradition of silicones, preceramic polymer routes to structural ceramics, sol/gel and other solution processing of electronic oxide ceramics including high-temperature superconductors, and silicone resin technology.



Maki Itoh, born in Osaka, Japan, received a B.S. (1976), M.S. (1979), and Ph.D. (1982) in organic chemistry from Kyoto University under Professor Y. Takegami. He then joined Sumitomo Metal Industries in the organic-coated steel sheets section in corporate research. After spending two postdoctoral years at the University of Massachusetts studying polymer chemistry under Professor R. W. Lenz, he joined Dow Corning in 1990 at the Japan Research Center, Dow Corning Asia, and has been working on organic polymer-modified polysiloxanes and silicone resins as a senior research specialist. He is currently a member of the steering committee of the Inorganic Polymer Division of the Society of Polymer Science, Japan.

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reviewed. Many of the applications are described in patents frequently only in a cursory way, and although an attempt has been made to describe applications, an exhaustive review of all patent literature was not undertaken.

Most of the precursors to silsesquioxanes find their origin in trichlorosilanes. These are frequently prepared from the silicone industry's direct process reaction of methyl chloride or hydrogen chloride with silicon metal, catalyzed with copper. Alkyl groups larger than methyl and organo-functional groups are formed by platinum-catalyzed hydrosilylation reactions with trichlorosilane or by organometallic coupling reactions with chlorosilanes. A review of this chemistry can be found in several text books or reviews on the subject.[5]

In this article, triorganosiloxy ($R_3SiO_{1/2}$), diorganosiloxane ($R_2SiO_{2/2}$), organosilsesquioxane ($RSiO_{3/2}$), and silicate ($SiO_{4/2}$) units may be referred as M, D, T, and Q units, respectively,[1] which is widely accepted description for the building blocks of polyorganosiloxanes. A significant amount of experimental detail is included in the preparation sections of this review because the resulting silsesquioxane materials are very process dependent.

II. Nonfunctional Silsesquioxanes

A. Phenylsilsesquioxane

In polyphenylsilsesquioxane, the substituent on the silicon atom is a phenyl group, and it is generally characterized by its high thermal stability. Some

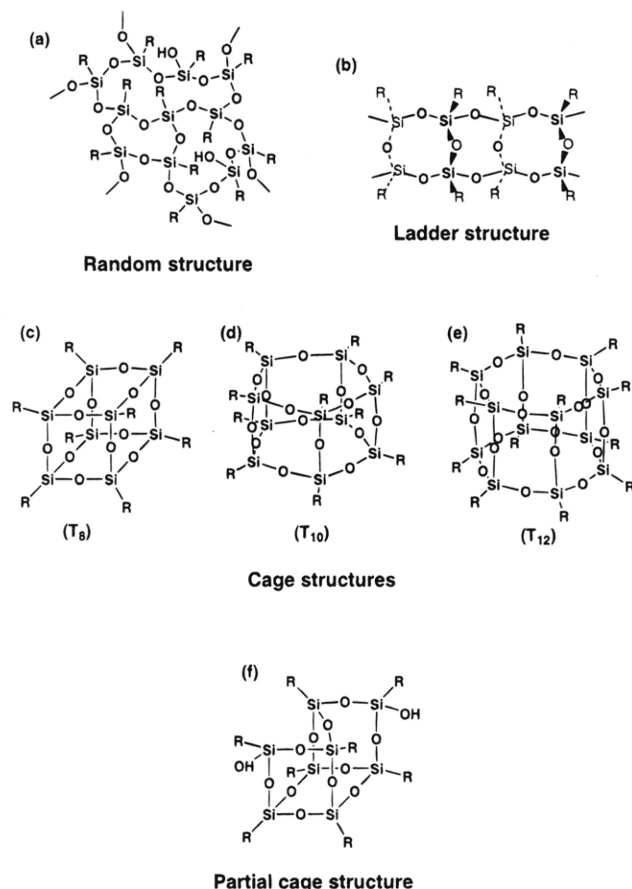


Figure 1. Structures of silsesquioxanes.

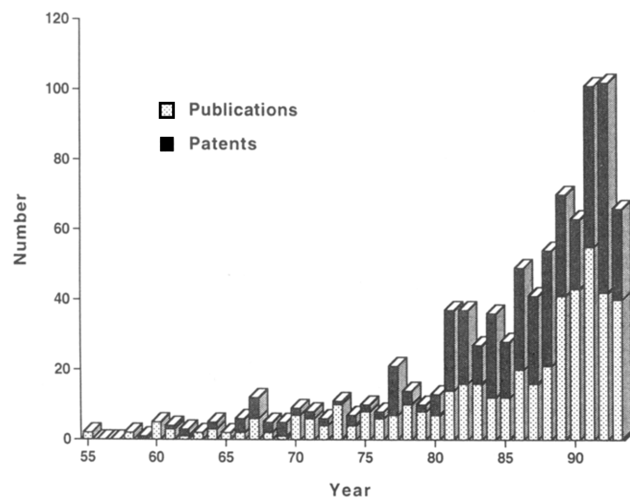


Figure 2. The number of patents and publications containing the term "silsesquioxane" versus the year.

specific polyphenylsilsesquioxanes are denoted as **PPSQ-X** in this section for the convenience of describing their synthesis and characterization.

1. Preparation

An alkaline equilibration of a phenyl hydrolyzate or a low molecular weight polyphenylsilsesquioxane including cages is the practical method for the preparation of polyphenylsilsesquioxane which can be summarized as follows: (1) hydrolysis of phenyltrichlorosilane in a solvent with excess water to give a hydrolyzate with a molecular weight of ~10^3, (2) equilibration of the hydrolyzate with potassium

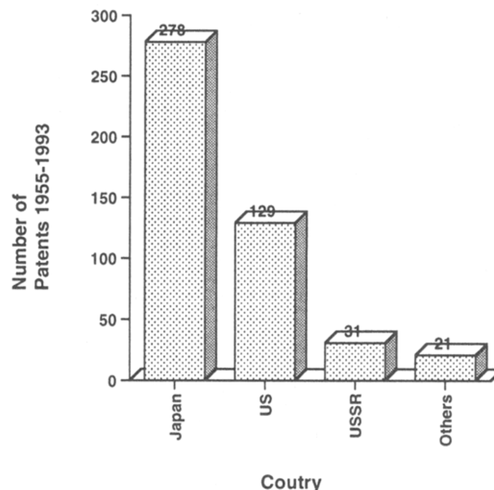


Figure 3. The total number of patents containing the word "Silsesquioxane" versus the country of the patent origin.

hydroxide at a relatively low concentration (~50%) and a low temperature (~100 °C) to give a prepolymer with a molecular weight of ~10^4, and (3) equilibration of the prepolymer at a high concentration (80−90%) and a high temperature (~250 °C) to give the polymer with a molecular weight of over 10^5. The critical factors in obtaining tractable high molecular weight polyphenylsilsesquioxane seem to be a high concentration and a high temperature. Usually a small amount of T_8 and T_{12} crystals (T_n denotes a cage structure with the number of the $SiO_{3/2}$ groups of n) are formed along with the prepolymer or the polymer, which are filtered off before precipitating the polymer in methanol.

The preparation of polyphenylsilsesquioxane is classified in terms of the starting materials in this section, and methods other than the equilibration are also presented.

From Phenyltrichlorosilane. Brown et al. reported the first high molecular weight tractable polyphenylsilsesquioxane in 1960[6] prepared by the equilibration method. The prepolymer had an intrinsic viscosity ([η]) of 0.12 dL/g, a number average molecular weight (M_n) of 1.4 × 10^4, and a weight average molecular weight (M_w) of 2.6 × 10^4. The degree of the silanol condensation was approximately 99.9%. The polymer, **PPSQ-1**,[6] was prepared from either the prepolymer, T_{12}, or the hydrolyzate by the step 3 described above. The [η] was 4.0 dL/g and the M_w was 4.1 × 10^6.

Many researchers followed this equilibration method to prepared polyphenylsilsesquioxane. Andrianov et al.[7] obtained polyphenylsilsesquioxane by starting from T_8 and first reacting it in a solvent, followed by heating at 250−270 °C without a solvent (**PPSQ-2**). Pavlova et al.[8] also prepared polyphenylsilsesquioxane from a phenyl hydrolyzate in various solvents. Adachi et al.[9,10] prepared a hydrolyzate in methyl isobutyl ketone (MIBK) or aliphatic solvents at 0−10 °C. They obtained the polymer by refluxing the hydrolyzate in xylene (50 wt % solid) catalyzed with potassium hydroxide (**PPSQ-3**). The polymer exhibited a M_w of 1.65 × 10^5 with a M_w/M_n of 3.3 as determined by gel permeation chromatography (GPC). The polymer was dried consecutively at 150 °C for 60 min and at 200 °C for 30 min. This "dried

polymer" became insoluble on curing at 350 °C for 60 min (cured polymer). Since their method corresponded with the prepolymer formation described by Brown et al.,[6] it is not likely that they obtained their reported molecular weight by their preparation method. Adachi et al. also claimed that a pure polyphenylsilsesquioxane for use in electronic devices was prepared by the alkaline equilibration method and by the use of ultra pure water.[11,12]

The use of a metal fluoride as the equilibration catalyst is claimed in a patent.[13] With shorter reaction time compared with the potassium hydroxide equilibration, polyphenylsilsesquioxanes with a M_w of 6×10^5 to 1.2×10^6 were obtained (**PPSQ-4**).

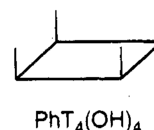
Zhang and Shi[14] studied the preparation of polyphenylsilsesquioxane under various conditions (**PPSQ-5**). They prepared a hydrolyzate from phenyltrichlorosilane in ether or toluene, with a M_n of $(1.08-2.82) \times 10^3$. The preparation of polyphenylsilsesquioxane was carried out in various combinations of benzene, toluene, xylene, tetrahydronaphthalene, and diphenyl ether using either potassium hydroxide or 1,3-dicyclohexylcarbodiimide as a catalyst. The reaction conditions were either by simple refluxing for 13 h or with azeotropic water removal at 260 °C for 7 h. The former gave polymers with an $[\eta]$ of 0.71−2.76 dL/g and a M_n of $(1.2-2.6) \times 10^4$, and the latter reaction afforded polyphenylsilsesquioxane with an $[\eta]$ of 8.0 dL/g and a M_w of 3.4×10^5. The use of 1,3-dicyclohexylcarbodiimide for the condensation of a phenyl hydrolyzate is actually dehydration without equilibration. This method was first disclosed in a patent.[15] Another dehydrating agent claimed in a patent is alkyl chloroformates.[16] One important feature of the dehydration methods is that the product polyphenylsilsesquioxane contains silanols.

A reaction at the interface of a ketone and a water layer was disclosed.[17] The water could contain an equivalent amount of a base to the hydrogen chloride produced from the chlorosilane. The two-layer system was refluxed for 2 h. The product had a low molecular weight exhibiting an $[\eta]$ of 0.07−0.11.

From Phenyltrialkoxysilane. Before Brown's study,[6] Sprung and Guenther[18] carried out the condensation of phenyltriethoxysilane but they focused on obtaining a lower molecular weight hydrolyzate. In a base-catalyzed reaction, phenyltriethoxysilane was refluxed with tetraethylammonium hydroxide and water in MIBK (~20% solid) for 11.7 h (**PPSQ-6**). The molecular weight was over 5×10^3 measured either cryoscopically or ebullioscopically. Brown later found the $[\eta]$ to be 0.14−0.26 dL/g.[6] A molecular weight of $(1.0-1.2) \times 10^3$ was obtained by an acid-catalyzed reaction using hydrochloric acid.

Nakahama et al.[19] prepared a hydrolyzate by the acid hydrolysis of phenyltrimethoxysilane and made the polymer by the alkali equilibration of the hydrolyzate in 90% solid concentration at 250 °C. The polyphenylsilsesquioxane, **PPSQ-7**, was obtained as a soluble polymer with a molecular weight of 9.0×10^4 as determined by GPC or vapor pressure osmometry (VPO).

Condensation of Phenylsilanetriol. Brown[20] noted that phenylsilanetriol undergoes polycondensation in a fairly selective manner, and the major route leads through the *cis,cis,cis*-cyclotetrasiloxanetetrol. Polymers formed upon complete condensation were linked polycyclic blocks, not the ladder structure, and were insoluble in cyclohexane.



