SILICONES

1. Introduction

Silicones are a class of polymers having the formula $[R_m Si(O)_{4-m/2}]_n$, where $m = 1–3$ and $n \geq 2$. The most common are the polydimethylsiloxanes (PDMS).

Silicones and silanes are the subject of many reviews (1–8). Commercial products include fluids, filled fluids and gums, greases, resins and rubber (1,2). Various forms of silicones and examples of applications are listed in Table 1.

The designations M, D, T, and Q, respectively, are used for mono-, di-, tri-, and quaternary coordination of oxygen around silicon in silicones. A T group can also be written as $CH_3SiO_{3/2}$; a Q group as SiO_2. When groups other than methyl are present, these groups are indicated with a superscript; eg, D^{Vi} represents a methyl vinyl siloxy group $(CH_3)CHCHSiO$. Resins are often referred to as M_xQ, M_xT, $M_xD_yT_z Q$, etc. This common shorthand notation for silicones is depicted in Fig. 2.

2. History of Silicones

Although silicon is quite abundant in nature, there are no natural forms of organosilicon. The first covalent compound of silicon, SiF_4, was made in 1771 (9). Berzelius, in 1823, was the first to make amorphous silicon by potassium reduction of SiF_4; he also found that the combination of SiO_2, CuO, and C had greater hardness than SiO_2 alone. In 1896, Morrison made silicon metal by the reaction of SiO_2 and C in an electric arc furnace, a process by which metallurgical-grade silicon has been produced commercially since the 1990s. Ironically, in 1900, Oswalt announced, "elementary silicon has no application or any interesting properties" (10). Six years later, in what would prove to be an important discovery, Vigreaux treated Na_2SiF_6 with copper at $1000°C$ to give Cu_xSi, a key intermediate in the modern preparation of methylchlorosilanes. Alkoxy silanes were first prepared in the mid-1800s (11,12).

Kipping is considered the father of organosilicon chemistry. He employed Grignard reagents to make compounds of the general class $R_{4-x} SiCl_x$ (13,14). Kipping reportedly remarked that the polymers obtained from the hydrolysis of chlorosilanes were "omnipresent nuisances" (15). In the 1930s Stock made significant contributions by carrying out gas-phase reactions to prepare silicon hydrides and compounds having Si–Si bonds (16).

The beginning of the silicone industry has been well documented (15,17). In 1930, Corning Glass made the first deliberate effort to find a use for silicones and in 1939 the company began the etherless methyl Grignard process as a method for making methyl silicones. One of the first commercial products, DC 4, was comprised of silica in PDMS fluid. It was used in high altitude aircraft applications. Another early product was DC 990A resin, $C_6 H_5 (C_2 H_5)Si(OH)_2$, which when cross-linked at high temperature had good dielectric strength, low dielectric loss, and good thermal stability.

In 1940, Rochow discovered the direct process, also called the methylchlorosilane (MCS) process, in which methyl chloride is passed over a bed of silicon and copper at high temperature ($250–300°C$) to produce a mixture of methylchloro-

silanes, including the industrially important dichlorodimethylsilane [75-78-5], $(CH_3)_2SiCl_2$. Working independently, Müller made a similar discovery in Germany. Consequently, the process is frequently called the Rochow process and sometimes the Rochow-Müller reaction. These discoveries were followed by two key publications describing the work that marked the beginning of the commercial silicone industry (18,19). Production increased rapidly with the need for silicones in World War II. In 1943, the Dow Corning Corp. was formed in Midland, Michigan, as a joint venture between Corning Glass and Dow Chemical. In 1947, GE opened a plant for manufacture of silicones in Waterford, New York, and in 1949 Union Carbide opened a silicone manufacturing plant in Tonawanda, New York.

3. Chemistry

The chemistry of silicones has been described in many textbooks (1,20,21).

3.1. Direct Process. Passing methyl chloride vapors through a bed of copper and silicon at temperatures near 300°C yields a mixture of methylchlorosilanes. The efficiency of this process is critically dependent on reactor design and chemistry. Optimization of the fluidized bed reactor is a critical part of the industrial process (22). The rate of MCS production and selectivity for dichlorodimethylsilane are significantly affected by trace elements in the catalyst bed; very pure copper and silicon give poor rate and selectivity (23−25).

Much of the early work on the direct process was devoted to understanding the structure of the active catalyst. Many reports have suggested that Cu_3Si, or η-phase, is a key catalytic species in the MCS reaction (9,26−29). Reactions employing Cu_3Si and Cu_5Si have been shown to be good models for the direct process (30). Copper transfer appears to be the first step in the MCS process (31). There is strong evidence to support the intermediacy of a silylene in the Cu-catalyzed direct process (Figure 3) (32).

In a single-crystal study of the surface interaction of Si with various forms of copper as models of the direct process (33), the highest selectivity obtained was for a mixture of 82% Cu and 18% Cu_2O, similar to the selectivity obtained in a fluidized-bed reactor (34). Other surface studies have shown that silicon is efficiently removed from the Cu−Si phase when the ratio of Me to Cl is ∼1:1 (35).

In one of the first comprehensive studies on the effect of trace elements on the direct process (34), the importance of zinc and tin and other trace elements as promoters was recognized. The effects of three promoters and their synergy have been investigated empirically (23). The results show that the reaction rate of the direct process decreases as a function of catalyst bed composition in the following order: SiCuZnSn > aged SiCu > SiCuAlSn >SiCuZn > SiCuAl > fresh SiCu > SiCuZn. The selectivity for the formation of $(CH_3)_2SiCl_2$ also depends on catalyst composition and decreases in the following way: SiCuZnSn > SiCuAlSn SiCuZn > aged SiCu > SiCuSn > SiCuAl > fresh SiCu. This study concluded that zinc functions as a methylating agent. Aluminum and tin are synergistic promotors of rate and selectivity, and it appears that aluminum modifies the alloy properties of CuZnAlSi. Finally, tin and zinc have a synergistic effect. The effect of aluminum on alloying properties has been discussed (36). Aluminum affects reactivity and

selectivity while calcium affects reactivity (37). Additional promoters include phosphorus, which acts as a strong selectivity enhancer (38–40), boron (41) and alkali metal halides (42). Optimization methods have been applied to the complex mixture of promoters used in the direct process (43).

Zinc and tin surface enrichment appears to be essential for high activity and reactivity. Additives that impede silicon and/or zinc surface enrichment have a negative impact on rate. Lead is an example of such a catalyst poison for this reason (44). Considerable fundamental work remains to be done to understand the direct process at the molecular level.

Not surprisingly, the particle size and composition of the silicon used in the direct process are important parameters. Optimum silicon particle size for the fluidized bed process is > 10 μ. Particles must also have low oxygen content (45). An interesting approach to optimizing the interaction of metal catalysts with the silicon surface is the pre-grinding of silicon with at least one of the metals used to catalyze the reaction (46). The elemental composition of the silicon input is critical to its performance in the direct process. Phosphorus can be added as a promoter or may be present as a component of the silicon (47). Significant effort has been made to improve the reactivity of silicon by a water granulation method during the production of silicon (48).

Alternatives to the methyl chloride based direct process have been reviewed (49). Direct-process chemistry has been used to make phenyl and ethyl silicones. For example, chlorobenzene can be used in place of methyl chloride to make phenylchlorosilanes (15). Phenylchlorosilanes can also be produced by the reaction of benzene, $HSiCl_3$, and BCl_3 (17,49). Ethylsilicones have been made primarily in the former Soviet Union, where the direct process is carried out with ethyl chloride in place of methyl chloride (50). Vinyl chloride can also be used in the direct process to produce vinylchlorosilanes (49). Vinylchlorosilanes can also be made by reaction of vinyl chloride with $HSiCl_3$ (51) or by platinum-catalyzed hydrosilylation of acetylene with $HSiCl_3$ (52,53).

Some new direct process-like reactions have been described. The reaction between methanol (CH_3OH) and Cu/Si gives $(CH_3O)_3SiH$ (Fig. 4), and the reaction of methanol over Si/B gives $(CH_3O)_4Si$ (54–56).

The reaction of alcohols other than methanol with silicon sources has been examined under direct process conditions as a method to make alkyl silicates (57). The use of HCl in the MCS reaction gas stream increases CH_3Cl_2SiH without decreasing the total combined yield of $(CH_3)_2SiCl_2$ and CH_3Cl_2SiH; no significant undesirable $SiCl_4$ or $HSiCl_3$ forms (58–60). Similar results are obtained by using hydrogen in place of HCl (61). Hydrogen in the direct process stream enriches SiH monomers, but promoters normally used in the direct process usually retard SiH monomer formation. Zinc is particularly deleterious to CH_3HSiCl_2 formation (62,63). Other forms of the direct process include the reaction of dimethyl ether and methyl halide over Si/Cu to give $(CH_3)_2Si(OCH_3)_2$ (64,65). More recently the reaction of $(CH_3)_2NH$ and silicon to give $((CH_3)_2N)_3SiH$ has been reported (66).

Methylchlorodisilanes are by-products of the direct-process. Commonly referred to as "residue", these are formed at a level of ∼4% of the total $(CH_3)_2SiCl_2$ produced. [In 1994, $(CH_3)_2SiCl_2$ production was ∼30,000 tons/year]. Disilanes are key constituents of the residue, and novel reactions forming Si–Cl bonds

have been described (67–69). Commercially, disilanes are redistributed to recover methylchlorosilane monomers (70). Some chemical reactions of direct-process disilanes are shown in Figure 5. Cleavage of Si–Si bonds with HCl has also been described and is practiced industrially (68).

A significant use of direct-process waste can be realized by C_6H_5 –Si bond formation via silylative decarbonylation (74,75). A novel route to C_6H_5 –Si bond formation has also been described (Fig. 6) (76).

3.2. Synthesis of Silicone Monomers and Intermediates.

Hydrosilylation Products.   In addition to the direct process and Grignard chemistries, a very important reaction for formation of Si–C bonds is the hydrosilylation reaction, which involves the addition of Si–H across an olefinic double bond (Fig. 7).

This reaction has been used for the formation of a wide variety of organo-functionalized silicones and for cross-linking silicone polymers by addition cure (77–83).

Recent examples that have utilized the hydrosilylation reaction to prepare very unique organosiloxanes are shown in Figures 8 and 9. Figure 8 depicts the hydrosilylation of phenylacetylene to provide β-vinyl silicones (84,85) and is a convenient route to high refractive index silicones.

Hydrosilylation reactions have also been used as the key step (86) in the synthesis of dendritic siloxanes (Fig. 9).

Alkoxysilanes.   Alkoxysilanes are important intermediates in the manufacture of silicone based materials. The prevalent method for forming the silyl ether linkage is alcoholysis of Si–Cl bonds (Fig. 10). Removal of the concurrently formed HCl is typically accomplished by addition of tertiary amines (87,88). Often NaOR is used instead of the corresponding alcohol to give the less corrosive and more easily removed NaCl as by-product (89,90). Use of alkyl orthoformates represents an alternative to alcohols or metal alkoxides (Fig. 11) (91–93).