$PhT_4(OH)_4$

Condensation of Tripotassium Phenylsilanetriolate. Takiguchi et al.[21] studied the condensation of tripotassium phenylsilanetriolate, $PhSi(OK)_3$, at the interface of a water layer and an organic layer (**PPSQ-8**). The purpose of the reaction system was to obtain structurally controlled polymers, *i.e.*, soluble polymers without crystalline cages and cross-linked gels. A prepolymer was obtained by the reaction of $PhSi(OK)_3$ and either acetic anhydride or chloroform with an $[\eta]$ of 0.06−0.13 dL/g. The prepolymer was then equilibrated with potassium hydroxide. The polymer thus obtained had an $[\eta]$ of 0.33 dL/g which corresponded to a molecular weight of 7.2×10^4 as calculated by the equation reported by Brown et al.[22]

2. Characterization and Properties

Structure. Polyphenylsilsesquioxane has been often referred as a ladder polymer since Brown et al.[6] reported the polymer to have *cis*-syndiotactic conformation as shown in Figure 1 (b). Although there is no ultimate evidence for this structure to date, it is likely that polyphenylsilsesquioxane has more or less rigid-rod nature at the molecular weight below ~10^5.

Brown et al.[6,23] assigned the structure by X-ray diffractometry (XRD), IR, UV,[24] bond angle calculation, and the a value in the Mark−Houwink equation. The XRD d-spacing data of oriented strips of 5.0 ± 0.5 Å and 12.5 Å show that the repeating distance is two chain units and that there are probably four monomer units per repeating segment. The observed UV hypochroism of 9% agrees with that calculated for the relative spacing of phenyl groups, although the hypochroismic effect is not very strong in polyphenylsilsesquioxane. The bond angle calculations show that the *cis*-syndiotactic double chain arrangement represents the only possible regular high polymer of polyphenylsilsesquioxane units which does not involve angular strain.

Among the characterization techniques mentioned above, the most direct information is the a value in the Mark−Houwink equation as determined in a dilute solution. Table 1 summarizes the a value for polyphenylsilsesquioxanes with various molecular weight range.[6,25−29] It is quite clear that the a value is close to 1 with the molecular weights lower than ~10^5 which means that the molecule is more or less a rigid-rod straight chain. In contrast, the molecule becomes branched with the molecular weights higher than ~10^5. As a matter of fact, Brown et al.[6] described that the curvature in the $[\eta]-M_w$ relations indicates that some branching is present at the M_w over 2×10^5.

In their dilute solution study, Helminiak et al. concluded that the conformation of polyphenylsilsesquioxane can be represented with a wormlike

Table 1. The a Value in the Mark–Houwink Equation[a] and the Molecular Weight for Polyphenylsilsesquioxanes

a	molecular weight	PPSQ no.	refs
0.92	1.4×10^4 (M_n)	PPSQ-1	6
1.10	$\leq 2 \times 10^5$	PPSQ-2	26
0.90	$\leq 0.6 \times 10^5$	PPSQ-2	26
0.9	$<(2.5-3) \times 10^5$	PPSQ-2	27,28
0.898	$(0.26-4.88) \times 10^5$ (M_n)	PPSQ-1	25
0.70	$>10^5$	PPSQ-2	26
0.54	$>3 \times 10^5$	PPSQ-2	27,28
some branching	$>2 \times 10^5$ (M_w)	PPSQ-1	6
distinct branching	$>10^6$		29

[a] $[\eta] = KM^a$ where M is molecular weight and K is a constant.

chain model with a persistence length of 75 Å for the same sample as in ref 25.[30] Andrianov et al.[27,28] also showed the rather rigid nature of the polymer by various properties: Kuhn's persistent length was estimated to be 100–200 Å, and the electrooptical effect in an electric field was 2 orders of magnitude greater than for flexible polymers. The observed Kerr effect was explained by the mechanism of rotation of a macromolecule as a whole. Small-angle light scattering showed 0.5 μm elongated particles. The XRD pattern exhibited a sharp reflection at 12.3 Å and a diffuse one at 4.6 Å, and the scanning electron microscope image presented fibrillar structures.

Frye and Klosowski[31] strongly opposed the linear double chain ladder structure and suggested a more or less randomly linked array of polycyclic cages. They pointed out that the slope of log–log plots of $[\eta]$ *vs* molecular weight was not so steep in the molecular weight range of 10^4–10^6 and suggested that the Brown's polymer which gave a steep slope was not a true equilibrate. However, their observation were consistent with the studies by Andrianov et al.,[26-28] Kovár et al.,[29] and even Brown et al.[6] that the slope was not very steep at the molecular weight over 10^5 as mentioned above. Frye and Klosowski also observed the occurrence of gelation of the system at a certain concentration which differed with temperature and solvents. However, this does not always support their conclusion that the polymer consists of linked cages since the gel is reversible, *i.e.*, a solution just below the gel point at 250 °C gels upon lowering the temperature, and the gel redissolves upon returning to the higher temperature.

Brown et al. concluded that the IR analysis was the most valuable tool for the assessment of the ladder structure: T_{8-12} cages give only one Si–O–Si band at 1121–1129 cm^{-1}, while the ladder polymer of at least 22–24 units exhibits two bands at 1135–1150 and 1045–1060 cm^{-1}.[22] Figure 4 shows the IR spectra of polyphenylsilsesquioxane during equilibration from a prepolymer to T_{12} at low concentration. The disappearance of the band at 1045 cm^{-1} is very distinct. Polyphenylsilsesquioxanes are sometimes simply characterized as a ladder polymer from the IR spectra as can be seen for **PPSQ-8**[21] and **PPSQ-3**.[9,32] However, there is no clear evidence for Brown's interpretation of the Si–O–Si bands. The characteristic Si–O–Si single band at 1120–1130 cm^{-1} for a cage would be due to its highly symmetric struc-

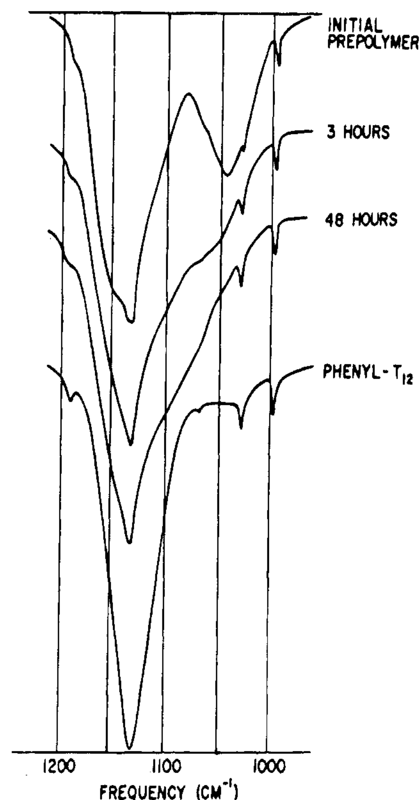


Figure 4. IR spectra of polyphenylsilsesquioxane during rearrangement of prepolymer to T_{12} at 0.60 mol/L in THF. (Reprinted from ref 22. Copyright 1964 American Chemical Society.)

ture, but the two bands at 1130 and 1040 cm^{-1} for a polyphenylsilsesquioxane can come from the breakdown in symmetry and not necessarily from the ladder structure.[33]

The broad peak for $PhSiO_{3/2}$ at −80 ppm in the ^{29}Si NMR spectra also suggests the presence of a variety of structures.[34] Adachi et al.[35] studied the initial hydrolysis process of phenyltrichlorosilane by NMR.

Structural studies of the phenyl T_8 cage have been carried out by XRD analysis, showing that six eight-membered rings are linked together to form a cage with Si atoms at the corners of a slightly distorted cube and O atoms bridging all 12 edges.[36]

Solubility. Sprung and Guenther[18] reported that **PPSQ-6** was soluble in benzene, chloroform, and tetrahydrofuran (THF), and insoluble in acetone, hexane, cyclohexane, ether, carbon tetrachloride, MIBK, and isobutyl ether. Brown et al.[6,23] reported that **PPSQ-1** was soluble in benzene, THF, and methylene chloride. Among the various reaction conditions to prepare **PPSQ-5** reported by Shi et al.,[14] some resulted in insoluble polymers, but most of them were soluble in benzene, toluene, and THF. Matsui[37] summarizes that polymers with molecular weights over several tens of thousand are soluble in benzene, dichloroethane, THF, chlorobenzene, and dimethylformamide and are insoluble in toluene, xylene, acetone, alcohol, and acetates. Oligomers with the molecular weight of several thousand are soluble in all these solvents. For **PPSQ-8** prepared by Takiguchi et al.,[21] the prepolymer is soluble in benzene, chloroform, carbon tetrachloride, ether,

Table 2. Mechanical Properties of Polyphenylsilsesquioxanes

PPSQ no.		T (°C)	tensile strength (MPa)	elongation (%)	ref
PPSQ-1		room temp	27.6–41.5	3–10	23
PPSQ-2[a]		100	39	25	28
PPSQ-4		room temp	18–30		13
PPSQ-3	dried	room temp	800	0.4	10
	cured	room temp	780	0.8	
	dried	250	400	2.7	
	cured	250	559	2.6	

[a] $[\eta]$ = 2.8 dL/g.

toluene, THF, methyl ethyl ketone, MIBK, and acetone and insoluble in methanol and ethanol. The polymer becomes insoluble in acetone.

Helminiak et al.[25] used benzene (25 °C), chloroform (25 °C), toluene (37 °C), ethylene dichloride (50.5 and 52 °C), and *o*-xylene (65 °C) for their characterization. Kovár et al.[29] determined the intrinsic viscosity in a mixed solvent of mesitylene and toluene and Andrianov et al.[26] in bromoform or benzene. Polyphenylsilsesquioxane does not melt upon heating.

Mechanical Properties. Test specimens can be prepared by solvent casting. However, Talcott et al.[38] report that efforts to prepare thick films resulted in wrinkling or voids due to "skinning over" of the polymer before all the solvent was evaporated. They removed the solvent from the solution by permeation through a solvent swelled silicone rubber sheet on a Büchner funnel attached to a suction flask for controlled evaporation of the solvent. Adachi et al.[10] prepared the specimen by slowly evaporating the solvent (the method not specified) over 14 days, giving 0.1–0.3 mm thick films. After cutting into strips, they were dried at 150 °C for 1 h and then at 200 °C for 30 min.

The values of tensile strength and elongation at break are summarized in Table 2. For most of the polyphenylsilsesquioxanes, the tensile strength value is in the range of 20–40 MPa and the elongation 3–20%. However, **PPSQ-3** exhibited 1 order of magnitude greater value for the strength with much less elongation. Since Adachi et al.[9,10] prepared the polymer by just refluxing in xylene at 50% solid concentration and reported the M_w to be 1.65×10^5, the mechanical property is surprising. It should be also noted that their soluble "dried" polymer and the insoluble "cured" polymer showed almost the same mechanical properties.

The dynamic storage modulus for both the dried and the cured sample of **PPSQ-3** at room temperature was 1.8 GPa which decreased to 200–300 MPa at 250 °C.[10] However no melting transition was observed up to 400 °C.

For Glass Resin produced by Owens Illinois, the pencil hardness of a polyphenylsilsesquioxane is reported to be 5 H, which is softer than that of a polymethylsilsesquioxane, 9 H, but the former is less brittle than the latter.[37]

Thermal Properties. Brown[23] reports that **PPSQ-1** does not lose its weight until 525 °C in air. On heating a resistance wire red hot with a strip of the polymer draped over, the strip stayed clear and hung for a minute or two at 650 °C.

Kitakohji et al.[39] compared the thermal stability of a polyphenylsilsesquioxane with that of a polyimide at a heating rate of 5 °C/min. The decomposition in air started at 460 °C for both samples, but the initial decomposition temperature for the polyphenylsilsesquioxane cured at 350 °C was 520 °C in air. The source and the nature of the polyphenylsilsesquioxane sample were not reported.

Table 3. Initial Decomposition Temperatures for PPSQ-5[a] (ref 40)

structure	initial decomp temp (°C)
ladder	525
with defects	507
branched	517
chlorinated	458

[a] In air, heating rate 20 °C/min.

The pyrolysis onset temperature was 480–500 °C in air at the heating rate of 10-20 °C/min and the 5% weight loss temperature was 550 °C for **PPSQ-3**.[9,10] Polyphenylsilsesquioxanes are more thermally stable than common polyimides by ~50 °C. On heating at 460 °C for 1 h, the weight loss was 1.0% for the cured polymer, while it was 3.0% for the dried polymer. The volatile pyrolysis products, 4.4% at 500 °C for 30 min and 5.7% for 1 h, were benzene as the main constituent with a small amount of carbon dioxide and propylene. The pyrolysis residue in air was identified as silica by IR and X-ray photoelectron spectroscopy.