Silyl ethers can also efficiently be prepared starting from Si–H bonds. Silanes containing one or more Si–H functional groups react with alcohols in the presence of a catalyst (Fig. 12). Typical catalysts include bases (eg, KOH, NaOH, KOR, NaOR, amines), strong acids, metals (colloidal copper) and metal complexes of Fe, Co, Ru, Rh, Pd, Ir, and Pt (94). Recently, a highly efficient catalyst (Ph_3PCuH) was reported to affect alcoholysis of hydrosilanes under mild conditions while also tolerating unsaturated alcohols (95). Tris-pentafluorophenylboron is also a very effective catalyst for silylation of alcohols with hydrosilanes (96).

Alkoxysilanes can also be prepared by exchange of an existing alkoxy group with another one (Fig. 13). Generally, alkoxy exchange requires a catalyst such as a mineral or organic acid (97), Lewis acid (alkyl titanate) (98), or strong base.

Acetoxysilanes.   A very important functional group in silicone chemistry is the acetoxysilane group. It is widely used during the manufacture of single component moisture curable room temperature vulcanizable sealants. These acetoxy-stopped polymers hydrolyze more readily than the corresponding alkoxy-stopped silicones, and release acetic acid during cure. Acetoxy-functionalized silicones are generally prepared by the acylation of a chlorosilane via addition of sodium acetate, acetic anhydride or acetic acid (99,100).

It is also possible to synthesize acyloxysilanes by reacting triorganohydrido-silanes with carboxylic acids (Fig. 14) in the presence of strong acids, aluminum, or nickel complexes as catalysts (101).

4. Polymerization

The manufacture of polydimethylsiloxane polymers is a multistep process. The hydrolysis of the chlorosilanes obtained from the direct process yields a mixture of cyclic and linear silanol-stopped oligomers, referred to as hydrolysate (Fig. 15). In some cases, chloro-stopped polymers can also be obtained (102).

The ratio of cyclic to linear oligomers, as well as the chain length of the linear siloxanes, is controlled by the conditions of hydrolysis, such as the ratio of chlorosilane to water, temperature, contact time, and solvents (1). Commercially, hydrolysis of dichlorodimethylsilane is carried out by either a batch or continuous process (1,2,103,107). In a typical industrial operation, dichloro-dimethylsilane is mixed with 22 wt% azeotropic aqueous hydrochloric acid in a continuous reactor. The resulting mixture of hydrolysate and 32 wt% hydro-chloric acid is separated by means of a decanter. After separation, the anhydrous hydrogen chloride is converted by reaction with methanol to methyl chloride, which is then reused in the direct process. The hydrolysate is washed to remove residual acid, then neutralized, dried, and filtered (104). The typical yield of cyclic oligomers is between 35 and 50%. The mixture of cyclic oligomers consists mainly of tetramer and pentamer. Only a small amount of cyclic trimer is formed.

The complete conversion of the dichlorodimethylsilane to only linear oligomers is also possible in a continuous hydrolysis operation (105). In this process, the cyclics are separated from linear oligomers by a stripping process and are mixed again with dichlorodimethylsilane. This mixture undergoes equilibration to chloro-terminated oligomers and is subsequently hydrolyzed. The silanol-stopped linear oligomers are directly used in the manufacture of silicone polymers.

Dichlorodimethylsilane can also be converted into siloxane silanol-stopped oligomers by a methanolysis process (Fig. 16).

In contrast to hydrolysis technology, the methanolysis process allows for the one-step synthesis of organosiloxane oligomers and methyl chloride without formation of hydrochloric acid (106,107). The continuous methanolysis can also yield quantitatively linear silanol-stopped oligomers by recycle of the cyclic fraction into the hydrolysis loop.

If the linear fraction of siloxane oligomers is used directly in the manufacture of silicone polymers, extremely pure ($>99.99\%$) dichlorodimethylsilane is required. A high content of trichloromethylsilane can produce significant amounts of trifunctional units and considerably affect the physical properties of the final products. If such high purity dichlorodimethylsilane is not utilized, an additional step, called cracking, must be included in the production scheme (108). In the cracking process, the hydrolyzate is depolymerized in the presence of strong base or acids to yield cyclic monomers, primarily octamethylcyclotetra-siloxane (D_4) and decamethylcyclopenta-siloxane (D_5), which are distilled from

the reaction mixture. The trifunctional by-products remain in the pot and are periodically removed.

4.1. Polycondensation.   The linear fraction of hydrolysate, dimethyloligosiloxane-α, ω-diols having a viscosity of $10-100$ mPa ($=$ cP), is converted further to silicone fluids and high molecular weight gums by polycondensation of the silanol end groups (Fig. 17). Polycondensation is an equilibrium process. In spite of the relatively high equilibrium constant for this reaction ($K_{eq@35°C} =$ 860 ± 90), water removal is required to obtain high molecular weight siloxane polymers (109).

Although the low molecular weight silanols such as trimethylsilanol and dimethylsilanediol undergo condensation thermally, the higher molecular weight oligomers are much more stable and their polycondensation must be catalyzed. Many catalytic systems capable of promoting polycondensation of siloxanediols have been described in patents and open literature (1,110–117). These catalysts include strong acids such as HCl, HBr, H_2SO_4, $HClO_4$, and CF_3SO_3H; phosphonitrilic chlorides such as $[Cl_3PN(PCl_2N)_nPCl_3]^+PCl_6{}^-$; oxygen-containing chlorophosphazenes such as $Cl_3PN(PCl_2N)_nP(OH)Cl_2$; strong bases such as KOH, NaOH, and $(CH_3)_4$ NOH; as well as amines, amine salts of carboxylic acids, ion exchange resins, and clays activated with mineral acids. The most selective, efficient and extensively used in industry are phosphonitrilic chlorides (112–114) and oxygen-containing chlorophosphazenes (115–117).

The first mechanistic studies of silanol polycondensation on the monomer level were carried out in the 1950s (118–120). The proposed mechanism of the acid-catalyzed condensation involves the protonation of the silanol group and subsequent nucleophilic substitution at the silicone (Fig. 18).

In the condensation catalyzed by a strong base, the rate-determining step is the attack of silanolate anion on the silicon atom in the silanol end group (118,119). Because of the high acidity of silanol (110), the alkali metal base (MtOH) is usually transformed into the silanolate anion (Fig. 19).

Early studies of the condensation reaction on the monomer level did not give the full picture of this process and only in the 1980s was the polycondensation of siloxanols studied by using oligomeric model compounds (121,122). These studies revealed that in the presence of strong protic acids three processes must be considered: linear condensation, cyclization, and disproportionation (Fig. 20). The relative contributions from these processes strongly depend on the reaction conditions, such as type of solvent, substrate, water concentration and acidity of catalyst (121–124). It was also discovered that in acid–base inert solvents, such as methylene chloride, another silanol group provides the basic assistance required for the condensation process. This phenomenon, called intra–inter catalysis, controls the linear/cyclic products ratio, which is constant at a wide range of substrate concentrations (121).

The behavior of oligosiloxanediols in the presence of strong bases is different. The contribution to the overall process of the disproportionation reaction, involving a migration of the ultimate siloxane unit between siloxane molecules, is much greater and may even completely dominate the polycondensation reaction (125). The reactivity enhancement of the siloxane bond adjacent to the silanolate anion can be understood in terms of $n(0) \rightarrow \sigma^*$ (SiO) conjugation.

4.2. Ring-Opening Polymerization. Ring-opening polymerization of cyclic oligodiorganosiloxanes is an alternative to the polycondensation method of manufacturing siloxane polymers. Commercially, the polymerization of unstrained octamethylcyclotetrasiloxane (D_4) is the most important (1,102,110). In the presence of catalysts such as strong acids or bases, D_4 undergoes equilibrium polymerization, which results in a mixture of high molecular weight polymer and low molecular weight cyclic oligomers (Fig. 21). The molecular weight of the polymer is easily controlled by the amount of chainstropper added and can be varied from very low molecular weight (MW) to very high MW.

The position of the equilibrium depends on a number of factors, such as concentration of siloxane units and the nature of substituents on the silicon, but is independent of the starting ratio of linear to cyclics or the polymerization conditions (126,127). For a bulk polymerization of dimethylsiloxane, the equilibrium concentration of cyclic oligomers is $\sim$18 wt% (128). The equilibrium mixture of cyclosiloxanes is composed of a continuous population to at least D_{400}, but D_4, D_5, and D_6 make up > 95 wt% of the total cyclic fraction (129).

The ring-opening polymerization of D_4 is controlled by entropy, because thermodynamically all bonds in the monomer and polymer are approximately the same (1,110,130). The molar cyclization equilibrium constants of dimethylsiloxane rings have been predicted by the Jacobson-Stockmayer theory (131). The ring-chain equilibrium for siloxane polymers has been studied in detail and is the subject of several reviews (127,128,132–135). The equilibrium constant for the formation of each cyclic is approximately equal to the equilibrium concentration of this cyclic, $K_n \sim [(SiR_2O)_n]_{eq}$. The total concentration of cyclic oligomers at equilibrium is thus independent of the initial monomer concentration. As a consequence, the amount of linear polymer decreases until the critical dilution point is reached, at which point only cyclic products are formed.

4.3. Anionic Polymerization of Cyclic Siloxanes. The anionic polymerization of cyclosiloxanes can be carried out in the presence of a wide variety of strong bases such as hydroxides, alcoholates, or silanolates of alkali metals (1,102,110). Commercially, the most important catalyst is potassium silanolate (98). The activity of the alkali metal hydroxides increases in the following sequence: LiOH $<$ NaOH $<$ KOH $<$ CsOH, which is also the order in which the degree of ionization of their ion pair increases (136). Another important class of catalysts is tetraalkylammonium and tetraalkylphosphonium hydroxides, and silanolates (137–139). These catalysts undergo thermal degradation when the polymer is heated above the catalyst decomposition temperature (typically $>150°C$) producing volatile by-products and the neutral, thermally stable polymer. Recently, a new class of super strong phosphazene bases such as $[(NMe_2)_3P=N-)_3P=NtBu]$ has been reported (140–142). The phosphazene bases allow for the synthesis high molecular weight polysiloxanes using extremely low catalyst levels with short reaction times and over a wide range of temperatures.

Anionic polymerization is widely used in the silicone industry for the manufacture of silicone polymers. The anionic polymerization of cyclic siloxanes can be conducted in a single-batch reactor or in a continuously stirred reactor (143,144). The viscosity of the polymer and type of end groups are easily controlled by the amount of added water or triorganosilyl chain-terminating groups.