Shi et al.[40] also studied the thermal behavior in detail for **PPSQ-5**. The onset temperature for the weight loss of 505 °C was obtained at the heating rate of 0 °C/min by extrapolating the data taken at different heating rates. The main pyrolysis mechanism was the formation of a phenyl radical followed by a hydrogen atom abstraction to form benzene. They also demonstrated that the initial decomposition temperature was lower for polyphenylsilsesquioxanes with defects or branching as listed in Table 3.

Other Properties. The thermal expansion coefficient for **PPSQ-3** was $(11-14) \times 10^{-5}$ below 220 °C for both the dried and cured polymers and decreased to 9×10^{-5} for the dried sample above 220 °C. Residual stress of 2.8×10^8 dyne/cm^2 was obtained from the warping of a coated silicon wafer.[10]

3. Applications

Polysilsesquioxanes, including polyphenylsilsesquioxane, are commercialized by Owens Illinois under the name of Glass Resin. In the following applications appearing in the literature (mostly in patents), this commercially available polyphenylsilsesquioxane was used in some of them. For those in which the polyphenylsilsesquioxane is prepared by

the authors/inventors, Brown's method is used in most of the cases. In some papers/patents, the source of the polyphenylsilsesquioxane was not reported.

On the basis of the number of publications, the use of polyphenylsilsesquioxane is focused on coatings, particularly in electronics and optical devices. Among these, the application in photoresists is outstanding.[41−49] Applications for interlayer dielectrics and protective coating films for semiconductor devices,[50−55] liquid crystal display elements,[56,57] magnetic recording media,[58,59] and optical fiber coatings[60,61] are disclosed. Other applications include their use in gas separation membranes,[62,63] binders for ceramics,[64] and carcinostatic drugs.[65]

It is not the purpose of the present review article to cover all of the application patents but rather to catch the application trends. It should be noted that there are a vast number of patents in this application-related area.

B. Methylsilsesquioxane

Preparation, characterization, properties, and applications of polymethylsilsesquioxane are described in this section. The initial thermal decomposition temperature of polymethylsilsesquioxane is somewhat lower than that of polyphenylsilsesquioxane, but polymethylsilsesquioxane can be characterized for its low weight loss on pyrolysis. Some specific polymethylsilsesquioxanes are denoted as **PMSQ-X** for the convenience of describing their synthesis and characterization.

1. Preparation

Although the first high molecular weight and soluble polyphenylsilsesquioxane was reported in 1960,[6] the method in a patent filed by Japan Synthetic Rubber[66] in 1978 mentioned below was the first to give a high molecular weight, soluble, and stable polymethylsilsesquioxane, probably because polymethylsilsesquioxane is very easily gelled during the course of its synthesis.

From Methyltrichlorosilane. The use of polar or oxygen-containing solvents seems to be essential for the production of polymethylsilsesquioxane. The inventors from Japan Synthetic Rubber mentioned above prepared the polymethylsilsesquioxane by adding water dropwise to methyltrichlorosilane dissolved in a mixture of MIBK and THF in the presence of triethylamine at 0 °C, followed by heating at 100−110 °C for 4 h (**PMSQ-1**).[66] The polymethylsilsesquioxane exhibited a M_n of 9×10^3 and was soluble in organic solvents such as THF or toluene even after standing for one month. The invention revised the process by using MIBK alone instead of the ketone/ether mixture, giving a polymethylsilsesquioxane with a M_w of $(1.1-1.4) \times 10^5$.[67] This method was modified by pressurizing with 1000−3000 Pa nitrogen (**PMSQ-2**).[68] **PMSQ-2** had a M_w of 10^5-10^6 and was soluble in toluene or MIBK even after standing for three months at room temperature.

Preparation of polymethylsilsesquioxane in a two-layer reaction system is claimed (**PMSQ-3**).[69] The reaction system consisted of a sodium acetate aqueous solution and toluene containing a small amount of 2-propanol, to which methyltrichlorosilane was added dropwise. **PMSQ-3** had a M_n of $(3-5) \times 10^3$ and was soluble in toluene, benzene, chloroform, carbon tetrachloride, and THF. It exhibited no change in the molecular weight distribution and solubility after being kept at 50 °C for one month.

A procedure starting from the preaminolysis of methyltrichlorosilane was reported (**PMSQ-4**).[70] Methyltrichlorosilane was reacted with ethylenediamine to give *N,N'*-bis(methyldichlorosilyl)ethylenediamine. This was hydrolyzed in a mixture of acetone, water, and dilute hydrochloric acid followed by heating at 60 °C for 6 h with xylene. After regulating the pH between 3 and 9 with tetramethylammonium hydroxide, the reaction was continued at 35 °C for 3 h. **PMSQ-4** was obtained as a colorless or yellowish solid with a molecular weight of 10^5-10^6.

From Methyltrialkoxysilane. Considerable work is found for the preparation of insoluble polymethylsilsesquioxane powder from methyltrialkoxysilanes. Toshiba Silicone filed many patents for truly globular, spherical, or fine clustered forms (**PMSQ-5**).[71] The powder was prepared by the polymerization of neat methyltrimethoxysilane at the interface with an aqueous ammonia solution. The volume ratio of methyltrimethoxysilane to water affected the shape of the powder. Shin-Etsu Chemical also described a method for preparing spherical polymethylsilsesquioxane powders with various diameters.[72] Methyltrialkoxysilane was hydrolyzed and condensed in an alkali metal hydroxide water solution at 20 °C, followed by neutralizing the solution with acetic acid. Recently Schmidt et al.[73] reported that the polycondensation of methyltrimethoxysilane in the presence of a surfactant afforded strictly spherical polymethylsilsesquioxane with the diameter in the range of 6−30 nm. The number of growing nuclei was constant with time or conversion, suggesting the phenomenon of a polycondensation into a micro emulsion. However, surface area per surfactant molecule studies revealed that the polymerization mechanism was very complex.

The preparation of a colloidal suspension of polymethylsilsesquioxane was disclosed by Dow Corning.[74,75]

Abe et al.[76] reported a film formable methyl hydrolyzate (**PMSQ-6**). They prepared the hydrolyzate by the partial hydrolysis and condensation of methyltrimethoxysilane in the presence of hydrochloric acid in methanol. The hydrolyzate dissolved in acetone was cast on a polymethylpentene plate, followed by curing at 100 °C for 1−50 days to give transparent films with thicknesses of 0.02−0.1 mm.

From Methyltriacetoxysilane. A novel synthetic method using methyltriacetoxysilane has been disclosed (**PMSQ-7**).[77] Methylethoxydiacetoxysilane prepared by the reaction of methyltriacetoxysilane with ethanol in MIBK was added to a suspension containing sodium bicarbonate and MIBK. Heating the reaction mixture at 100 °C for several hours gave a prepolymer with a M_n of 3.5×10^3. By reacting the prepolymer in MIBK with 1 wt % of potassium hydroxide at 60 °C for 1 h, **PMSQ-7** having a M_n of 1.41×10^5 was obtained. The polymer was soluble in benzene, toluene, ethyl acetate, *n*-butyl acetate, MIBK, and cyclohexane.

From Redistribution Reaction of Methylhydridosiloxanes. Laine et al.[78,79] described a novel method of titanium-catalyzed redistribution of methylhydridooligo- and polysiloxanes. The resulting polymer, **PMSQ-8**, was a copolymer with an approximate composition of $[MeHSiO]_{0.3}[MeSiO3/2]_{0.7}$.

2. Characterization and Properties

Structure. Contrary to polyphenylsilsesquioxane, there is little literature focused on the structure of polymethylsilsesquioxane. Polymethylsilsesquioxanes are simply described to have ladder structures based on their IR spectra. For example, **PMSQ-1**,[66] **-2**,[68] **-3**,[69] **-4**,[70] and **-7**[77] exhibit the characteristic Si–O–Si bands at 1180/1020, 1130/1035, 1125/1040, 1120/1030, and 1090/1015 cm^{-1}, respectively. As described for polyphenylsilsesquioxane, however, IR study cannot be the sole evidence for a ladder structure.

Maciel et al.[80] studied the ^{29}Si CP-MAS NMR spectra for solid polymethylsilsesquioxanes, which were prepared by the hydrolysis of methyltrichlorosilane with a large excess of water and the hydrolysis of methyltriethoxysilane in ethanol with hydrochloric acid. A strong peak at −65 ppm and a weak peak at −55 ppm were observed which they assigned to $CH_3SiO_{3/2}$ and $CH_3Si(OH)O_{2/2}$ units, respectively. For the polymethylsilsesquioxane prepared from methyltriethoxysilane, a shoulder appeared on the low-shielding side of the peak at −65 ppm which was identified as a $CH_3Si(OC_2H_5)O_{2/2}$ unit. Engelhardt et al.[81] also reported a ^{29}Si NMR study for a methyl silicone resin, in which $CH_3SiO_{3/2}$ appeared as a peak at −65.6 ppm in the solid-state NMR and at −65.3 ppm in a carbon tetrachloride solution. The ^{29}Si NMR spectrum of **PMSQ-4**[70] showed peaks at −55.3 and −64.8 ppm.

The XRD analysis of **PMSQ-4**[70] presented broad reflections assigned to the plane-to-plane distance at 8.7 Å and the thickness of the molecular chains at 3.6 Å.

Thermal Properties. Polymethylsilsesquioxane is characterized by its low weight loss at high temperatures, ~800 °C, although the initial decomposition temperature is somewhat lower than that of polyphenylsilsesquioxane. Theoretically 10.5% of the weight is lost by the conversion of $CH_3SiO_{1.5}$ to SiO_2, while that from $C_6H_5SiO_{1.5}$ to SiO_2 gives 53.5% weight loss.

Adachi et al.[82] evaluated the thermal property of a polymethylsilsesquioxane with a M_w of 5.0×10^4 which was prepared by the hydrolysis of methyltrichlorosilane in a cooled organic solvent, followed by condensing the hydrolyzate in the presence of triethylamine. The initial decomposition temperature of the polymethylsilsesquioxane was 460 °C in air which was lower than that of a polyphenylsilsesquioxane, 520 °C. However, the weight loss of the polymethylsilsesquioxane at 800 °C was only 9% which was much smaller than that of the polyphenylsilsesquioxane, ~50%. Kitakohji et al.[39] reported the initial decomposition temperature of a polymethylsilsesquioxane was 400 °C in air and at 660 °C under nitrogen for a heating rate of 5 °C/min. The weight loss at 900 °C was 7%. **PMSQ-3** showed a weight loss at 400 °C of 5% under nitrogen and 9% in air.[69] **PMSQ-4**[70] showed only 2% weight loss at 700 °C under nitrogen and 10% weight loss at 460 °C in air at the heating rate of 20 °C/min.

Matsui[37] reported the mass spectra of the gases released by heating polymethylsilsesquioxanes (Owens-Illinois, Glass Resin GR650) at 400−600 °C in vacuo. Polymethylsilsesquioxanes cured at 250 °C in air for 30 min gave water, hydrogen, carbon monoxide, and carbon dioxide at 500 °C. Methane and ethanol were additionally released at 550 °C. Those cured at 350 °C began to release water, methane, hydrogen, carbon monoxide, and carbon dioxide at 550 °C.

The pyrolysis mechanism was investigated by Li and Hwang[83] using thermogravimetry both under isothermal conditions and by increasing the temperature at 10 °C/min. The thermal degradation of a polymethylsilsesquioxane under isothermal conditions was interpreted as a non-chain-scission mechanism containing initiation, propagation, and termination. In the initiation step, the activated silicon and methyl groups are formed. The propagation occurs at the Si−C bond conjugating with the activated silicon atom. The activated silicon reacts with oxygen immediately to form silica, and the methyl group oxidizes to give carbon dioxide and water. A linear relationship between the rate of weight loss and time in the early stage of pyrolysis and the presence of a maximum value in the rate curve supports the above proposed mechanism. (See section V. B.2 for other mechanisms.)

Mechanical Properties. There is little information on mechanical properties of polymethylsilsesquioxane in contrast to that for polyphenylsilsesquioxane. Cured polymethylsilsesquioxane coatings showed a pencil hardness of 9 H[37] but were very brittle. The description that **PMSQ-1**[67] and **-2**[68] attained a coating film thickness up to only 2 and 3.5 μm, respectively, by the improvement in the patents also reveals the brittleness of polymethylsilsesquioxanes.

Tensile strength and elongation were measured on **PMSQ-6** films[76] cured at 100 °C, in which the units with hydroxy or methoxy groups were still remaining. The degree of bridging, $CH_3SiO_{3/2}/(CH_3SiO_{3/2} + CH_3Si(OR)O_{2/2})$ in which R is H or CH_3, was 78% at the maximum. The film with the degree of bridging of 78% showed a tensile strength of 28 MPa.

Other Properties. A polymethylsilsesquioxane (GR650) was optically transparent between 250 and 600 nm.[37] The refractive index is 1.42. This resin was also characterized by its relatively high volume resistivity, low dielectric constant, and low hygroscopicity.[37]

3. Applications

Although the application of polyphenylsilsesquioxane is mainly focused on coatings in electronic and optical devices as mentioned above, the use of polymethylsilsesquioxane is much more diversified. Several representative applications are described below.

The review article describing organosilicon resists reports the use of polymethylsilsesquioxane.[41] A novel chemical amplification resist for electron beam lithography, which consists of an onium salt cationic

initiator and a polymethylsilsesquioxane, was developed by Matsushita Electric.[84] **PMSQ-1** was applied as an insulating films for an integrated circuit. The film on a silicon wafer was heated at 350 °C for 1 h followed by further heat treatment at 450 °C for 30 min. This treatment gave a 2-μm-thick coating without cracking.[66,67] **PMSQ-2**[68] and **3**[69] are also aimed at the insulating layers on electronic circuit boards.

The polymethylsilsesquioxane powder, **PMSQ-5**, is used for additive to materials such as cosmetics,[85] polypropylene films,[86] and methacrylic resins.[87] The use of polyorganosiloxane compositions containing polyorganosiloxanes, amino- and epoxy-containing silanes/siloxanes, and polymethylsilsesquioxane powder are also disclosed in a patent.[88] This composition, which adheres well to rubber and plastics, can be used to provide nonsticking, water repellent, and abrasion resistant films on papers, rubbers, plastics and metals.

Sumitomo Electric[89] applied polymethylsilsesquioxane to a polymer clad on the outer periphery of a silica or optical glass fiber. The clad fiber exhibited good strength, light transmission characteristics, heat resistance, and flexibility. The polymethylsilsesquioxane was prepared by the Japan Synthetic Rubber method.[66]

Polymethylsilsesquioxane is also used as a binder for ceramics.[90] **PMSQ-8** was reported to produce a black glass, discussed in more detail below, by heating to 900 °C at 5 °C/min in nitrogen with an apparent composition of SiO_2 (70%), SiC (20%), and C (10%).[78] Kamiya et al.[91] prepared nitrogen-containing SiO_2 glass fibers by ammonolysis of gels obtained by the hydrolysis and condensation of methyltriethoxysilane by the sol–gel process.

C. Copolymer of Phenylsilsesquioxane and Methylsilsesquioxane

Copolymers of phenyl- and methylsilsesquioxanes are disclosed in several patents. This can be used as a method to prevent a polymethylsilsesquioxane from gelation by the incorporation of the phenylsilsesquioxane unit and to provide the brittle polymethylsilsesquioxane with some toughness.

Several patents were issued to Owens Illinois[92–94] describing the cohydrolysis and the condensation of a mixture of methyltriethoxysilane and phenyltriethoxysilane in the presence of vanadium, iron, and aluminum chelate catalysts.

Methyltriethoxysilane and phenyltrimethoxysilane in a 9 to 1 molar ratio were hydrolyzed in the presence of hydrogen chloride at 50 °C for 30 min and at 70 °C for 2 h.[95] The hydrolyzate was reacted with triethylamine in MIBK (15% solid) at 80 °C for 3 h, followed by neutralizing with hydrogen chloride. A polymer with a M_n of 3.5×10^5 was obtained.

Commercially available copolymers are also described in other patents.[96,97]

D. Others

1. Substituted Phenyl- and Benzylsilsesquioxanes

In their work on the molecular conformations, hydrodynamics, and optics of polysilsesquioxanes described in the polyphenylsilsesquioxane section,[27,28] Andrianov et al. studied poly[(*m*-chlorophenyl)-silsesquioxane] along with copolymers of phenylsilsesquioxane with 4-methylpentyl- and isobutylsilsesquioxane.

Papkov et al. studied poly(*m*-tolylsilsesquioxane).[98,99] They prepared the polymer in a two-step equilibration using potassium hydroxide from the chlorosilane via T_{8-16} cages and observed mesomorphic super molecular structures during the polymerization. By the hydrolysis in 95% ethanol, Feher and Budzichowski[100] prepared the octameric cage of *m*-tolylsilsesquioxane together with those of benzyl- and 3,5-dimethylphenylsilsesquioxanes.

Terunuma and Murakata[101] reported the preparation of polyphenylsilsesquioxanes substituted with *n*-butyl, *n*-pentyl, and *n*-nonyl groups at the para position for improving the brittleness of polyphenylsilsesquioxane. The first two gave oils with a M_w of 7.0×10^3, but the last one resulted in mostly a T_8 cage.

Karchkadze et al.[102] obtained a high molecular weight poly(α-naphthylsilsesquioxane) by an alkaline equilibration of the oligotetrols at 270–280 °C. The oligotetrols are the hydrolyzate of the corresponding chlorosilane. The polymer showed a weight loss onset at 400–450 °C and a 40% weight loss at 650 °C by TGA.

Substituted phenyl- and benzylsilsesquioxanes are found as a component for photoresists.[41] Onose and Tanaka developed a positive photoresist using a copolymer of phenyl- and (*p*-acetylphenyl)silsesquioxane.[103] A positive resist utilizing poly[(*p*-hydroxybenzyl)silsesquioxane] is reported by Sugiyama et al.[104–106] The phenolic OH was protected as a methoxy group during the polycondensation catalyzed by potassium hydroxide, and the (*p*-methoxybenzyl)-trichlorosilane was synthesized either by the Grignard reaction between (*p*-methoxybenzyl)magnesium chloride and silicon tetrachloride or by the reaction of *p*-methoxybenzyl chloride and trichlorosilane. The phenolic hydroxy group was introduced to give the polymer alkali solubility, and the benzyl group was employed to prevent the cleavage of the silicon–phenol bond. Positive resists containing poly[(*p*-hydroxybenzyl)silsesquioxane-*co*-(*p*-methoxybenzyl)-silsesquioxane] were prepared by Sachdev et al.[107] They partially replaced OH groups with [(1,2-diazonaphthoquinonyl)sulfonyl]oxy moiety and obtained bilayer resist formulations having higher sensitivity and contrast.

A large number of substituted polyphenylsilsesquioxanes are claimed for carcinostatic drugs.[65] The substituents include *p*-bromo-, methyl-, methoxy-, *p*-phenoxy-, *o*-trifluoromethyl-, *p*-cyano-, and carboxylic groups.

2. Aliphatic Silsesquioxanes

In their effort to obtain stable low molecular weight hydrolyzates by the presence of large substituents, Sprung and Guenther[18] obtained a poly(*n*-amylsilsesquioxane) by the acid- or base-catalyzed reaction of the corresponding triethoxysilane. The average molecular weight was 9.0×10^2 to 1.0×10^3.

In addition to those described in the former section, Andrianov et al.[26,27] studied the properties of poly(3-methyl-1-butenylsilsesquioxane).

Low molecular weight cages of various alkylsilsesquioxanes are summarized in a review article.[108] Studies include ethyl,[109] *n*-propyl,[109] isopropyl,[108] *n*-butyl,[109] *n*-hexyl,[110] *n*-heptyl,[110] *n*-octyl,[110] and isononyl[110] substituents. The latter four are applied as damping fluids and structural plasticizers for polymeric ceramic materials.[108]

Feher et al. prepared incompletely condensed oligosilsesquioxanes (see Figure 1f) having cyclopentyl, cyclohexyl, cycloheptyl, and cyclooctyl substituents which contains silanol groups[111] and studied these compounds as models for the hydroxy groups on silica surface. They suggested that the most reactive site for silylation of silica surface may be those possessing at least three mutually hydrogen-bonded hydroxy groups based upon the reaction with trimethylchlorosilane.[112] They copolymerized a cyclohexyl partial cage, by using the hydroxy groups, with bis(dimethylamino)silanes.[113] The polymer had a M_w of 1.5×10^4 to 2.0×10^5 and the 10% weight loss temperature by thermogravimetry under nitrogen was 490–510 °C. They also prepared Cr- and V-containing silsesquioxanes by reacting the above molecules with CrO_3 and $(n\text{-PrO})_3VO$ as a model for silica-supported olefin polymerization catalyst.[114]

3. Hydridosilsesquioxane

Hydridosilsesquioxane is a silsesquioxane in which the substituent on silicone is hydrogen, thus is totally inorganic. This material is conventionally called "silsesquioxane" in a similar manner that SiH_4 is called silane. In this article, however, we specify the name of this silsesquioxane as hydridosilsesquioxane to make the term unambiguous.

Frye and Collins[115] were the first to obtain a soluble hydridosilsesquioxane containing T_{10-16} oligomers in a practical yield. They prepared the oligomer by slowly adding a benzene solution of trichlorosilane to a mixture of benzene, concentrated sulfuric acid, and fuming sulfuric acid. They also obtained the T_8 cage by the reaction of trimethoxysilane in a mixture of acetic acid, cyclohexane, and hydrochloric acid.

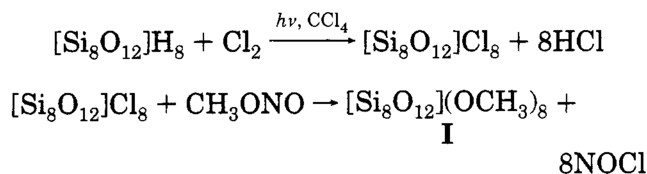
The preparation of polyhydridosilsesquioxane by slowly adding trichlorosilane to MIBK containing 2 wt % of water, followed by bubbling nitrogen carrying water vapor is described in a patent.[116] The unreacted silanol was capped with dimethylchlorosilane. The product was soluble in benzene.

Corriu et al.[117] reported the thermal reactivity under argon, air, and ammonia of hydridosilsesquioxane gels prepared from trichloro- or trialkoxysilane. Under argon, the cleavage of Si–H bonds to give a loss of hydrogen and a redistribution reaction of Si–H and Si–O bonds to give SiH_4 was described. They also reported that the thermal nitridation of the gel with ammonia provides an efficient route to a silicon oxynitride ceramic containing nitrogen higher than 3 wt %.[118]

Hydridosilsesquioxane can be converted to a silica coatings for application in the environmental protection and as an interlayer dielectric for integrated circuits.[119,120] The silica coating is formed either by the rapid thermal processing at a temperature as low as 400 °C[119] or by processing at temperatures from 175 to 250 °C.[120] The silsesquioxane is produced by the method of Frye and Collins.[115] A number of related patents were issued to Dow Corning.[121] The preparation of silica thin films using CVD from hydridosilsesquioxane is also reported by Nyman et al.[122] They synthesized the T_8 by adding a pentane solution of trichlorosilane to a mixture of hydrochloric acid, sodium dodecyl sulfate, anhydrous ferric chloride, and methanol in pentane.

The silanol of a partial hydrolyzate of trichlorosilane was alkoxylated with methanol or ethanol, which was claimed to be reacted with allyl acetate to acetylate 70–90% of the Si–H group.[123] The compounds are used in a formulation for coatings that are highly weather resistant.

In an effort to synthesize a silica consisting of a building block of rigid cubic $[Si_8O_{12}]$, Klemperer et al. prepared $[Si_8O_{12}](OCH_3)_8$ (**I**) by the following two-step reaction:[124]



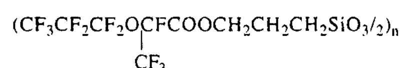
$$[Si_8O_{12}]H_8 + Cl_2 \xrightarrow{h\nu,\ CCl_4} [Si_8O_{12}]Cl_8 + 8HCl$$

$$[Si_8O_{12}]Cl_8 + CH_3ONO \rightarrow \underset{\mathbf{I}}{[Si_8O_{12}](OCH_3)_8} + 8NOCl$$

I was sol–gel polymerized to afford very high surface area silica xerogels, for which transmission electron microscope confirmed the retention of the $[Si_8O_{12}]$ cubic core structure.[125]

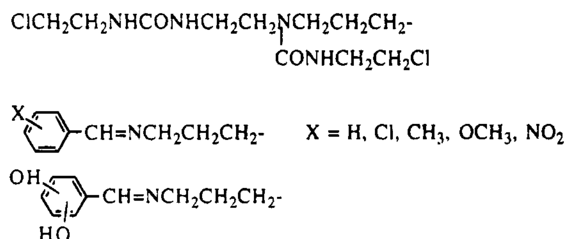
4. Other Silsesquioxanes

Polyfluoroalkylsilsesquioxanes are reported by Kobayashi.[126] Poly[(3,3,3-trifluoropropyl)silsesquioxane] was prepared by hydrolyzing the corresponding trichlorosilane in THF with hydrochloric acid, and poly[(3,3,4,4,5,5,6,6,6-nonafluorohexyl)silsesquioxane] was obtained by hydrolyzing the chlorosilane in 1,3-bis(trifluoromethyl)benzene containing 2-propanol. The M_w of the polymers was 6.55×10^3 and 2.16×10^3, respectively, relative to polystyrene. The IR spectrum of the poly[(3,3,4,4,5,5,6,6,6-nonafluorohexyl)silsesquioxane] showed somewhat less defined bands for the Si–O–Si bonds at 1132 and 1074 cm^{-1}. The ^{29}Si NMR spectrum of the same polymer exhibited peaks for $C_4F_9C_2H_4Si(OH)O_{2/2}$ at −58 ppm and $C_4F_9C_2H_4SiO_{3/2}$ at −66 ppm. The surface tension was 20.0 mN/m for the poly[(3,3,3-trifluoropropyl)silsesquioxane] and 6.6 mN/m for the poly[(3,3,4,4,5,5,6,6,6-nonafluorohexyl)silsesquioxane], while it was 21.5 mN/m for a polymethylsilsesquioxane. A polysilsesquioxane in which the substituent is 3-[[[1-(*n*-heptafluoropropoxy)perfluoroethyl]carbonyl]oxy]propyl of the following formula is claimed in a patent for carcinostatic drugs:[127]



[(2-Benzimidazolylthio)methyl]-, [(2-benzoxazolylthio)methyl]-, and [(2-benzthiazolylthio)methyl]-silsesquioxanes[128] are described as sorbents for metal ions.