The mechanism of anionic polymerization of cyclosiloxanes has been the subject of several studies (145,146). The first kinetic analysis in this area was carried out in the early 1950s (147). In the general scheme of this process, the propagation/depropagation step involves the nucleophilic attack of the silanolate anion on the silicon, which results in the cleavage of the siloxane bond and formation of the new silanolate active center (Fig. 22).

The kinetics of this process is strongly affected by an association phenomenon. It has been known that the active center is the silanolate ion pair, which is in equilibrium with a dormant ion pair complex (148,149). The polymerization of cyclosiloxanes in the presence of potassium silanolate shows the kinetic order 0.5 with respect to the initiator, which suggests the principal role of dimer complex (150).

The synthesis of new, high performance materials requires the synthesis of well-defined, narrow molecular weight distribution, cyclic-free, homo- and copolymers. This can be accomplished by the kinetically controlled polymerization of the strained monomers, hexaalkylcyclotrisiloxanes. In the presence of the proper initiator and under the right reaction conditions, the polymerization of hexamethylcyclotrisiloxane (D_3) can proceed as a classical living polymerization. The most frequently used initiator, lithium silanolate, provides fast and quantitative initiation and a propagation that is free of depolymerization or chain-scrambling processes (151−153). However, the rate of D_3 polymerization in the presence of lithium silanolate is slow. To accelerate the polymerization process, a cation-interacting solvent such as tetrahydrofuran (THF) is commonly employed (154,155). Nucleophilic additives such as hexamethylphosphoric triamide (HMPT) or dimethyl sulfoxide (DMSO), as well as chelating agents such as cryptates, can also be used (156−161). These additives interact strongly with the lithium cation and convert the intimate ion pair into a more reactive, separated one.

4.4. Cationic Polymerization of Cyclic Siloxanes.   The cationic polymerization of cyclic siloxanes is often a preferred method for the synthesis of siloxane polymers. This process, which can be performed at relatively low temperature, can be applied to the synthesis of polysiloxanes having base-sensitive substituents such as Si−H, and the catalyst can be easily deactivated. The first high molecular weight siloxane polymer was prepared by the cationic ring-opening polymerization of D_4 in the presence of sulfuric acid (162). Since that time many catalytic systems have been reported in patents and open literature. These include strong protic acids such as CF_3SO_3H (triflic acid), $HClO_4$, H_2SO_4, aryl- and alkylsulfonic acids, heterogeneous catalysts such as ion-exchange resins, acid-treated graphite, and acid-treated clays, as well as some Lewis acids such as $SnCl_4$ (1,110,163−172). Polymerization in the presence of Lewis acids is a subject of controversy. Strong protic acids such as $HSnCl_5$, the product of the reaction of Lewis acid with water or other protic impurities, are proposed in most cases as the true catalyst (173). However, it has been reported that some nonprotic systems such as ethylboron sesquitriflate (174), and antimony chloride — acid chloride pairs (175) are able to initiate polymerization of cyclotrisiloxane. Also, electron-deficient organosilicone reagents such as trimethylsilyl triflate (176,177) and $Me_3SiH/(C_6H_5)_3C^+B(C_6 F_5)_4^-$ (178) have been proven effective as initiators for cationic ring-opening polymerization of cyclosiloxanes.

Despite a long history of commercial application and in-depth studies (110, 163,178–184), the mechanism of cationic polymerization of cyclic siloxanes is not as well understood as the anionic process. Several unusual kinetic results have been observed, such as the apparent negative order in the monomer concentration, negative activation energy, or a strong effect of water on the kinetics of polymerization (171,182–185). The proposed complex mechanism of acid-catalyzed polymerization consists of four processes: initiation-ring opening, step growth by homo- and heterofunctional condensation, chain propagation by direct monomer addition, and end group interconversion. Hydrogen-bond association plays a crucial role in this process (148,185,186). The cationic ring-opening polymerization initiated by the electrophilic trialkylsilyl species proceeds by the simpler addition mechanism, which involves a single "long-lived" oxonium ion end group (178).

4.5. Emulsion Polymerization.   Even though siloxane bond formation is an equilibrium process, it is possible to form siloxane polymers by polycondensation or ring-opening polymerization in aqueous emulsions (187–189). D_4 can be converted into high MW polymer by emulsion polymerization in the presence of dodecylbenzenesulfonic acid (DBSA), which acts as both emulsifying surfactant and catalyst (190). It is also possible to obtain high MW polymers by polycondensation of α, ω-dihydroxy-stopped oligosiloxanes in an aqueous emulsion employing DBSA (191) or benzyldimethyldodecylammonium hydroxide (BDDOH) (192) as the surface-active catalysts. The polycondensation involves the reaction of a complex of silanol and two molecules of DBSA with another silanol end group (193). The anionic emulsion polymerization of D_4 in the presence of BDDOH as a surface-active catalyst has been reported (192,194) and a reaction scheme proposed, which involves a quaternary ammonium silanolate as an active species.

4.6. Radiation-Induced Polymerization.   In 1956, it was discovered that D_3 can be polymerized in the solid state by γ-irradiation (195). Since that time a number of papers have reported radiation-induced polymerization of D_3 and D_4 in the solid state (196,197). The first successful radiation-induced polymerization of cyclic siloxanes in the liquid state (198) and later work (199) showed that the polymerization of cyclic siloxanes induced by γ-irradiation has a cationic nature. The polymerization is initiated by a cleavage of Si–C bond and formation of silylenium cation (Fig. 23).

The γ-irradiation-induced polymerization requires an extremely high purity reaction system. Trace amounts of water can terminate a cationic reaction and inhibit polymerization. Organic bases such as ammonia and trimethylamine also inhibit polymerization. The γ-irradiation-induced polymerization of rigorously dried D_4 exhibits a square-root dependence of the rate on the dose rate as predicted by the Hayashi-Williams equation for completely pure systems (200).

4.7. Plasma Polymerization.   Plasma polymerization as a method for modifying surfaces of materials has been known for at least 25 years. The need for well-defined, thin polymer films for applications in optics, electronics, or biomedicine stimulated the development of plasma-induced polymerization but to date, relatively few large-scale applications exist. However, in recent years increased awareness of energy consumption and hazardous waste disposal concerns have stimulated the interest in this technique as method for manufacturing or depositing polymers on various substrates (201). The special interest

that has developed in organosilicon monomers may be because many of these monomers are generally volatile, nontoxic, nonflammable, and relatively inexpensive. Also, plasma-polymerized organosilicone films have a natural chemical affinity for adhesion to single-crystal silicon, and the properties of these films can be varied widely by the choice of monomer and polymerization parameters (202). The mechanism of plasma polymerization is still not well understood as of this writing and differs substantially from the conventional ring-opening polymerization of cyclic monomers. The dissociation and ionization of organosilicone monomers by low energy electron impact is the dominant source of radical fragments and a variety of ion−molecules and ion−radicals. In the case of hexamethyldisiloxane, extension of the monomer molecule by one dimethylsiloxane unit and elimination of the trimethylsilylium ion, $(CH_3)_3Si^+$, was proposed as a crucial step in the polymer film formation. The building of Si−C−Si links also plays an important role in the polymerization. Cyclic monomers such as D_4 polymerize via the formation of a network of siloxane chains and rings. The resulting films are usually hard and scratch-resistant but often show considerable stress (203). Such films can be used as corrosion-resistant coatings on metals or as membranes in gas sensor devices (204,205). The plasma polymerization of tetramethyldisiloxane was recently employed to deposit scratch-resistant and antifogging films on transparent polycarbonate substrates (206) and more generally when the formation of silicone films with uniform thickness and without any dust interference was required.

5. Silicone Network Formation

Silicone rubber has a three-dimensional (3D) network structure consisting of cross-linked polydiorganosiloxane chains. Three reaction types are generally employed for the formation of silicone networks (207): peroxide-induced free-radical processes, hydrosilylation addition reactions, and condensation reactions. Silicones have also been cross-linked using radiation to produce free radicals or to induce photoinitiated reactions.

5.1. Peroxide Cure.   The use of peroxide catalysts at elevated temperatures is one of the most common methods for the preparation of silicone networks (208). Typical peroxides include acyl derivatives such as dibenzoyl (209), bis-*p*-chlorobenzoyl, and bis-2,4-dichlorobenzoyl peroxides; aryl−alkyl derivatives such as dicumyl peroxide; and dialkyl derivatives such as di-*tert*-butyl peroxide and 2,5-dimethyl-2,5-di-*tert*-butylperoxyhexane. The amount and type of peroxide used determine the cure temperature of the composition as well as its ultimate properties. Diaroyl peroxides can be used with either polydimethysiloxanes or with vinylmethylpolysiloxanes. Bis-2,4-dichlorobenzoyl peroxide has the highest rate of decomposition and the lowest decomposition temperature. Cross-linking by peroxides is initiated by the generation of free radicals via homolytic cleavage of the peroxide at elevated temperatures. The peroxy radicals can abstract hydrogen atoms from methyl groups, forming ethylenic linkages between siloxane chains (210). Model studies have confirmed the formation of $SiCH_2CH_2Si$ as the predominant cross-linking reaction (211) (Fig. 24).

The cross-linking of vinyl containing polydimethylpolysiloxanes can be achieved using alkylaryl or dialkyl peroxides (1,212). A radical can be formed at either the methyl or vinyl site; it is generally agreed that the reaction through the vinyl group is energetically favored. Several mechanisms have been proposed to explain the reaction. One suggestion is that the radical is first formed on a methyl group that can then attack either a methyl or a vinyl group (213). Another proposal is that the cross-link occurs primarily through the vinyl group (214). The first step is addition of the peroxy radical to the vinyl moiety (215). The resultant radical can then attack either another vinyl group or a methyl group. Termination can occur by coupling or by hydrogen abstraction from adjacent peroxide molecules. Rheometric studies indicate that methylvinylsilicone resins do undergo cross-linking via the methyl groups but at a slower rate than through the vinyl groups (216).

5.2. Hydrosilylation. Hydrosilylation, the reaction between a silicone hydride group and an olefin to form an alkylenic linkage, is extremely important for the formation of silicone networks (77,83,217–219). Cross-linking and network formation occur by reaction of multifunctional silicon hydride groups with multifunctional silicone olefinic groups. Typically, vinyl groups attached to silicon are employed, however, there are reports of network formation by reaction of multifunctional silicone hydride polymers with hexenyl-terminated siloxanes (220). No by-products aside from Pt residue are produced by this type of curing and no shrinkage is observed. Addition of the hydride to the olefin may be either Markovnikov or anti-Markovnikov, depending on the choice of the silicone–olefin group and catalyst. With silicon bound vinyl groups, the reaction produces 95% of the β-addition product (Fig. 25).

Hydrosilylation is generally catalyzed by Group 8–10 (VIII) metal complexes or supported metal catalysts. Platinum complexes are the most widely used, although rhodium(I) complexes have also been reported (83). Typical industrial catalysts include soluble platinum species such as the platinum–divinyltetramethyldisiloxane complex (Karstedt's catalyst) (221). These catalysts exhibit high turnover rates and are useful in concentrations as low as 1–2 ppm.

Side reactions or postcuring reactions are possible in the formation of silicone networks. In most cases, the silicon bound hydride is in stoichiometric excess to enhance reaction rates. Disproportionation reactions involving terminal hydride groups have been reported (222). A major side reaction consumes Si–H to give redistributed siloxane in the resulting polymers and gaseous silane as a by-product.

Excess silicon hydride may undergo hydrolysis. The silanol thus formed can then condense with another hydride resulting in networks with a higher cross-link density (223–225). Isomerization of a terminal olefin to a less reactive internal olefin has been noted (222). Vinylsilane–hydride interchange reactions have been observed particularly when less active catalysts are employed (217) (Fig. 26).

Several mechanisms have been proposed for the platinum-catalyzed homogeneous hydrosilylation reaction. The most commonly invoked mechanism, proposed by Chalk and Harrod in 1965 (226), consists of elementary steps similar to homogeneous hydrogenation, oxidative addition, migratory insertion, and reductive elimination. However, this mechanism fails to describe the induction

period or the presence of colloidal species at the end of the reaction. Lewis proposed an alternative mechanism based on the intermediacy of colloids that were detected by transmission electron microscopy after evaporation of catalytically active solutions (227,228).

More recently, extended X-ray absorption fine structure (EXAFS) has been used to identify the actual catalytic species in both model systems and networks (229). At the completion of the hydrosilylation reaction, the state of the platinum species is dependent on the reaction conditions. With a stoichiometric excess of olefin, a mononuclear platinum species containing six platinum–carbon bonds, such as platinum coordinated to three olefin groups, is obtained. However, in the presence of high silicon hydride concentrations or in reactions employing poorly coordinating olefins such as hexenes, the platinum product is multinuclear and contains platinum–silicon bonds. Upon addition of the deficient reagent (olefin or silicon hydride), the platinum products can interconvert to the catalytically active form. Colloids have been found in a post mortem analysis of hydrosilylation reactions upon evaporation or destabilization of the reactant solutions. EXAFS analysis of solutions frozen during model reactions of cross-linking systems (functional siloxane monomers) showed that regardless of reactant stoichiometry, the platinum intermediates during the catalytic portion of the reaction were mononuclear and contained both platinum–silicon and platinum–carbon bonds. A mechanism was therefore proposed that incorporates the Chalk-Harrod postulate with the addition of exchange and hydrosilylation of the ligands on the platinum during the induction period, and a pathway to colloid formation at the end of the reaction. Ab initio calculations reported on the platinum-catalyzed hydrosilylation of ethylene support the Chalk-Harrod mechanistic steps of oxidative addition, migratory insertion, and reductive elimination during the catalytic cycle (230) (Fig. 27).

Catalyst inhibitors are often included in formulations to increase the pot life of these systems. An ideal silicone addition cure composition would combine instant cure at elevated temperature with infinite pot life at ambient conditions. Unfortunately, real systems always deviate from this ideal situation. One mechanism of inhibition consists of equilibrium between the inhibitor (I) and catalyst ligands (L) (231) (Fig. 28).

Hydrosilylation with inhibited complexes is generally less rapid than with platinum(0) olefin compounds. Complexing ligands such as phosphines and amines are excellent inhibitors but often form complexes so stable that they act as poisons and prevent cure even at elevated temperatures. Unsaturated organic compounds such as acetylenic alcohols, acetylene dicarboxylates, maleates, fumarates, and eneynes are preferred inhibitors (231–242). Steffanut and co-workers have reported the use of platinum(0) complexes with electron deficient olefinic ligands as hydrosilylation catalysts (243). Some of these complexes are self-inhibiting. Platinum–fumarate or maleate complexes formed from the reaction of platinum(0) compounds with dimethyl fumarate or dimethyl maleate, must undergo reduction of the fumarate or maleate ligand with silicon hydride prior to becoming active hydrosilylation catalysts (244). An alternative inhibition strategy is to encapsulate the platinum catalysts with cyclodextrin, thermoplastics, or silicones (245–247).

5.3. Condensation Cure. The condensation of silanol groups to form siloxanes is an extremely important industrial reaction and may be represented in its simplest form as follows (Fig. 29)

Unfortunately, because self-condensation of silanols on the same silicone can occur readily, the controlled reaction of disilanol or trisilanol compounds with telechelic silanol polymers to form a 3D network is not feasible. Instead, networks are derived from reactions of telechelic polymers with cross-linkers containing reactive groups such as alkoxysilanes, acyloxysilanes, silicon hydrides, or ketoximinosilanes, as in the reactions in Figures 30, 31, 32, 33 (207). The choice of cross-linking agent depends on the specific product characteristics desired.

Condensation catalysts include acids and bases, as well as organic complexes of metals. Both tin(II) and tin(IV) complexes with oxygen-donor ligands are extremely useful. It has been suggested that the tin(IV) catalyst is converted to its active form by partial hydrolysis followed by reaction with the hydrolyzable silane to yield a tin–silanolate species (Fig. 34 and 35) (248,249).

The organotin silanolate reacts with the polydimethylsiloxane diol by either attack on the SiOC bond or by silanolysis of the SnOC bond (248,249). Other metal catalysts include chelated salts of titanium and tetraalkoxytitanates, which have also been shown to form silanolate species similar to those postulated for tin catalysts (250,251). Formation of a cross-linked matrix involves a combination of the three steps in Figures 36, 37, 38.

The role of water in condensation cross-linking is dependent on whether the material is a one- or two-component curing system (252). One-component systems do not cure until they are exposed to water. Two component systems usually contain water in one of the components and begin to cure as soon as the components are mixed. Other work suggests that tin(II) catalysts can function in the absence of water (253). Studies of the relative rates of hydrolysis and condensation of multifunctional silanes, $R_xSi(OR)_{4-x}$, in the presence of acidic or basic catalysis have shown that the first Si–OR group hydrolyzes much more rapidly than subsequent groups (254). Silanol–silanol condensation is much slower than silanol–alkoxysilane condensation, even if the alkoxysilane is monofunctional, thus suggesting that in the presence of a cross-linker chain extension will not occur to a significant extent (255–258).

Condensation cure can also be carried out in emulsions (259–271). In this case, the cross-linker and polydimethylsiloxane are emulsified using anionic, cationic, or nonionic surfactants in water, and a condensation catalyst such as dibutyltin dilaurate is added. The formulation can also be cured without a tin-catalyst if self-catalytic hydrolyzable silanes are included (265). The polymer can then undergo cross-linking, forming a continuous film when the water is evaporated.

5.4. High Energy Radiation Cure. Silicones can be vulcanized by high-energy radiation examples of which include γ-irradiation, X-ray, and electron beam. High energy radiation interacts with shell electrons of atoms of the silicone materials and induces ionization. The generated radical cations and free radicals initiate chemical reactions that lead to cross-linking (272). The properties of silicones cross-linked by high-energy irradiation are indistinguishable from those vulcanized with peroxides (273). But silicone rubber cross-linked by

γ-irradiation does, however, have two advantages: better resistance to aging in humid environments and greater hydrolytic stability at elevated temperatures because the compositions are catalyst-free (274). Radiation cure of methylvinyl silicone rubber is a random cross-linking process with no differentiation between methyl and vinyl groups (275). Substitution of phenyl for methyl groups on the siloxane chain increases the radiation resistance. Silicone hydride groups are highly sensitive to radiation (276).

5.5. Photoinitated Radiation Cure.   Attachment of reactive functional groups such as mercaptans, acrylates, and oxiranes to a polysiloxane backbone can be used to render a silicone susceptible to curing by lower energy electromagnetic radiation such as ultraviolet (uv) or low energy electron beam (277). Thiols can be added across an olefin using an aromatic ketone as the photoinitiator (278,279). Unfortunately, the odor associated with thiols has limited the commercial acceptance of this technology. Two systems, which are widely used in the industry for silicone release and protective coatings, are silicones containing pendant acrylate groups (free-radical cure mechanism) and oxirane or vinylether functional siloxanes (acid catalyzed). The acrylate functional polysiloxanes are prepared by allowing epoxy-functional siloxanes to react with acrylic acid or from the esterification of siloxane containing alcohol groups with acrylic acid (280–283). Cross-linking occurs upon the generation of free radicals by electron beam (EB) irradiation of the silicone matrix or by uv-initiated decomposition of benzophenone-based photoinitiators. The most important limitation of this process is sensitivity to oxygen. The typical industrial coating line requires oxygen levels <50 ppm.

Silicones functionalized with oxiranes or vinyl ethers groups and can be cured by uv irradiation in the presence of diaryliodonium or sulfonium salts containing triflate, PF_6 or SbF_6 counterions (284–290). Decomposition of the onium salt under uv irradiation leads to the formation of strong acid that initiates very rapid polymerization of oxiranes or vinyl ether groups (291–293). Recently, a new class of onium salts prepared with the tetrakis(pentafluorophenyl)borate (TPFB) anion has been introduced as a uv photoinitiator (294–296). The presence of the large, weakly nucleophilic TPFB anion improves the solubility of the iodonium salts in the siloxane matrix and increases the reactivity of the formed acid (297,298). The cationic polymerization of oxiranes and vinyl ethers is not sensitive to the presence of oxygen and can be carried out under ambient conditions. Cycloaliphatic epoxies are highly reactive in the ring-opening polymerization reaction initiated by strong acids, so the typical commercial system is based on polysiloxanes with pendant cyclohexeneoxide moieties. Such polymers are readily prepared by the hydrosilylation of 4-vinylcyclohexeneoxide with hydrogen functional polysiloxane in the presence of a catalytic amount of platinum or rhodium (299) (Fig. 39).

Formation of a siloxane network via hydrosilylation can also be initiated by a free-radical mechanism (300–302). A photochemical route makes use of photosensitizers such as peresters to generate radicals in the system. Unfortunately, the reaction is quite sluggish. Several complexes of platinum such as (η^5-cyclopentadienyl)trialkylplatinum(IV) compounds have been found to be photoactive. The mixture of silicone polymer containing alkenyl functional groups with silicon hydride cross-linker materials and a catalytic amount of a cyclopentadienylpla-

tinum(IV) compound is stable in the dark. Under uv radiation, however, the platinum complex undergoes rapid decomposition with release of platinum species that catalyze rapid hydrosilylation and network formation (303–308). Other uv-active hydrosilylation catalyst precursors include (acetylacetonate)-PtMe$_3$ (309), (acetylacetonate)$_2$Pt (310–312), platinum triazene compounds (313,314) and other sytems (315,316).