A number of patents for polysilsesquioxanes bearing the following groups are filed for carcinostatic drugs:[129–131]



Poly(trimethylsilyl)silsesquioxane was reported by Yamane et al.[132] The monomer, 1,1,1-trimethyl-2,2,2-trichlorodisilane was synthesized from triphenylchlorosilane by converting it to sodium triphenylsilane, reacting the sodium triphenylsilane with trimethylchlorosilane to form trimethyltriphenyldisilane and finally converting the phenyl groups to chloro groups. The polymer was obtained either by the potassium hydroxide equilibration or by the 1,3-dicyclohexylcarbodiimide condensation, giving a M_n relative to polystyrene of $(1.3-5.0) \times 10^3$. Photoreactivity is expected for this polysilylsilsesquioxane.

Polymethyl-, polypropyl-, and polyphenylsilsesquioxanes were used as precursors for ceramic fibers or ceramic matrices[133] and are described in more detail below. By blending those with varying substituents, both the melt rheology and the composition of the fired ceramic can be controlled. The use of polysilsesquioxane-derived Si–C–O as the matrix for Nicalon fiber composite[134] and polysilsesquioxane-derived ceramic fibers[135] is reported by the same group.

Kreuzer et al.[136] prepared liquid crystalline silsesquioxanes by the hydrosilylation of octa(hydridodimethylsiloxy)octasilsesquioxane and various terminally unsaturated mesogens. Most of the products exhibited smectic phases, while the lateral connection of a mesogen resulted in a nematic phase. The optical microscopic textures were similar to those of calamitic liquid crystals. The concept provides a new type of backbone for side chain liquid crystalline polymers ranging from cages to high molecular weight polysilsesquioxanes.

III. Organo-Functional Silsesquioxanes

Most of the silsesquioxanes described in this section are prepared from silanes having the following structure $YRSiX_3$, where Y is an organo-functional group and X is a hydrolyzable moiety. These types of silane compounds are particularly known as silane coupling agents. The hydrolyzable group X includes alkoxy groups, halogen, and acetoxy groups, which form silanol on hydrolysis. The interaction of silane coupling agents with an inorganic material is the strongest when a chemical bonding is formed by the condensation of the silanol with a hydroxy group on the inorganic surface. The silanol can also condense to form a silica-like hard surface. The functional group Y is exemplified with amino, methacryl, vinyl, epoxy, and mercapto groups. The use of a silane coupling agent is again the most effective when a chemical reaction takes place with the organic polymer to form a covalent bond. The effect of the organo-functional group also includes the increasing compatibility of an inorganic material to an organic material by changing the surface energy and providing a layer with intermediate modulus between the inorganic material with a high modulus and the organic material with a low modulus. Thus, by the use of a silane coupling agent in organic–inorganic composites, mechanical properties can be improved, the inorganic filler content can be increased, electric insulation can be maintained, water resistance can be improved, and aggregation of the filler can be avoided. The details of silane coupling agents are not within the scope of the present article but are described elsewhere.[137]

A. Vinyl- and Allyl-Functional Silsesquioxanes

1. Vinyl-Functional Silsesquioxanes

A polyvinylsilsesquioxane with a M_n of 3.8×10^3 was reported by Wagner et al. in 1953.[138] They prepared the polymer by adding an ether solution of vinyltrichlorosilane to ice water and shaking the ether solution containing the product with aqueous ammonium hydroxide. The polymer was a brittle, white solid with a softening point of 85–90 °C, soluble in alcohol, ether, acetone, and benzene but insoluble in hydrocarbons such as heptane or cyclohexane.

Nakahama et al.[19] obtained a hydrolyzate with a M_w of 1.0×10^3 by a hydrogen chloride-catalyzed hydrolysis of vinyltriethoxysilane. The alkaline equilibration of the hydrolyzate resulted in gelation at 250 °C with a 90% concentration and it gave the same result even at 120 °C with 50% solid content. Copolymerization with phenylsilsesquioxane, with the phenyl/vinyl ratio of 7/3 to 9/1, gave polymers with a M_w of $(5.0-8.0) \times 10^4$. These authors then prepared polystyrene-grafted polysilsesquioxanes either by the reaction of a butyl lithium-initiated styrene living polymer with a poly(phenylsilsesquioxane-*co*-vinylsilsesquioxane) or by the radical copolymerization of styrene and the polysilsesquioxane.

A polyvinylsilsesquioxane was prepared by hydrolyzing vinyltrichlorosilane in MIBK, followed by polycondensation at room temperature using triethylamine as a catalyst.[139] The polymer with a M_w of 1.5×10^4 was copolymerized by a free radical process with chloromethylstyrene to give a copolymer with a M_w of 2.5×10^4.

Vinylsilsesquioxane cages appear in many reports. Voronkov et al.[140,141] describes the preparation of a T_8 cage from vinyltrichlorosilane. Vinylphenylsilsesquioxanes with a formula of $(PhSiO_{3/2})_x$-$(ViSiO_{3/2})_{8-x}$, where $x = 1-3$, are also reported.[142] Bromination[143] and hydrobromination[144] of T_8 are reported as examples of reactions of the cages.

Dielectric films for integrated circuits were prepared by Korchkov et al.[145,146] by the vapor deposition of the T_8 cage. The use of vinyl-T_8 as a resist for the electron lithographic manufacture of semiconductor microreliefs, in which the electron lithography is performed as a dry process, has been described in the review article.[108] The interaction of vinyl-T_8 films with hydrogen ions and the applicability as an ionic resist in the dry vacuum process of ion lithography were investigated.[147]

Poly(vinyl-*co*-phenylsilsesquioxane) was applied to a negative bilevel resist for deep-UV lithography.[148]

The polymer has high resistivity to reactive ion etching in oxygen plasma, and the cross-linking involved the radical formation by the fission of a silicon–phenyl bond, followed by an attack of the radical on the vinyl group. The poly(polyvinylsilsesquioxane-*co*-chloromethylstyrene) mentioned above[139] is utilized as an electron beam resist.

Abe et al. reported film-formable vinyl hydrolyzates.[149] These authors prepared the hydrolyzate by the partial hydrolysis and condensation of vinyltrimethoxysilane in the presence of hydrochloric acid in ethanol. Oligomers with a M_w of 6.0×10^2 to 2.2×10^4, which still contained methoxy groups, were obtained . Further condensation of cast films at 80 °C for several days afforded transparent films having a tensile strength of 7–15 MPa. In another approach, these authors first conducted the vinyl polymerization of the silane followed by the hydrolysis. Radical polymerization of vinyltrimethoxysilane using di-*tert*-butyl peroxide gave a polyvinyltrimethoxysilane with a M_w of 2.2×10^3. Hard or flexible gels, depending on the difference in the water/hydrogen chloride/polymer ratio, were obtained by the hydrolytic polycondensation of the trimethoxy group of the polymer.

2. Allyl-Functional Silsesquioxanes

Octaallylsilsesquioxane was synthesized by hydrolyzing/condensing allyltrichlorosilane in ethanol.[150] The yield was increased by bubbling liquid nitrogen vapor through the reaction mixture. Vacuum thermal evaporation resulted in the production of thin films which polymerize upon electron beam irradiation.

The preparation of polyallylsilsesquioxane was disclosed in a patent.[151] Allyltrichlorosilane was first hydrolyzed in a suspension containing ether or THF, water, and sodium hydrogen carbonate to give a hydrolyzate with the degree of polymerization 8–12. The hydrolyzate was condensed in MIBK using a tertiary amine at room temperature to afford polymers with a M_w of 3.0×10^3 to 5.0×10^4. The same inventors claim negative photoresists containing the poly(allylsilsesquioxane) and a bisazide.[152] The resist was characterized by its high sensitivity, high resolution, and resistivity to oxygen plasma.

B. Methacryl-Functional Silsesquioxanes

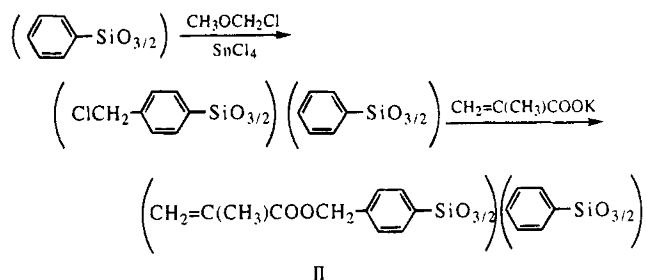
Nakahama et al.[19] obtained a hydrolyzate with a M_w of $(1.2-1.5) \times 10^3$ from [γ-(methacryloxy)propyl]triethoxysilane in the same way as described in the vinylsilsesquioxane section. The alkaline equilibration of the hydrolyzate at 120 °C at 50% solid content gave a polymer in the molecular weight range of $(1.0-1.2) \times 10^4$. Copolymers with phenylsilsesquioxane with the phenyl/vinyl ratio of 7/3 were also obtained with a M_w of $2.5-3.0 \times 10^4$. Polystyrene-grafted polysilsesquioxanes described above were also prepared.

The preparation of copolymers of [γ-(methacryloxy)propyl]silsesquioxane and methylsilsesquioxane was claimed in a recent patent.[153] These inventors prepared the polymer by condensing the corresponding alkoxy silanes in water in the presence of *p*-methoxyphenol to give a prepolymer with a M_w of $(1.4-1.9) \times 10^3$. On further condensing with *n*-butylamine, a polymer with a M_w of $(1.5-1.7) \times 10^4$ was obtained. The polysilsesquioxane is used in ultraviolet curable compositions,[154] in coatings for cement,[155,156] UV-curable adhesives,[157] and coatings for optical fibers.[158]

The preparation of spherical fine powder of poly[γ-(methacryloxy)propyl-*co*-methylsilsesquioxane] is claimed in a patent.[159] The powder, having a controlled diameter of 0.5 to 6 μm, was formed by hydrolyzing/condensing the alkoxysilanes or the partial hydrolyzates in an anionic surface active agent aqueous solution. The silsesquioxane powder is useful for imparting durable lubricity, water repellency and release and stress relaxing properties to plastics and rubber without loss of the inherent properties of the materials.

A methacryl-functional methylfluoroalkylsilsesquioxane which has excellent compatibility and copolymerizability with fluorine-containing acrylic monomers and oligomers was disclosed in a patent.[160] In an example from the patent, a mixture of (3,3,3-trifluoropropyl)trimethoxysilane, [γ-(methacryloxy)propyl]trimethoxysilane, and methyltriethoxysilane was hydrolyzed in a water/ethanol mixture in the presence of hydrochloric acid, followed by equilibrating with *n*-butylamine, to give the product with a M_w of 4.7×10^3. The polysilsesquioxane was photocurable.

A methacryloxy-functional polyphenylsilsesquioxane (**II**) was utilized as a negative photoresist.[161] A polyphenylsilsesquioxane was first chloromethylated and was then reacted with potassium methacrylate to form a polyphenylsilsesquioxane in which a part of the phenyl ring was substituted with a methacryloxymethyl group. The photoresist showed a higher sensitivity to near UV light and excellent resistance to reactive ion etching with oxygen.