5.6. Characterization of Silicone Networks.   The cross-linking of silicones as a function of time can be monitored using a variety of techniques such as infrared (ir) spectroscopy, dynamic mechanical analysis, dielectric spectroscopy, ultrasound, differential scanning calorimetry, and thermomechanical analysis (317–324). Infrared spectroscopy is especially useful with addition cure systems because the disappearance of the SiH peak in the starting silicone hydride can be readily monitored. Dynamic mechanical analysis has been used to study the critical time for gelation of a polydimethylsiloxane network (317). Fourier-transform infrared (FTir) dichroism has been used to investigate the molecular orientation of polydimethysiloxane networks. In a study of the isothermal dielectric properties of condensation-cured networks at room temperature as a function of catalyst concentration during cure, the effect of catalyst concentration was reflected in the value of the loss factor (318). The gel point of an addition-cured network can be determined using ultrasound techniques (320). A step-like increase in the longitudinal wave velocity is exhibited at the sol–gel transition point. Differential scanning calorimetry has been used with hydrosilylation-cured systems to determine rates of conversion and to develop a kinetic model for the rubber injection-molding process (322).

In addition to the above techniques, inverse gas chromatography (gc), swelling experiments, tensile tests, mechanical analyses, dynamic light scattering and small-angle neutron scattering have been used to determine the cross-link density of cured networks (325–332). Solid-state ^{29}Si nmr and chemical degradation methods have been used to characterize cured networks structurally (333). ^{1}H and ^{2}H nmr as well as spin echo experiments have been used to study the dynamics of cured silicone networks (334–338). Stress relaxation experiments have been employed to examine the chemistry of vulcanized silicone networks (339).

5.7. Model Networks.   Construction of model networks allows development of quantitative structure property relationships and provides the ability to test the accuracy of the theories of rubber elasticity (340–343). By definition, model networks have controlled molecular weight between cross-links, controlled cross-link functionality, and controlled molecular weight distribution of cross-linked chains. Silicones cross-linked by either condensation or addition reactions are ideally suited for these studies because all of the above parameters can be controlled. A typical condensation-cure model network consists of an α,ω-polydimethylsiloxanediol, tetraethoxysilane (or alkyl-trimethoxysilane), and a tin-cure catalyst (344). A typical addition-cure model is composed of α,ω-vinylpolydimethylsiloxane, M$^H_4$Q, and a platinum-cure catalyst (345–347).

Using both condensation- and addition-cured model systems, it has been shown that the modulus depends on the molecular weight of the polymer and that the modulus at rupture increases with increased junction functionality (348). However, if a bimodal distribution of chain lengths is employed, an

anomalously high modulus at high extensions is observed. Finite extensibility of the short chains has been proposed as the origin of this upturn in the stress–strain curve. Calculations have been performed on the effect of including a trimodal distribution of chain lengths on ultimate properties. The study concluded that incorporation of very long chains into a bimodal network of long and short chains could lead to elastomers with improved properties (349). Monte Carlo simulations of the elastic behavior of polydimethylsiloxane networks have been performed (350–351).

The effect of pendant chains on the mechanical properties of model polydimethylsiloxanes has been studied. It was found that the loss modulus of these networks was a function of the concentration and molecular weight of the dangling chains. The elastic properties of networks with pendant chains were found to be lower than those that were completely cross-linked (352).

Monodisperse model networks have been prepared using prepolymers with polydispersivities close to 1.0. Equilibrium tensile measurements on such networks prepared from fractionated polydimethylsiloxane show single-curve elastic moduli of all the networks (353,354). Simulations of the effect of molecular weight distribution on the equilibrium modulus indicated that with increasing polydispersity, the affine structure factor is found to decrease. Low extents of reaction were observed for the more monodisperse systems. The observed low extent of reaction is due to the reduced number of cross-links with increased molecular weight of chains in the system (355). Dynamic mechanical measurements have been reported for networks prepared by telechlelic condensation of monodisperse polydimethylsiloxane with tetraethoxysilane (356). The tensile and swelling behaviors of polydimethylsiloxane networks of high junction functionality have been determined using hydride terminated and hydride on chain siloxane reactions with vinyl-stopped polydimethylsiloxanes (357). In an examination of the mechanical behavior and swelling properties of networks prepared by cross-linking fractionated vinylmethylpolydimethylsiloxane with pentamethylcyclopentasiloxane (358), the dynamic mechanical properties measured were in good agreement with the swelling rates. It has been found that a lowering of the elastic modulus increases broadness of the molecular weight distribution of networks (359). There is a good correlation between theoretical predictions and the experimental value of the tensile modulus for monodisperse networks prepared from vinyl-terminated silicones and M_4^HQ (333).

5.8. Filled Silicone Networks.   Few applications use silicone elastomers in the unfilled state. The addition of fillers results in a several-fold improvement in properties. Fillers can be broadly categorized as reinforcing and nonreinforcing (or semireinforcing). Reinforcing fillers increase tensile strength, tear strength, and abrasion resistance, whereas nonreinforcing fillers are used as additives for reducing cost, improving heat stability, imparting color, and for increasing electrical conductivity (360).

Nonreinforcing fillers include calcium carbonate, clays, silicates, and aluminates. They are primarily used as extending fillers; ie, they serve the purpose of reducing cost per unit volume. Pigment-grade oxides, especially ferric oxides, are used as fillers and stabilizers for high temperature compounds used in oxidizing environments. Other fillers such as fumed titania, alumina, and zirconia find applications for extended heat stability, for imparting color, and for improving

the electrical conductivity of the formulation. Although carbon black is the most common reinforcing filler for other vulcanized rubber/elastomeric applications, it is not commonly used as a reinforcing filler in silicones. Instead, it finds applications in improving electrical conductivity and pigmentation (361).

Fillers that are used for providing reinforcement include finely divided silicasprepared by vapor-phase hydrolysis or oxidation of chlorosilanes, dehydrated silica gels, precipitated silicas, diatomaceous silicas, and finely ground high assay natural silicas (362–366). The size, structure, and surface chemistry of the filler all play important roles in determining the final degree of reinforcement (367–369). The most important criteria for reinforcement are the availability of sufficient surface area and a strong van der Waals or hydrogen-bonding interaction between the polymer and the filler (a covalent linkage is not essential (370,371). Fillers made by the fumed process have typical surface areas around 200 m^2/g and provide the maximum reinforcement. Several comparative studies of the effectiveness of fumed versus precipitated silica show that for fumed silicas, interaction with siloxane occurs by randomly distributed silanols whereas for precipitated silica, a more complex structure is involved probably involving short chains of polysilicic acid (365,372,373).

Several properties of the filler are important to the compounder (374). Properties that are frequently reported by fumed silica manufacturers include surface area, the acidity of the filler, nitrogen adsorption, oil absorption, and particle size distribution (375,376). Adsorption techniques provide a measure of the surface area of the filler, whereas oil absorption is an indication of the structure of the filler (377). Measurement of the silanol concentration is critical, and some techniques that are commonly used in the industry to estimate this parameter include methyl red absorption and methanol wettability tests (367,368,372). Other techniques to characterize fillers include weight loss, various spectroscopies, such as diffuse reflectance ir spectroscopy (drift), inverse gas chromatography (igc), photoacoustic ir, nmr, Raman, and surface forces apparatus (372,378–385).

Structuring refers to the formation of an elastic mass before cure that impedes normal processing operations such as molding and extrusion. Intensive working may be required to restore plasticity. Plasticity and process aids are therefore incorporated as monomeric or oligomeric organosilicon compounds. Alternatively, the silanol concentration on the silica surface can be controlled by filler treatment to prevent structuring (386,387). Reaction of the silica particles with hot vapors of chlorosilanes, low molecular weight cyclic siloxanes, and hexamethyldisilazane (HMDZ) are some of the commonly used filler treatments in the industry (361,388). It has been proposed that pretreatment of the filler reduces the strength of silica–silica and silica–polymer interactions (389).

Polymer–filler interactions have been studied by deuterium nmr spectroscopy. In unstrained networks, two regions of local chain mobility were identified, that within the absorption layer and that outside. In a uniaxially strained sample, the chains were immobilized near the filler surface. Chain order is increased in filled systems relative to unfilled systems (390). Molecular orientation in stretched networks was also studied using FTir dichroism. Filler introduction led to an increase in orientation that was attributed to a higher microscopic strain in the elastomeric network (391).

The final mechanical properties of the elastomer compound are a function of the concentration of the reinforcing filler in the formulation. In the small strain limit, Einstein relationships have been proposed for changes in viscosity and modulus as a function of volume fraction of the filler (392,393). Although these relationships work well for spherical and low structure fillers, they do not correctly predict the final properties of systems filled with high structure nonspherical particles. The high structure of the filler leads to a system that is not free draining, resulting in an augmentation of the filler concentration caused by the rubber trapped in the internal void space (occluded rubber) (394−397). An empirical modification to the Einstein relationship for modulus has been proposed (398). However, these relationships do not account for the secondary agglomeration that results in highly non-Newtonian and thixotropic behavior (399−406). The reasons for improvement in the failure properties of these systems are not well understood (405,407,408). Some mechanisms that have been proposed include the ability of a filled system to increase energy dissipation at the tip of the crack through viscoelastic processes, and the ability of the dispersed particles in cooperatively arresting or deflecting the growth of cracks, thereby delaying the onset of catastrophic failure. Results of tensile, ir dichroism, and birefringence experiments show strong upturns in the stress with increasing elongation while segmental-orientation-strain properties remain linear. The upturn in the stress results from limited extensibility of the chains. A model based on Monte Carlo calculations show strong differences between stress and orientation effects (409). A phenomenon often discussed in connection with filler reinforcement is stress softening, which probably arises because of the progressive detachment, or breaking, of network chains attached to filler particles (410).

Fillers have also been shown to influence abrasive wear of silicone rubbers. The wear rates increase slowly with filler concentration until a critical volume fraction is reached after which wear rates increase significantly with increasing filler loading. A model, which included the stress concentration induced by the filler, showed a positive correlation between the wear rate and the damage zone volume (411).

A good dispersion of the filler particles is essential for ensuring satisfactory ultimate properties (412−418). The first processing step involves the initial incorporation of the filler in the polymer matrix, and is limited primarily by the wettability of the filler. The next step involves a fracture of the aggregates and their uniform dispersion under shear. Heat treatment is often used to promote wetting and improve polymer−filler interactions (419). Dispersion is measured in terms of the remaining agglomerates, which cause premature failure in tensile testing and other ultimate properties. A trend in obtaining uniform dispersions is *in situ* precipitation of silica by catalytic hydrolysis of tetraethyl orthosilicate (TEOS) in a preformed silicone matrix using sol−gel techniques (420). Dynamic mechanical losses in addition cured polydimethylsiloxane networks containing *in situ* precipitation of silica indicated that the glass transition temperature showed only a slight dependence on the presence of the filler particles but the filler reduced both the degree and rate of crystallization for the *in situ* filled networks (421).

6. Properties and Uses

Silicone properties and uses have been discussed extensively (1,422–425).

6.1. Silicone Fluids.   Silicone fluids are used as damping fluids, dielectric fluids, polishes, cosmetic and personal care additives, textile finishes, hydraulic fluids, paint additives, photocopy fuser oils, and heat-transfer oils. Polydimethylsiloxane oils are manufactured by the equilibrium polymerization of cyclic or linear dimethylsilicone precursors. Monofunctional organosilane end groups, typically trimethylsilyl (M), are used, and the ratio of end group to chain units (D), ie, the ratio M/D, controls the ultimate average molecular weight and viscosity (162). Low viscosity fluids, $< 10^5$ cSt, are generally prepared by acid-catalyzed equilibration. The reaction can be run continuously or in a glass-lined batch reactor at temperatures up to 180°C. Solid acidified montmorillonite (Filtrol) or sulfuric acid on carbon catalysts are removed by filtration, and the end products are stripped under high vacuum and temperature to remove residual low molecular weight cyclic or linear siloxanes (426).

High molecular weight ($>10^6$ cSt) silicone oils and gums are prepared by base-catalyzed, ring-opening polymerization of cyclicdiorganosiloxanes, such as D_4, or by condensation polymerization of silanol-terminated PDMS. Both methods are practiced commercially. Potassium silanoate, prepared from $HO-(D_n)-OH$ and KOH, or transient catalysts such as tetramethylammonium or tetrabutylphosphonium hydroxide, are used in the ring-opening polymerization method (147,427,428). The potassium silanoate is quenched at the end of reaction, eg, with phosphoric acid. The transient catalysts can be decomposed at temperatures >150°C. Condensation polymerization also requires a catalyst, eg, linear phosphonitrilic chlorides (LPNC) (112–115). Ultimate molecular weight is controlled by the removal of water. LPNC catalysts can be deactivated thermally or by the addition of bases such as hexamethyldisilazane.

The physical properties of polydimethylsiloxane fluids have been extensively studied (1,429–431). The properties of a typical 50-cSt silicone oil (the silicone industry commonly uses centistokes, cSt, as a measure of the viscosity of a silicone polymer where 1 cST = 1 mm^2/s) are presented in Table 2. Linear silicone fluids have low melting points and second-order (glass) transition temperatures. High molecular weight PDMS has a T_m of −51°C and a T_g of −86°C (432). The low intermolecular forces in silicones also lead to low boiling points, low activation energies for viscous flow, high compressibility, and generally Newtonian flow behavior. High molecular weight polymers ($M_w > 35,000$) exhibit non-Newtonian flow, especially at high shear rates. This same phenomenon also results in a material having relatively poor physical properties at high molecular weight.

Unlike the linear analogues, cyclic dimethylsiloxanes are low melting solids and the T_m generally decreases with increasing ring size. Physical properties for a series of M-stopped oligomers, MD_xM, and cyclic compounds, D_x, are listed in Table 3.

Many of the applications for silicone oils are derived from the wide temperature range over which they can be used. Addition of a small amount of phenylsiloxane in the form of diphenyl or phenymethylsiloxy groups, and/or

incorporation of a slight amount of branching, suppresses the T_m of the dimethyl-silicones and can reduce the pour points to as low as $-100°C$ (433,434). Methyl-silicone oils are stable in air at 150°C for extremely long periods of time (435) and undergo only slow degradation up to 200°C. In vacuum or inert atmospheres, dimethylsilicone oil can be heated to 300°C for limited amounts of time (436). The thermal properties of silicones are important for medical applications (437). Heat-resistant silicone fluids have increasing amounts of phenyl-containing substituents. High molecular weight methylphenylsilicones can be used in air at temperatures up to 250°C for several hundred hours and can withstand brief exposures up to 450°C in the presence of inert gases (438). Table 4 compares silicone polymers with equivalent petroleum-based materials, and demonstrates the wide range of temperature over which they can be used.

Dimethylsilicone fluids decompose via two principal mechanisms: retrocyclization to low volatile cyclic siloxanes such as D_3 and D_4, and thermal oxidation of the alkyl side chains to give formaldehyde, CO_2, water, and T groups (430). The retrocyclization process is catalyzed by acids or bases and can occur at temperatures $> 140°C$. Catalytic acidic or basic sites on glassware and metallic containers are often the source of degradation of PDMS fluids. Heating in air to $200-250°C$ causes thermal oxidation of PDMS, and the cross-linking from T and Q group formation ultimately results in gellation. Stabilizers such as p-aminophenol, naphthols, metal acetonylacetonates, and iron octoate are commonly used to improve thermal stability (439–443).

For higher molecular weight polydimethylsiloxanes ($M_n > 2500$), the number-average molecular weight is related to the bulk viscosity by the following formula:, where the viscosity units are cSt (Fig. 40).

The number-average molecular weight of dimethylsiloxane can also be determined from the intrinsic viscosity dL/g (extrapolated to zero viscosity) in toluene or methyl ethyl ketone according to Figure 41 (444,445):

Compared to petroleum-based fluids, silicone oils show relatively small changes in viscosity as a function of temperature (1,430). A common measure of the viscosity change with temperature is the viscosity–temperature coefficient (VTC). Typical dimethylsilicone VTC is 0.6 or less. Phenylsilicones are slightly higher. Organic oils are typically 0.8 or greater. The viscosity temperature curves relationship is expressed in Figure 42 where a, b, and c are constants.

Figure 43 shows viscosity–temperature curves for a series of silicone oils from 20 to 10,000 cSt, an SAE 10 petroleum oil, and a diester-based oil (368). Silicones with phenyl, trifluoropropyl, or larger alkyl groups show larger viscosity changes with increasing temperature than dimethysilicone oils. Low molecular weight silicone oils (<1000 mm^2) exhibit Newtonian flow behavior and undergo only small changes in viscosity under shearing conditions (446). Higher viscosity PDMS fluids shear thin at higher shear rates. The fluids are stable to shear stress, however, and recover to their original viscosity after being passed through small capillaries under pressure. Figure 44 shows the effect of shear rate on viscosity for a series of PDMS fluids of different molecular weights.

Many of the unique properties of silicone oils are associated with the surface effects of dimethylsiloxanes. Silicones impart water repellency to fabrics, act as antifoaming agents (447) as release liners for adhesive labels and as

polishes and waxes (448). Dimethylsilicone oils can spread onto many solid and liquid surfaces to form films of molecular dimensions (449,450). This phenomenon is greatly affected by even small changes in the chemical structure of siloxane in the siloxane polymer. Increasing the size of the alkyl substituent from methyl to ethyl dramatically reduces the film-forming ability of the polymer (449). Phenyl-substituted silicones are spread onto water or solid surfaces more slowly than PDMS (451).

Dimethylsilicone polymers are often described as having a combination of silicate and paraffin structures. The orientation of the polymer chains onto surfaces, physically, by chemical affinity, or bonding, can contribute to the observed surface properties. The surface tension of hexamethyldisiloxane, MM, is 15.7 mN/m (dyn/cm). Increasing incorporation of D-units (MD_xM) increases the value to ~20 dyn/cm for higher viscosity fluids. Silicone fluids are characterized by their hydrophobicity (resistance to water), and the contact angle between PDMS and water is between 100 and 110°. Carefully deposited dimethysilicone on soda lime glass has a contact angle of ~60° at room temperature; the angle increases with increasing temperature to ~100° at 390°C and then decreases at the decomposition temperature (1).

Gases are very soluble in dimethylsilicone polymers and PDMS is permeable to water vapor. The solubility of air, nitrogen, and carbon dioxide at 101.3 kPa (1 atm) is 0.17, 0.19, and 1.00 cm^3/cm^3, respectively (452). About 250−300 ppb of water can dissolve in dimethylsiloxane at 25°C and 95% relative humidity (453). The water solubility of silanol-terminated oligomers increases with decreasing molecular weight; the lowest silicone monomer, dimethylsilanediol, is water-miscible. Silicone oils are soluble in nonpolar organic solvents such as benzene, toluene, dimethyl ether, chloroform, methyl ethyl ketone, methylene chloride, or kerosene. Incorporation of phenyl and especially trifluoropropyl or β-cyanoethyl groups onto the polymer decreases the solubility of siloxane in nonpolar organic solvents (446). These derivatives are slightly soluble in acetone, ethanol, and butanol, and relatively immiscible in methanol, ethylene glycol, and water. Exposure to strong acids or bases leads to reequilibration of the polymer.

Silicone fluids have good dielectric properties, loss factor, specific resistance, and dielectric strength at normal operating conditions, and the properties vary only slightly with temperature (1,430,454). These properties in combination with relatively low flammability have led to the use of silicones in transformers and other large electrical appliances (455). The dielectric constant of a 1000-cSt oil is 2.8 at 30°C and 2.6 at 100°C. The loss factor is low, 1.2×10^{-4} at 20°C, and varies irregularly with frequency. Specific resistance is 4×10^{15} Ω-cm at 20°C and decreases with increasing temperature or with exposure to moisture. The dielectric strength is 120 kV/cm (20°C, 50 cP, 6 kV/s).

Silicone oils are good hydrodynamic lubricants but have generally poor frictional lubricating properties (456−458). The latter can be improved by incorporating chlorophenyl groups into the polymer side chains (459). For steel on steel, the coefficient of friction is ~0.3−0.5. The load-bearing capacity of PDMS (Almen-Wieland machine) is only 50−150 kg, compared with ~1000 kg for polychlorophenylmethylsiloxane and up to 2000 kg for mineral oil.

The thermal conductivity of dimethylsilicone with viscosities >100 cSt is 15.5 J/s/cm/°C (3.7×10^{-4} cal^{-1}cm^{-1}°C^{-1}), and is roughly constant with increasing viscosity (460). The specific heat is 1.55–1.70 J/g/°C (0.37–0.41 cal/ g/°C) over the 20–200°C range and is practically independent of viscosity. Thermal expansion of PDMS is ~0.1%/°C (460).

Liquid silicone oils are highly compressible and remain liquid over pressure ranges where normal paraffin oils have already solidified (461). This property, combined with a wide temperature use range, is the reason for silicone use in a large number of hydraulic applications. The adiabatic compressibility of 1000-cSt dimethylsilicone oils is ~1000 Pa^{-1}(100 cm^2/dyn). This value decreases slightly with increasing viscosity, similar to paraffin oils. PDMS oils can withstand pressures > 3.4 GPa (35,000 kg/cm^2) even though they are compressed >30%.