Compositions containing poly[γ-(methacryloxy)propyl-*co*-methylsilsesquioxane] were disclosed for anaerobic-curing polysiloxane sealing materials.[162] By using cumene hydroperoxide as a free radical catalyst, the formulation remained uncured for several days in the presence of oxygen but was cured on the removal of oxygen.

Schmidt et al. prepared sol–gel inorganic/organic nanocomposites from compositions based on zirconium alkoxides, methacrylic acid, and [γ-(methacryloxy)propyl]silsesquioxane, with 4-nitro-4′-[[(trimethoxysilyl)oxy]propyl]azobenzene chemically bonded to the matrix.[163] The composite exhibited a second-order nonlinear optical property. (See section V.B.1 for the more details for the sol–gel inorganic/organic composites.)

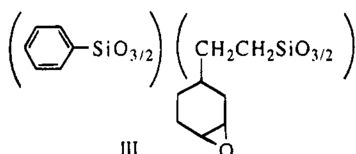
C. Amino-Functional Silsesquioxanes

The use of amino-functional silsesquioxanes is found in several patents. An insulating layer of a polysilsesquioxane formed by hydrolyzing silanes such as (γ-aminopropyl)triethoxysilane and [γ-[(2-aminoethyl)amino]propyl]triethoxysilane is claimed for electronic devices.[164,165] The same type of silsesquioxanes are claimed to provide curl retention for hair.[166] Antitumor silsesquioxane derivatives are disclosed which are formed by the dehydrative condensation of poly[(γ-aminopropyl)silsesquioxane] and specific carbonyl compounds.[130,131,167] [γ-[(2-Aminoethyl)amino]propyl]triethoxysilane is hydrolytically polymerized in the presence of SiO_2 or Al_2O_3 and treated with $PdCl_2$ to give silsesquioxane-supported transition metal catalysts.[168]

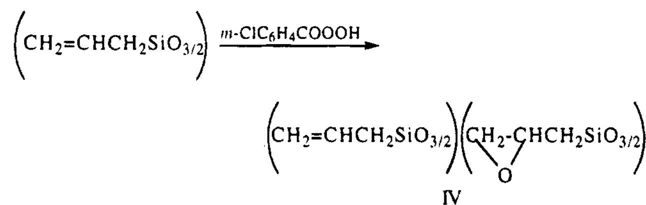
D. Epoxy-Functional Silsesquioxanes

Nakahama et al.[19] obtained a hydrolyzate with a M_w of 1.0×10^3 from (γ-glycidoxypropyl)trimethoxysilane in the same way as described in the vinylsilsesquioxane section.

[2-(3,4-Epoxycyclohexyl)ethyl]trimethoxysilane was co-hydrolyzed with phenyltrimethoxysilane to form a corresponding alkali-soluble silsesquioxane copolymer (**III**).[41] The polysilsesquioxane is reported to behave as a sensitive negative bilayer deep UV resist in the presence of a photo acid generator. [2-(3,4-Epoxycyclohexyl)ethyl]trimethoxysilane is also used in the above-mentioned insulation layer application.[164]



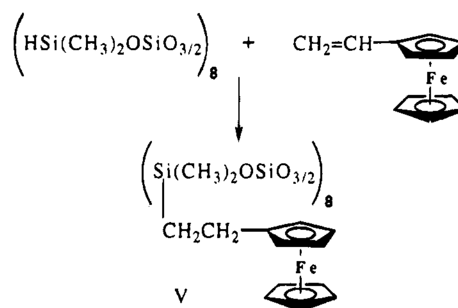
The polyallylsilsesquioxane described above[151] with a M_w of 1.47×10^4 was epoxidized by reacting with 3-chloroperoxybenzoic acid.[169] The degree of epoxidization was about 50%, which means that the product was a copolymer of allylsilsesquioxane and glycidylsilsesquioxane in a 1:1 ratio (**IV**). The composition containing a photo acid generator was curable with UV light for photolithography.



E. Others

The polysilsesquioxane spherical fine powder mentioned in the methacryl-functional silsesquioxane section was also prepared using (mercaptopropyl)trimethoxysilane.[159] Poly[(mercaptomethyl)silsesquioxane][170] is reported to separate silver ions from other heavy metal ions by sorption onto it. Poly[(ω-sulfoalkyl)silsesquioxanes] were prepared from $HS(CH_2)_nSi(OR)_3$, where $n = 1-3$, by treating the silane with hydrogen peroxide for oxidation of the SH group to SO_3H, which was accompanied by hydrolysis of the alkoxysilane with subsequent polycondensation.[171] The products were insoluble and nonswelling in water and organic solvents and selectively sorbed Fe^{3+} from aqueous solutions.

Soluble poly[(γ-chloropropyl)silsesquioxane] in the molecular weight range of $(1.0-1.2) \times 10^4$ was prepared by Nakahama et al.[19] Copolymers with phenylsilsesquioxane with a phenyl/vinyl ratio of 7/3 were obtained with a M_w of 1.22×10^5. The chloropropyl group was reacted with living polystyrene to give polystyrene-grafted polysilsesquioxanes. Porous xerogels of poly(chloromethylsilsesquioxane) were reported for hydrocarbon sorption.[172]



The ferrocenyl-substituted T_8 cage (**V**) was synthesized by the hydrosilylation of vinyl ferrocene with octakis(hydrodimethylsiloxy)octasilsesquioxane, and polymers containing skeletal ferrocene together with silsesquioxane frameworks were prepared by the hydrosilylation of the hydrosilsesquioxane and 1,1′-divinylferrocene.[173] The electrochemical behavior of the products was studied by cyclic voltammetry.

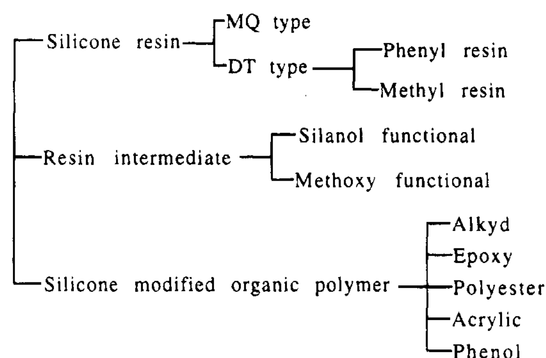
Carbofunctional polysilsesquioxanes, $\{X(CH_2)_nSiO_{3/2}\}_m$ and $\{O_{3/2}Si(CH_2)_nY(CH_2)_nSiO_{3/2}\}_m$, where X = $H_2N(CH_2)_2S-$, $H_2N(CH_2)_3S-$, CH_3CONH-, $CH_3C(S)NH-$; Y = $-S(CH_2)_2S-$, $-NHSSNH-$, $-NHSONH-$, $-NHSO_2NH-$, where $n = 2, 3$, were prepared by hydrolytic polycondensation in a water or an ammonium hydroxide solution.[174] These silsesquioxanes showed high sorption activity in the separation of Au(III), Pt(IV), and Pd(II) from HCl solutions in the presence of Zn(II), Cu(II), Fe(III), and Ni(II).

IV. Commercial Silicone Resins

The term "silicone resin" refers to a class of nonlinear, largely silsesquioxane-containing polyorganosiloxanes and formulations therefrom. In this article, however, formulations will not be included for simplicity. Usually silicone resins before curing are solvent-soluble solids or liquids. While the base polymers of silicone oils and elastomers mostly consist of D units, silicone resins contain T, silsesquioxane, or Q, silicate, units as essential building blocks. This means that silicone resin polymers possess cross-linked (network) structures and thus are three dimensional.

In this section, classification, structures, preparation, properties, and application of silicone resins are reviewed by referring to some broad general publications including Japanese publications[175-177] since detailed published literature on this area, other than

Scheme 1. Classification of Commercial Silicone Resins (Reprinted from Ref 187 and Translated into English. Copyright 1993 Dow Corning Toray Silicone Co., Ltd.)



trade literature, is very limited. Information about applications can be also found in the literature.[178-186]

A. Classification

Scheme 1 illustrates the classification of silicone resins in terms of building units.[187] Silicone-modified organic polymers are copolymers of silicone and organic polymers, which are prepared using resin intermediates. Resin intermediates are relatively low molecular weight silicone resins containing silanol or alkoxy functionality. The organic polymers used for silicone modification include alkyd resin, epoxy resin, polyester, etc., which are applied according to their feature. Resin intermediates and silicone-modified organic polymers will not be discussed in this article.

Commercial silicone resins can be classified into a DT type, which mainly consist of D and T units, and an MQ type, which comprise M and Q units. MQ resins are prepared by using sodium silicate as the starting material for the Q unit which is capped by trimethylsilyl group, and are mostly used internally in silicone industry as raw materials for adhesives, etc. Thus, commercial silicone resin in general means the DT-type resins, for which the rest of the description in this section will be presented. The DT-type resins are classified into phenyl resin, which contains phenyl and methyl groups as the organic radical, and methyl resin, which consists exclusively of methyl substituent.

B. Structures

The structural factors affecting the properties of commercial silicone resins are the type of the organic radicals (R), the R/Si ratio, the phenyl/methyl ratio, and the molecular weight. Unlike linear polymers, it is very difficult to "visualize" the structure of a specific resin polymer molecule using chemical drawing. It is especially difficult to show the size of the molecule because it is three-dimensional, and the concept of "repeating units" can hardly be applied. Researchers in this area often use compositional formulas for describing resin polymers such as $[C_6H_5SiO_{3/2}]_x[(CH_3)_2SiO]_y$ where x and y show only the molar ratio of the components. Using the expression of M, D, T, and Q units, the molecule shown above would be conveniently expressed as $T^{Ph}{}_xD^{Me2}{}_y$, or more concisely $T^{Ph}{}_xD_y$ because methyl groups are often treated as default.

Table 4. Half-Lives of Organic Groups at 250 °C (ref 188)

organic group bonded to Si	approximate half-life at 250 °C in air
phenyl	>100000
methyl	>10000
ethyl	6
propyl	2
butyl	<2
pentyl	4
nonyl	8
decyl	12
dodecyl	8
octadecyl	26
cyclohexyl	40
vinyl	101

Table 5. Feature Properties for Methyl and Phenyl Resins (Reprinted from Ref 189 and Translated into English. Copyright 1993 Dow Corning Toray Silicone Co., Ltd.)

methyl resin	phenyl resin
hydrophobic	thermally stable
small weight loss on pyrolysis	oxidatively stable
flexible at low temperature	softens at high temperature
chemically resistant	becomes tack free at room temperature
arc resistant	compatible with organic polymers

1. Type of Organic Radicals

The organic substituents used for commercial silicone resins are essentially methyl and phenyl because the thermal stability is inferior for those containing other organic moieties as listed in Table 4.[188] The constituents of phenyl and methyl resins are D^{Me2}, D^{Ph2}, D^{PhMe}, T^{Ph}, and T^{Me}. Table 5 summarizes the feature properties of methyl resins and phenyl resins.[189] Phenyl resins are often used for heat resistant coatings because of their thermal stability and flexibility after heat aging. On the other hand, methyl resins are used for hydrophobic and nonsmoking applications.

2. R/Si Ratio

R/Si ratio is the molar ratio of all organic groups against all silicon atoms. A pure T resin has an R/Si of 1.0 and a pure D resin has the value of 2.0. Thus a copolymer of T and D has an R/Si between 1.0 and 2.0. The smaller the R/Si, the more cross-linked the resin is. Usual commercial resins have R/Si values between 1.0 and 1.7.[190] A polymer having an R/Si more than 1.7 has a more linear polymer nature rather than being network like. Applications for resins having different R/Si ratios are listed in Table 6.[191]

Similarly, "% SiO_x content" is used to describe the structure of the resins. This shows the inorganic portion of the resin by weight percent after converting all the siloxane moiety into SiO_2. This "% SiO_x" can show the difference in the size of the organic groups while R/Si cannot. For example, the "% SiO_x" of phenylsilsesquioxane is 46.5 ($60/129 \times 100$, $SiO_2 = 60$ and $PhSiO_{3/2} = 129$) and that of methylsilsesquioxane is 89.6 ($60/67 \times 100$), while the R/Si is 1.0 for both.

Table 6. Applications for Commercial Silicone Resins with Different R/Si Ratios (Reprinted from Ref 191 and Translated into English. Copyright 1993 Dow Corning Toray Silicone Co., Ltd.)

R/Si ratio	major applications
1.0–1.2	silicone–glass laminate sheets, binders for mica, hard coatings
1.3–1.6	heat resistant coatings, varnishes for electrical insulation
1.5–1.7	textile coatings

A different way of looking at the weight of inorganic portion is "weight of resin per Si". This is literally the molecular weight of the resin per one silicon atom. The weight of resin per Si of phenylsilsesquioxane is, as shown above, 129. Thus, the higher this value is, the lower the inorganic content.