Dimethylsilicone fluids are transparent to visible light and microwave but absorb ultraviolet radiation at wavelengths < 280 nm (462). Siloxanes absorb strongly in the ir between 1000 and 1100 cm^{-1} (Si$-$O stretching), 1300–1350 cm^{-1} (Si$-$C stretching), and 2950–3000 cm^{-1} (C$-$H stretching) (463). The speed of sound in PDMS is 987.3 m/s for a 1000-cSt fluid at 30°C and decreases with increasing temperature (464). Methylsilicone fluids are cross-linked when exposed to gamma ray or electron beam irradiation (465). Polymers containing aromatic substituents are more resistant than dimethyl silicone polymers.

Silicone Heat-Cured Rubber. Silicone elastomers are made by vulcanizing high molecular weight (>5 x 10^5 gm/mol) linear polydimethylsiloxane polymer, often called gum. Fillers are used in these formulations to increase strength through reinforcement. Extending fillers and various additives, eg, antioxidants, adhesion promoters, and pigments, can be used to obtain certain properties (1,466).

Peroxides are typical vulcanizing agents and the mechanism of cure involves free-radical abstraction of a proton from a silicon methyl group followed by dimerization of the methyl radicals to form ethylene cross-links (Fig. 24) (219,467,468). Higher cure speed can be obtained with a mixture of peroxides (469). Vinyl-containing polymers are often used to control the cross-linking reaction and to accelerate the cure rate. Commonly used peroxides include di-tert-butyl peroxide [110-05-4], benzoyl peroxide [94-36-0], di(p-cumyl) peroxide, and di(p-chlorophenyl) peroxide. The choice of peroxide is based on the desired cure temperature and rate. Table 5 lists some common peroxide curing agents, typical cure temperatures, and some recommended processing conditions.

Recent work on peroxide curing agents (470) suggests that bis-peroxides such as that shown in Figure 45 are especially efficient agents for curing silicone rubber.

Unlike natural rubber, silicone rubber does not stress-crystallize when elongated, which leads to relatively poor physical properties. Unfilled silicone rubber has only a 0.35-MPa (50-psi) tensile stress at break, thus silicone rubber must be compounded with 10–25 wt % reinforcing fillers, typically fumed silica, to improve the final rubber product properties (471–474). Other common fillers include precipitated silica, titanium dioxide, calcium carbonate, magnesium

oxide, and ferric oxide. Pigments and colorants are also used. The addition of fillers to the gum stock can result in structuring during storage, which decreases the workability of the material. To prevent structuring, the filler is often treated with agents such as hexamethyldisilazane to reduce surface hydroxyl functionality, or with processing aids such as silanol functional silicone oils, diphenylsilanediol, or dimethylpinacoloxysilane, Figure 46 (361,475).

The processing methods for silicone rubber are similar to those used for natural rubber (1,476–478). Polymer gum stock and fillers are compounded in a dough or Banbury-type mixer. Catalysts are added and additional compounding is completed on water-cooled roll mills. For small batches, the entire process can be carried out on a two-roll mill.

Heat-cured silicone rubber is commercially available in several forms; as gum stock, reinforced gum or partially filled gum. These compounds can be uncatalyzed, catalyzed, or contain catalyst dispersions. Catalyzed compounds are ready for use without additional processing. Silicone rubber is often freshened, ie, the compound is freshly worked on a rubber mill until it is a smooth continuous sheet. The freshening process eliminates the structuring problems associated with polymer-filler interactions. Rubber can be extruded on wire and cured in place (479).

It is common practice in the silicone rubber industry to prepare specific or custom mixtures of polymer, fillers, and cure catalysts for particular applications. The number of potential combinations is enormous. Improved properties of the rubber can be achieved if a premix of some of the inputs is performed. A premixing process for fumed silica, eg, involves the breaking down of gum particles into a fine dispersion in a bed of fumed silica. As the process continues, fumed silica coats the gum surface preventing reagglomeration of these particles (480).

In general, the mixture is selected to achieve some special operating or processing requirement, and the formulations are classified accordingly. Table 6 lists some of the commercially important types of silicone rubbers.

Silicone rubber is most commonly fabricated by compression molding of catalyzed formulated gum compounds at 100–180° C under 5.5–10.3 MPa (800–1500 psi) pressure. Mold release compounds are usually employed. Under these conditions the rubber is cured in a few minutes. Extrusion processing is used in the manufacture of tubes, rods, wire and cable insulation, and continuous profiles. Initial properties, so-called green strength, are obtained by curing in hot air or steam tunnels from 276 to 690 kPa (40–100 psi) at 300–450° C for several minutes. Final physical properties are achieved by postcuring in air or steam, typically for 30–90 min. When silicone rubber must be bonded to other surfaces, eg, metals, plastics, or ceramics primers are used. Silicate or titanate esters from the hydrolysis of tetraethoxysilane or tetraethoxyltitanium are often used as primers. Silicone rubber-coated textiles and glass cloth are made by initially dissolving gum stock in solvent and applying the rubber by dip coating. The fabric is then dried and the rubber cured in heated towers. Tubes and hose can be formed on mandrels from this fabric into complex shapes. Foamed or sponge silicone rubber can be made by incorporating chemical blowing agents into the rubber stock, which typically eliminate nitrogen or carbon dioxide

under the thermal curing conditions. Sponge silicone rubber made in this way has a closed-cell structure and densities of 0.4−1.0 g/cm^3.

Vulcanized silicone rubber is characterized by its wide temperature use range (−50 to >200° C), excellent electrical properties, and resistance to air oxidation and weathering conditions (484). Improvements in properties such as heat aging can be achieved by *in situ* treatment of the filler during rubber manufacture (480). Silicone rubber is also extremely permeable to gases and water vapor. The mechanical properties of silicone rubber are generally inferior to most organic (butyl) rubbers at room temperature. Tables 7, 8, 9 list some typical physical properties for vulcanized silicone rubber. Silicone rubber can be made with varying degrees of hardness. Shore A values from 20 to 90 are typical; the best physical properties are generally obtained with values from 50 to 70. The properties of silicone vary with temperature (483). The Young's modulus drops from 10^5 to 2×10^2 MPa (14.5×10^4 to 2.9×10^4 psi) from −50° C to room temperature and then is fairly constant to 260°C. Tensile strength at break decreases from 6.9 MPa (1000 psi) at 0°C to 2.1 MPa (300 psi) at 300°C. Typical elongation at break values range from 300 to 700%, depending on the composition.

The compression set of silicone rubber is similar to organic types of rubber at low (0−50°C) temperatures, ranging from 5 to 15% (489). Above 50°C, silicone rubber is superior, but compression set increases with time and temperature. Improvements in the compression set of silicone rubber are achieved with *in situ* treatment of the filler (490). Silicone rubber is more tear-sensitive than butyl rubber, and the degree of sensitivity is a function of filler size and dispersion, cross-link density, and curing conditions. The electrical properties of silicone rubber (491,492) are generally superior to organic rubbers and are retained over a temperature range from −50 to 250°C (76). Typical electrical values for a heat-cured silicone rubber are shown in Table 9.

Silicone rubber film is 10−20 times more permeable to gases and water vapor than organic rubber (489). The water permeability of silicone rubber is ∼14×10^6 mol/m^2·s·Pa, which means that silicone rubber can absorb ∼35 mg of water per square centimeter of surface area after 7 days' exposure (486). Table 7 shows the permeability of silicone to common gases. Organic solvents can diffuse into and swell silicone rubber, significantly decreasing the physical properties of the material. The degree of swelling depends on the solubility parameters of the solvent and the rubber, as illustrated in Figure 47.

Solvent-resistant rubber based on either trifluoropropylmethylsiloxane or β-cyanoethylmethylsiloxane has been developed for special applications, eg, as fuel tank sealants, where the material will be exposed to aggressive solvents. Those based on trifluoropropylmethylsiloxane are more important commercially. Pure water has little effect on silicone; however, long exposures in the presence of acid or base catalysts causes degradation and reversion of the rubber to a sticky gum (493,494). Prolonged exposure to temperatures ∼300°C in air causes the rubber to stiffen and ultimately to become brittle (483). As with silicone oil, the principal chemical pathways of degradation are retrocyclization and oxidation of the polymer alkyl groups. Heating in air at 125° C causes a decrease in elongation and an increase in hardness, but no important changes in tensile properties are observed.

Silicone rubber burns with a high char yield, and the residual material is nonconducting silicon dioxide. The limiting oxygen index for a typical rubber formulation is ∼20. Flame-retardant versions are available with oxygen index values as high as 40−50 (481). In general, silicone rubber is not resistant to gamma or electron beam radiation and undergoes cross-linking, which leads to embrittlement (495). Increasing levels of phenyl-containing silicone in the rubber improves the radiation resistance (496).

6.2. Silicone Liquid-Injection-Molding Rubber. An increasingly important processing technique for silicone rubber is liquid injection molding. These materials are also referred to as liquid silicone rubber (LSR). Unlike heat-cured rubber, which is typically compression-molded from high viscosity gum compounds, liquid-injection-molded (LIM) rubber is made from low viscosity starting materials, 1000−20000 mPa·s(= cP), and is cured in molds similar to those used for plastic injection molding. The principal advantages of LIM include rapid cycle times and the ability to fill complex mold shapes because of the low viscosity of the inputs. Rubber parts can be cured in 10−40 s using low molding pressures, ∼2−20 MPa (300−3000 psi), and low curing temperatures, typically 150-260°C (501). The LIM processing is increasingly being used for applications such as electrical connectors, O-ring seals, computer keypads, baby bottle nipples, valves, electrical components, health care products, and sporting equipment such as goggles and scuba masks.

Silicone LIM rubber is made from a two-component polymer system. One part (Part B) contains a linear polydimethysiloxane polymer with pendent Si−H functionality, reinforcing fillers such as fumed silica, extending fillers, pigments, and stabilizers. The second part (Part A) contains linear polydimethylsiloxane with terminal and pendent vinyl groups; reinforcing and extending fillers; a platinum hydrosilylation catalyst; and a catalyst inhibitor, commonly olefins, alkynes, amines, or phosphines. Incorporation of trifluoropropylsilyl groups is possible if solvent resistance is desired (497).

After the components are mixed and heated, the catalyst initiates the cross-linking reaction by addition of the Si−H group to the double bond (Fig. 48). Latent cure catalysts have been developed that allow the formulation of one-component products (498). These systems work by incorporation of platinum ligands that deactivate the platinum hydrosilylation catalysts at room temperature. When heated to temperatures > 100°C, these catalysts become active.

Cured silicone LIM rubber can be fabricated with physical properties equivalent to heat-cured rubber (499). Shore A hardness can range from 30 to 70, depending on formulations. Typical physical properties include tensile strengths as high as 9.7 MPa (1400 psi), elongations at break of 500−775%, and tear strengths > 30 N/mm (180 lb/in.). Compression sets of < 10% can be achieved if the material is baked after processing.