3. Phenyl/Methyl Ratio

As described before, the phenyl resins contain both phenyl and methyl groups. Their properties thus are affected by the phenyl/methyl ratio according to the features listed in Table 5.[189]

Traditionally, "R/Si", "% SiO_x", "weight of resin per Si", "phenyl content", and "methyl content" have been the major parameters describing structures and properties of silicone resins.[190] Brown prepared four different T^{Me}–T^{Ph}–D^{Me2}–D^{Ph2} resins having the same values in these parameters by varying T^{Me}/T^{Ph} and D^{Me2}/D^{Ph2} ratios and showed that they have very similar properties.[192]

4. Molecular Weight

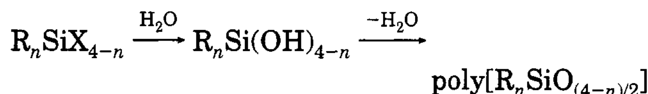
Molecular weights of commercially T-based resins vary from several thousand to more than one hundred thousand.[190] Due to the three-dimensional nature of the molecules, polydispersity indices of the resins as calculated by M_w/M_n are usually very large. GPC is conveniently used for determining molecular weights of resins but the M_n and M_w values relative to standard polystyrene are considerably different from the actual ones. VPO and laser light scattering are recommended for determining exact molecular weights.[193]

Compared to high molecular weight silicone resins of the same R/Si ratio and phenyl/methyl ratio, the low molecular weight resins are more compatible with organic polymers, while the high molecular weight resins are superior in thermal stability and weatherability.[191]

Structural characterization other than what was mentioned above includes NMR techniques, especially ^{29}Si NMR. Owing to the recent advancement of solid state NMR techniques, insoluble materials such as cured silicone resins can be analyzed easily.[194]

C. Preparation

Commercial silicone resins are prepared by hydrolysis of chlorosilanes or alkoxysilanes (mostly methoxysilanes or ethoxysilanes) to form silanol species which successively undergo condensation to give polysiloxanes. The chemistry can be described as follows:



$$R_nSiX_{4-n} \xrightarrow{H_2O} R_nSi(OH)_{4-n} \xrightarrow{-H_2O} \text{poly}[R_nSiO_{(4-n)/2}]$$

where R = methyl, phenyl etc. and X = Cl or alkoxy.

While the hydrolysis of chlorosilanes is usually done without a catalyst (hydrochloric acid is produced as a byproduct and acts as an in situ catalyst), alkoxysilanes are hydrolyzed with an acidic or a basic catalyst.[195] The most commonly used catalyst is hydrochloric acid. In the case of the hydrolysis of chlorosilanes, it is very rare that the resulting polysiloxane contains residual Si–Cl groups. On the other hand, in the alkoxysilane-based resins, residual alkoxy groups are often observed when the catalyst is not strong or the amount of water is not large enough.

The silanol species resulting from hydrolysis of Si–Cl or Si–OR groups undergo condensation to form Si–O–Si bonds. This process takes place almost simultaneously with hydrolysis especially when chlorosilanes are used as starting materials. Since it is not practical to try to isolate silanol species as intermediates, usually the hydrolysis and condensation are carried out in a one-pot process. The resulting resin molecules normally have uncondensed silanol groups, the amount of which is about 2–6 wt % (as OH groups).[196] As mentioned above, these silanol groups are often utilized in cross-linking or modifying the resin. The molecular weight of the resin at this stage is several thousand at most.

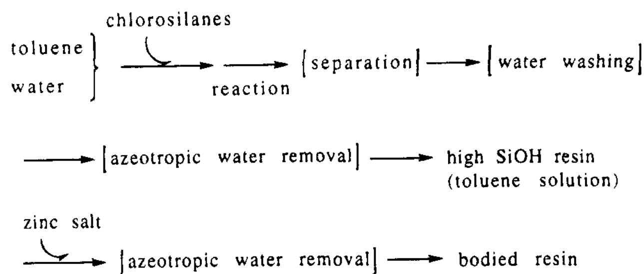
It is often necessary to reduce the amount of uncondensed silanol groups in order, for example, to avoid gelation of the resin during storage caused by self condensation. This is achieved by either "capping" or the condensation of silanol groups. Capping is typically done by allowing hexamethyldisilazane to react with the resin molecule. The condensation, called "bodying" in the industry, is preferred because molecular weights greater than several thousand are desired in many applications. For example, a low molecular weight resin is not good for coating applications because of poor film forming ability and physical strength. This condensation is achieved by refluxing a resin solution in toluene or xylene with azeotropic removal of water in the presence of a catalyst. The catalysts typically used for bodying are metallic salts such as zinc octoate.[196] This bodying is a combination of intermolecular and intramolecular condensation reactions. Obviously the former gives rise to an increased molecular weight and ultimately gelation of the resin. Gelation is controlled by adjusting the concentration of the resin solution during bodying. The higher the concentration, the higher the extent of intermolecular condensation.[196]

The hydrolysis/condensation process can be either batchwise or continuous. A typical batch procedure is shown in Scheme 2.

D. Cross-Linking

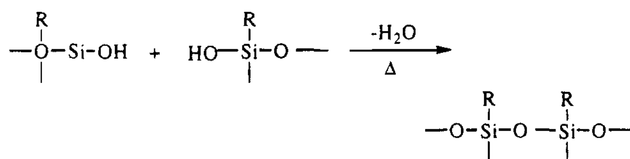
Silicone resins can be cross-linked (cured) to give insoluble and nonmeltable cured materials. The curing methods include silanol–silanol condensation, addition reactions (hydrosilylation), and radical reac-

Scheme 2. Typical Resin Manufacturing Process

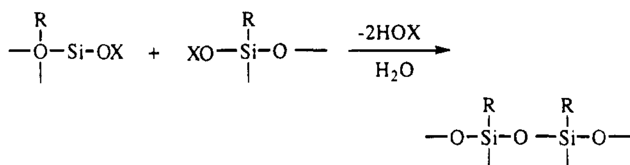


Scheme 3. Curing Methods of Silicone Resins (Reprinted from Ref 198 and Translated into English. Copyright 1993 Dow Corning Toray Silicone Co., Ltd.)

Silanol condensation

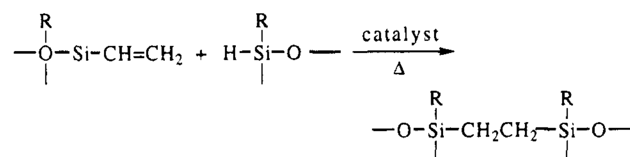


(Room temperature cure)

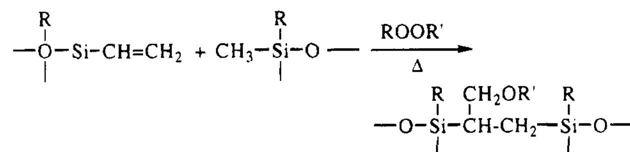


$X = -CH_3$: alkoxy-functional;
$X = -N{=}CRR'$: oxime-functional

Addition reaction



Radical reaction



tions (induced by thermal decomposition of peroxide)[197] as shown in Scheme 3.[198] Among the condensation methods, the alkoxy- and oxime-functional types for which the reaction is induced by the moisture in air are differentiated as room temperature cure system.

Commercially, however, silanol–silanol condensation is used almost predominantly. The condensation reactions, utilizing the residual silanol groups of the resin molecules and forming Si–O–Si bonds with the elimination of water, are effected by heat and catalyst. Even after bodying, silanol groups are available for condensation. The catalysts for cross-linking are again metal salts, among which lead, zinc, and cobalt salts are often used.[199] Usually a high temperature is necessary to obtain complete cure because of the lower reactivity of silanol groups caused by steric hindrance and limited molecular motion. A typical cure temperature ranges between 150 and 250 °C and cure time is 0.5 to 10 h.

E. Properties

It is very difficult to describe properties of silicone resins in a limited space because they vary depending on the composition and application of the resins. Thus, very general aspects of properties of silicone resins will be discussed below.

1. Oxidative Stability

The major reason that silicone resins were accepted by the market in the early days was their oxidative thermal stability.[1-4] Compared with organic resins with C–C backbones, silicone resins have already oxidized backbones, *i.e.*, Si–O–Si, and thus they are inherently resistant to oxidation. Unlike polydimethylsiloxane, silicone resins are not prone to “tail-biting” depolymerization (to form cyclics) or random thermal chain scission owing to the three-dimensional structure. Therefore, it can be concluded that the oxidative stability of silicone resins is mostly governed by the stability of organic groups attached to silicon atoms (see Table 4[188]). It is seen that phenyl and methyl groups are remarkably stable. When organic groups are oxidized, they tend to be substituted with oxygen to form siloxane bonds. Therefore, methyl silicone resins do not lose much weight and increase their cross-link density upon oxidation. This is taken as an advantage and positively utilized in some applications such as high-temperature coatings. For example, some silicone resin-based paint containing aluminum as a pigment can endure more than 500 °C for a long period of time. Oxidized resins are thought to form highly stable composites with aluminum through Si–O–Al bonding.[200] Furthermore, in the early days of the silicone industry, the oxidation of ethyl groups was utilized as a cross-linking reaction in some of the commercial products.

2. Mechanical Properties

While most silicone resins are solid at room temperature, some are liquid. The solid resins are usually soluble in organic solvents and meltable with their typical softening temperatures ranging from 25 to 150 °C. Cured silicone resins are fairly brittle and not suitable for structural materials when reinforcement fillers are not incorporated. Thus, only limited data have been collected regarding the mechanical strength of bulk silicone resins. Instead, there have been numerous data compiled for silicone–glass cloth laminates, silicone–silica–(glass fiber) composites and etc.[201] For coating resins, a great number of coating-specific data such as pencil hardness, bending–cracking, and cross-hatch adhesion have been collected. These data can be typically found in product brochures.

It can be generalized that silicone resins are harder and more brittle with more % SiO_x content. This means that flexibility can be imparted by the incorporation of D or M units or bulky substituents.

3. Weatherability

Synergistic effect of the strong Si–O–Si bond, transparency to UV light, and chemical resistance

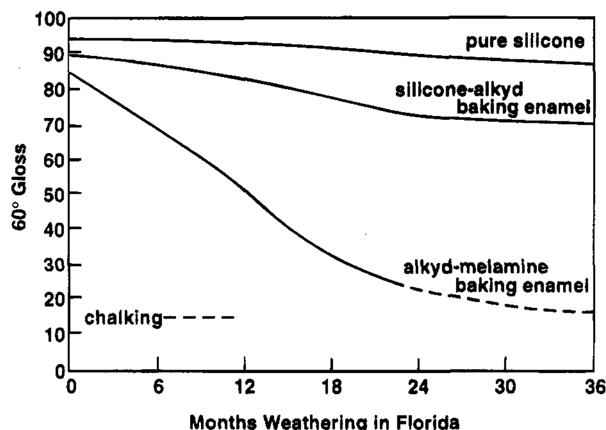


Figure 5. Comparison for the weatherability of a silicone resin coating and an organic coating by outdoor exposure. (Reprinted from ref 202 and translated into English. Copyright 1993 Dow Corning Toray Silicone Co., Ltd.)

Table 7. Surface Tension of Cured Silicone Resins (Reprinted from Ref 203 and Translated into English. Copyright 1993 Dow Corning Toray Silicone Co., Ltd.)

silicone resin	critical surface tension (dyne/cm)	water contact angle (deg)
methyl resin	22.2	108
phenyl resin	27.7	94

gives silicone resins good weatherability as one of the most promising features. Figure 5 illustrates the gloss retention of various coating films for outdoor exposure.[202]

4. Hydrophobicity

Silicone resins are more hydrophobic than organic polymers, and thus are superior in moisture resistance and water repellency. Table 7 lists critical surface tension and water contact angle for a methyl resin and a phenyl resin.[203] Methyl resins have quite low surface tension, and the value increases with increasing phenyl content.

5. Chemical Resistance[204]

Generally, cured silicone resins are resistant to aqueous solutions of acid, base (except for ammonia), or neutral salts. They are also resistant to aliphatic alcohols (except for methanol) and mineral oils. Aromatic solvents, aliphatic solvents, chlorinated solvents, ketones and esters deteriorate silicone resins significantly unless the resin is highly reinforced with fillers.

6. Electrical Properties

In addition to the oxidative stability and weatherability, the electrical properties of silicone resins make them superior to other resins. Table 8 exhibits electrical properties for a phenyl resin and a methyl resin.[205] Their high dielectric strength, high volume resistivity, low dielectric constant, and low dissipation factor make silicone resins very suitable for insulating coatings.[206] More importantly, the temperature dependence of these properties is much smaller than that for common organic materials such as alkyd, polyurethane, and epoxide. Silicone resins maintain good electrical properties even at elevated temperatures while organic materials tend to lose their properties.[205]

Table 8. Electrical Properties of Silicone Resins (Reprinted from Ref 205 and Translated into English. Copyright 1993 Dow Corning Toray Silicone Co., Ltd.)

	phenyl resin	methyl resin
dielectric strength (kV/mm)	45	48
dielectric constant/1 MHz	2.8	2.6
dissipation factor/1 MHz	0.0014	0.0020
volume resistivity (Ω cm)	6.0×10^{15}	4.0×10^{15}

Table 9. Application of Commercial Silicone Resins

- protective coatings
  - heat-resistant coatings
  - weather-resistant coatings
  - release coatings
  - coatings on rubbers
  - surface-protective coatings
  - abrasion-resistant coatings
- electrical insulating coatings
  - electrical insulating varnishes
  - protective coatings for electronics
- adhesive-related materials
  - additives for pressure-sensitive adhesives
  - additives for release paper coatings
- resists for microlithography

F. Application

Silicone resins are used in various applications summarized in Table 9 upon the basis of the properties described above.

Silicone resins are used as heat resistant coatings in chemical plants, automobile exhausts, engine components, heating systems, kitchen appliances, rockets, etc.[207] Silicone resins without organic polymer modification are used for household appliances and heaters in which the service temperature is below 300 °C. For the temperature range between 300 °C and 500 °C, silicone-modified epoxy resin or polyesters are frequently used. Pure silicone resins are again used above 500 °C in combination with pigments as described before.

Silicone-modified organic resin coatings have been mainly used for weather-resistant coatings from the viewpoint of balancing performance, price, and easy processability.[207]

The low surface tension of silicones allows them to be used as release coatings.[207] The major application is for pan glaze. Relatively flexible silicone resins are used for rubber coatings to give the rubber luster, slipping ability, and release ability.[207] Room temperature curable silicone resins are used for easily processable protective coatings for metals and plastics surface.[207]

A hard, clear coating film was developed by hydrolyzing/condensing methyltrimethoxysilane in a water/alcohol solvent system in the presence of colloidal silica. The coating is used for abrasion resistant coating on various substrates including plastics.[208]

Besides the coating application, silicone resins are used as additives for pressure sensitive adhesives and release coatings for the adhesive tapes.[207]

The multilayer resist process was developed to overcome the limitations on resolution imposed by topographic variations on the wafer surface. A

second thin resist film is coated on top of the first planarizing coating in this process. This second resist film needs resistivity to oxygen-reactive ion etching. Silicone-containing resists are quite useful in this application because silicones form protective silica layers when exposed to oxygen glow discharges.[41]

V. Materials Science and Emerging Applications of Silsesquioxanes

A. Bridging Silsesquioxanes

An area of silsesquioxane materials science receiving significant attention in recent years is the use of alkyl or aryl bridged di-, or in some cases, trisubstituted silsesquioxanes represented by the cartoon shown below:

where the shaded box is an arylene, alkylene or alkynyl bridging group. The subject of this class of silsesquioxanes will be part of another review by K. J. Shea and D. A. Loy included in this issue and, therefore, will be treated here only in a cursory way for completeness of the subject on silsesquioxanes.

These materials are generally formed in a solution by acid- or base-catalyzed hydrolysis of the corresponding alkoxy silanes.[209,210] The solvent is removed to form amorphous xerogels with high specific surface areas ranging up to around 1000 m^2/g and nanoporosity from 20 Å and up depending on the size of the bridging group. These clear materials are reported to have thermal stability to 400 °C. These nanopores have been used as scaffolding for quantum confinement materials such as CdS.[211]

B. Ceramic Precursors

1. Inorganic/Organic Hybrids

One very active area of research in recent years has been the formation of inorganic/organic hybrid materials generally utilizing silsesquioxanes as the link between the inorganic and organic components. Phase-separated composite materials will not be reviewed in this section. The review will be confined to molecular level covalently bonded materials or nanometer level composites. These materials are often referred in the literature under the names: ormosils,[212] ormocers,[212] ceramers,[213] and polycerams.[214]

Much of the early work on the ormocers or ormosils originated with Schmidt who coined the term to describe *or*ganically *mo*dified *sil*icates or *cer*amics.[212] Several reviews have been written on molecular levels[212,215] and nanometer size[216–218] particle level materials. Schmidt classifies these into four general types of "ormocers".[215] These are (a) penetrating porous glass by organic monomers and polymerizing them (which does not involve silsesquioxanes[219]), (b) in situ polymerization of inorganic precursors into silicone matrices (which also do not generally involve silsesquioxane moieties),[213] (c) synthesizing independent interpenetrating networks,[220] and (d) linking of inorganic moieties to organo-functional groups where the groups are organo-functional silsesquioxanes, organo-functional bidentate ligands and organo-functional acelylates.[215]

The organo-functional silsesquioxanes frequently employed by Schmidt and associates are (aminopropyl)-, [γ-(methacryloxy)propyl]-, or (3-glycidoxypropyl)silsesquioxanes. A typical "ormocer" formulation would involve silicate moieties generated from tetraalkoxysilanes, titanate moieties generated from tetraalkoxy titanium, epoxy functionality generated from (3-glycidoxypropyl)trimethoxysilane, γ-(methacryloxy)propyl functionality from [γ-(methacryloxy)propyl]trimethoxysilane and a methylmethacrylate monomers.[215] Some formulations also included diphenylsilyl moieties.[215]

The proposed applications for "ormocers" are wide. These range from monolithic forms such as optical lenses to embossing.[221] They have been used as adhesives[219] and abrasive resistant coatings[222] for plastic ophthalmic lens, for human skin abrasives and SO_2 sensors.[215] Numerous other applications are also described by Schmidt.[215b]

Metal salts have been incorporated into silsesquioxane-based ceramers. The gelation of "ormosils" has been followed by studying rigidochromism with incorporated $Re(CO)_3$−2,2′-bipyridine.[223] Metal salts of copper or rhodium have been incorporated into poly(ethylenediaminopropylsilsesquioxane) and then fired to 450 °C in air to give approximately four nanometer size metal particles catalytically active in silica particles.[224]

Larger organic polymeric segments have also been incorporated into the silsesquioxane cores.[214,225] Silica generated from tetramethoxysilane or tetraethoxysilane was combined with (triethoxysilyl)polybutadiene, *N*-(triethoxypropyl-*O*-polyethylene oxide) urethane, or $(MeO)_3Si(CH_2)_2$-substituted polyethyleneimine to produce transparent "polycerams" which could incorporate nonlinear optic dyes such as *p*-nitroaniline or 2-methyl-4-nitroanaline to produce materials with a strong second-harmonic generation.

Polyphenyleneterephthalamide containing carbonyl chloride ends were reacted with (aminophenyl)trimethoxysilane, and the resulting polymer was used to prepare hybrids with chemically bonded silica prepared by the addition of tetramethoxysilane followed by hydrolysis.[226] Tough transparent films were produced.

2. Pyrolysis of Silsesquioxanes to Silicon Oxy Carbide Ceramics

The use of polysilsesquioxanes as precursors to silicon oxy carbide and silicon carbide ceramics through pyrolysis at elevated temperatures in inert atmospheres has become a very active field of research in recent years. Previously, most organosilicon precursors to silicon carbide, silicon nitride, silicon oxy nitride and silicon oxy carbonitride ceramics were polysilanes, polycarbosilanes, or polysilazanes.[227] Other precursors to silicon oxy carbide involving, for example, hydrosilylation reactions, but not involving silsesquioxanes are reported in the literature but not included in this review.

The conversion of silsesquioxanes to silicon oxy carbide ceramics, frequently referred to as "black glass", was first reported about 10 years ago by Chi and associates.[228] A typical procedure employed by these researchers involved hydrolyzing methyltrimethoxysilane in a 6:1 ratio of water and at a pH of about 7. The mixture was allowed to slowly gel for about 3 days, and then the solvent (water and methanol) was allowed to slowly evaporate over a period of 3 weeks. The gel was further dried at 60 °C for 24 h and then at 120 °C for an additional day to produce a low density gel. The slow gelation and drying were conducted to prevent the cracking of the monolithic pieces. Pyrolysis in argon to 1200 °C produced a black amorphous glassy appearing solid with a density of 1.6 g/cm^3 and an empirical formula of $SiO_{1.5}C_{0.5}$.

White and associates at Standard Oil converted a series of silsesquioxanes to silicon carbide.[229] These researchers prepared gels of methyl-, ethyl-, propyl-, hexyl-, vinyl-, allyl-, and phenylsilsesquioxanes by three processes. These processes were ammonium hydroxide-catalyzed hydrolysis of the corresponding alkoxysilanes, acid-catalyzed hydrolysis of the alkoxy silanes followed by ammonia-catalyzed gelation or hydrolysis of the corresponding chlorosilanes. The gels were characterized by FTIR, XRD, TGA, and ^{13}C and ^{29}Si MAS-NMR. The gels were then pyrolyzed in argon to 1500 °C until most of the oxygen was removed by carbothermic reduction to form CO. XRD studies showed that the phenyl-, allyl-, and vinylsilsesquioxanes produced small crystallites of β silicon carbide while the saturated alkyl silsesquioxanes produced broad amorphous peaks in the region of beta silicon carbide and cristobalite. Their TGA studies showed that the decomposition occurred in two steps: loss of carbon hydrogen species and carbothermic reduction with the loss of CO.

Hurwitz and associates[133,134] have studied the pyrolysis by TGA of polymethylsilsesquioxane, polyphenylsilsesquioxane, and the copolymers of phenyl and propylsilsesquioxane and phenyl- and vinylsilsesquioxanes. Initial weight loss occurred around 200 °C probably due to loss of cage silsesquioxanes and formation of thermosets followed by an extensive weight loss beginning at 525 °C. Carbothermic reduction with loss of CO was observed as with the previously mentioned studies at the highest pyrolysis temperatures.

Fibers were drawn from the polysilsesquioxane melts, cross-linked by UV radiation, and fired into ceramic fibers.[133,134] The polysilsesquioxanes were also used as ceramic matrices for silicon carbide fiber and platelets.[133,134] These researchers studied in detail the spinning properties of a phenylsilsesquioxane/propyl silsesquioxane system.[230] They found by IR, ^{29}Si, and ^1H NMR that the silsesquioxane system obtained from Petrarch Systems was a mixture of oligomers with few copolymers present. Shear thinning during spinning was attributed to phase separation.

^{29}Si MAS-NMR studies by Corriu and his associates[231] have revealed that inert gas pyrolysis of methyl silsesquioxane gels first leads to loss of methane and hydrogen up to about 1000 °C and solid-state bond redistribution of Si−C and Si−O bonds at higher temperatures. Similar pyrolysis chemistry was observed for polymethylsilsesquioxane up to 1000 °C.[232] The solid-state redistribution of Si−C and Si−O identified by Corriu was found to occur in other silsesquioxane-based polymers.[233] ^{29}Si MAS-NMR studies showed that similar high-temperature solid-state bond redistribution takes place when a copolymer of phenylsilsesquioxane and methylsilsesquioxane capped with vinyl dimethylsiloxy units was pyrolyzed in an inert atmosphere above 1200 °C.[234]

In addition to the amorphous Si−C−O ceramics produced when polysilsesquioxanes are pyrolyzed to above 1000 °C, an appreciable amount of "free" carbon is also formed in the ceramic matrix.[235] The "free" carbon content was determined by MAS-NMR and elemental analysis. This "free" carbon can be greatly reduced by the presence of Si−H bonds from polysilsesquioxane during pyrolysis. When a 2:1 ratio of $HSiO_{3/2}$ and MeHSiO material was pyrolyzed to 1000 °C in argon, the amount of free carbon was reduced almost to zero.[236]

Glossary of Terms and Symbols

CP	cross-polarization
D	diorganosiloxane ($R_2SiO_{2/2}$) unit
FTIR	Fourier-transform infrared (spectroscopy)
GPC	gel permeation chromatography
M	triorganosiloxy ($R_3SiO_{1/2}$) unit
MAS	magic-angle spinning
MIBK	methyl isobutyl ketone
M_n	number average molecular weight
M_w	weight average molecular weight
PMSQ	polymethylsilsesquioxane
PPSQ	polyphenylsilsesquioxane
Q	silicate ($SiO_{4/2}$) unit
T	organosilsesquioxane ($RSiO_{3/2}$) unit
TGA	thermogravimetric analysis
THF	tetrahydrofuran
T_n	cage structure with the number of the $SiO_{3/2}$ groups of n
VPO	vapor pressure osmometry
XRD	X-ray diffractometry
[η]	intrinsic viscosity

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