New applications for LIM are being developed due to advances in uncured rheological properties, property improvements achieved from fillers and advances in molding and processing (500). The rheological properties of the uncured LIM can vary from manufacturer to manufacturer (501). Fillers can enhance or degrade the thermal stability of the cured LIM (502). The final properties of LIM materials can be tailored. These properties include adhesion, hardness, green strength, elongation, and tensile strength. In addition, the

pre-cured viscosity, rheological properties, and cure speed can be modified (503). Finally, improvements in mold design (504) processing conditions (505) and advances in mold filling simulations have greatly improved the utilization of LIM materials.

6.3. Foam Rubber. Flexible foamed silicone rubber can be fabricated with flame retardancy greatly superior to that of the urethane-type foam. A self-blowing, low-to-medium density 80-240 kg/cm^3 (5–15 lb/ft^3) silicone foamed rubber can be prepared using polymers similar to those used in LIM products (506–509). Two components are mixed at room temperature: one part contains polydimethylsiloxane with pendent SiH functionality and fillers, and the other consists of terminal and pendant vinyl containing PDMS, reinforcing and extending fillers, a platinum hydrosilylation catalyst and inhibitor, water, alcohol, and an emulsifying agent. Typical time for foam formation is < 20 min.

Two chemical reactions occur simultaneously when the components are mixed. One is the platinum-catalyzed reaction of hydroxyl groups from water or alcohol with polymer SiH to give hydrogen gas (Fig. 49). This reaction is the source of the blowing agent that forms the foam. The second reaction is the cross-linking of SiH and Si–vinyl, which increases the polymer viscosity ultimately leading to gelation and curing to give an elastomer. Proper control of the kinetics of these two reactions is critical to achieving foam having good physical properties. Emulsion-derived foam is possible as well (510).

Silicone foam thus formed has an open cell structure and is a relatively poor insulating material. Cell size can be controlled by the selection of fillers, which serve as bubble nucleating sites (511). The addition of quartz and other fillers (512) greatly improves the flame retardancy of the foam; char yields of > 65% can be achieved. Cone calorimetry, UL 94 and other measurements have shown the excellent flammability properties of silicone foam (513). Because of its excellent flammability characteristics, silicone foam is used in building and construction fire-stop systems and as pipe insulation in power plants, in transportation systems as carpet underlay and in seating. Typical physical properties of silicone foam are listed in Table 10.

6.4. Silicone Resins. Silicone resins are an unusual class of organosiloxane polymers. Unlike linear poly(siloxanes), the typical silicone resin has a highly branched molecular structure. The most unique, and perhaps most useful, characteristics of these materials are their solubility in organic solvents and apparent miscibility in other polymers, including silicones. The incongruity between solubility and three-dimensional structure is caused by low molecular weight ($M_n < 10,000$ g/mol) and broad polydispersivity of most silicone resins.

A wide variety of organosilicone resins containing a combination of M, D, T, and/or Q groups have been prepared and many are commercially manufactured. In addition, resins containing hydrosilation-reactive SiH and SiVi groups or other functionalities, including OH and phenyl groups, are known. Three classes of silicone resins are most widely used in the silicone industry: MQ, TD, and T resins.

MQ Resins. These resins are composed of clusters of quadrafunctional silicate Q groups end-capped with monofunctional trimethylsiloxy M groups. The structure of an MQ resin molecule is defined by three characterization parameters: M/Q ratio, molecular weight, and % OH. Standard analytical techniques

have been used to quantify these parameters, including[29] Si nmr to determine M/Q ratio, GPC for molecular weight, and FIir for % OH (515). Most commercially useful MQ resins have an M/Q ratio between 0.6 and 1. Ratios < 0.6 result in insoluble solids, whereas those > 1 produce liquids (516). Molecular weight is related to M/Q ratio; higher molecular weights are associated with lower M/Q ratios. Typical molecular weights are M_n = 10,000 g/mol for a resin with an M/Q of 0.6, and M_n = 2000 g/mol for an M/Q of 1.0 (515,516). The silanol content (% OH by weight) of these resins, typically ranging between 0 and 3%, is process dependent. An ir study indicates that OH groups are intramolecularly associated through hydrogen bonding (516). A computer-generated molecular structure of a common commercially prepared MQ resin has been reported (517). This structure, shown in Figure 50, consists of a chain of silicate clusters end-capped with trimethylsiloxy groups.

MQ resins are commercially manufactured by one of two processes: the ethyl silicate or the sodium silicate process. In the ethyl silicate process, the resins are prepared by cohydrolysis of tetraethoxysilane and trimethylchlorosilane in the presence of an aromatic solvent (Fig. 51). This process is versatile and reproducible; it can be used to prepare soluble MQ resins with M/Q ratios ranging from 0.6 to 4 (518,519). The products of these reactions typically contain high levels of residual alkoxysilane groups.

A more economical route to MQ resin uses inexpensive sodium silicate and trimethylchlorosilane (Fig. 52) (520). The sodium silicate process is initiated by acidifying an aqueous sodium silicate solution to pH 2. The resulting hydrosol quickly builds molecular weight. The rate of this increase is moderated by the addition of an alcohol such as 2-propanol. The hydrosol is subsequently silylated by the addition of trimethylchlorosilane. This process, which is kinetically sensitive and limited to synthesizing M/Q ratios of 1 or less, is preferred when high OH (> 1%) MQ resins are required (521).

Both the ethyl and sodium silicate processes can be modified by substituting SiH- or SiVi-functional chlorosilanes or combinations of chlorosilanes to produce hydrosilation-reactive MQ resins (521,522).

The most prominent use of MQ resins is as the tackifying agent for silicone pressure-sensitive adhesives (PSA) (523–525). The other main component of silicone PSA is a silicone gum. This mixture of MQ resin and silicone gum is applied to a tape backing such as polytetrafluoroethylene (PTFE) or poly (ethylene terephthalate) (PET) and cured in the presence of a peroxide catalyst to provide an adhesive tape. MQ resins are also commonly used as control-release additives for silicone paper release products, as reinforcing agents for LIM silicones, in masonry sealants, and in leather/textile water-repellent coatings (523,526–530). An additional use of MQ resins is as a surfactant. MQ resins are commercially attractive for use in defoaming applications as well as for stabilizing frothed urethane for high hyphen;density carpet backing. Virtually every use for MQ resins is as a blend with a poly(dimethylsiloxane). These blends have been characterized as interpenetrating networks (517,531,532). Both MQ resin/ PDMS blends are microphase separated. One phase is PDMS-rich and has a T_g of −107°C. This T_g does not change with changes in the blend ratio. The other phase is an MQ resin/PDMS-miscible phase, the T_g of which varies linearly from −100 to 200°C as the composition of the blend is changed from 30 to 90%

MQ resin (517). These unique viscoelastic properties contribute to the versatility of silicone products containing MQ resin.

TD Resins.   The other important class of silicone resins is TD resins. These materials are simply prepared by cohydrolyzing mixtures of chlorosilanes in organic solvents (Fig. 53), where R is typically CH_3 or C_6H_5 (533). TD resins with T > 60m% are substantially less soluble in polydimethylsiloxanes than MQ resins.

A variety of liquid and solid resins can be prepared by varying the T/D ratio. Commercial TD resins are available containing from 5 to 95% T groups. Mixtures of methyl and phenylchlorosilanes are also frequently used. Some TD resins are modified by the addition of catalysts to reduce the silanol content, thereby increasing the molecular weight. Contrary to MQ resins, which are very stable, TD resins are unstable toward silanol condensation reactions.

TD resins are used as protective coatings, electrical coatings, saturants, laminates, and water repellents (1). TD resins are also useful in high performance paints. Compositions high in silanol content are utilized in reactive formulations. Low silanol TD resins are used as a nonreactive additive to alkyd paint formulations. Attractive features of TD resin-based protective coatings include superior, uv-resistant weatherability, and excellent high and low temperature properties. Silicone electrical coatings are preferred when good dielectric insulation is required over a broad temperature range. TD resins are also used to saturate glass or Kevlar fabrics. After curing, these flexible composites are used in a variety of applications. TD resin-based water repellents are used chiefly with siliceous substrates. Some typical TD silicone resin properties are as follows: dielectric strength = 68,000 V/mm; dielectric constant = 2.9 at 60 Hz and 25°C; dissipation factor = 0.006 at 60 Hz and 25°C; surface resistivity = 1×10^{14} Ω/in^2.; and volume resistivity = 1×10^{14} Ω· cm.

T Resins.   T resins are have been historically called silsesquioxanes. Crystalline polyhedral silsesquioxsanes can be synthesized by hydrolytic condensation of $RSiCl_3$ (Fig. 54), where R = c-C_6H_{11} (534−538).

These cage structures can be derivatized with heteroatoms (539) to form catalysts or organic ligands that can act as precursors to hybrid organic/inorganic materials (540) or ligands (536).

A unique, amorphous T resin particle has been reported (541). This material, known by the tradename Tospearl (Tospearl is a trademark of the General Electric Company), is a spherical resin particle made by the controlled, base catalyzed hydrolysis and condensation of $MeSi(OMe)_3$ (Fig. 55).

Highly cross-linked spheres with an average particle size from 0.5 to 12.0 μ have been produced. Extremely narrow particle size distributions are possible. The particle size and degree of monodispersivity are controlled by kinetic factors during the hydrolysis. Applications for Tospearl powders include wear resistance, antiblocking properties, light-diffusion control, and lubrication (542).

T resins are also an important component of silicone powder coatings and are useful in powder coatings obtained by the hydrolysis of $MeSiCl_3$ or the cohydolysis of CH_3SiCl_3 and $C_6H_5SiCl_3$. These silicone formulations provide high temperature (service temperatures > 800° F) and impact resistance (543,544) in solvent-free coatings.

Another key application for silsesquioxanes is in electronic insulating films having ultra-low dielectric constants (< 2.7) (545−548). A solution of T resins in organic solvents is synthesized by cohydrolysis of $MeSiCl_3$ and $HSiCl_3$ in the presence of a nonpolar solvent, a polar solvent (alcohol), and a phase transfer catalyst (547). The resulting polymer has a caged structure with essentially no hydroxyl or alkoxy substituents. A film with a low dielectric constant is prepared by spin coating the organic solution of resin onto an integrated circuit device, followed by thermal curing at $\sim$450° C. Films, having thicknesses of $\sim$1.0 μ and low levels of internal stress, insulate the individual circuit elements of the integrated circuit.

6.5. Organosilicone Coating Products.   Silicone products are used in a large variety of coating applications; most prominent among these are silicone PSA, plastic hardcoats, and paper release coatings (523−525).

Pressure-Sensitive Adhesives.   Silicone PSAs are used primarily in specialty tape applications that require the superior properties of silicones, including resistance to harsh chemical environments and temperature extremes (523−525). Silicone PSAs are also used in applications requiring long service life, electrical insulation, and protection from moisture. Another distinct advantage of silicone PSAs is their ability to wet low surface energy tape substrates such as PTFE.

Silicone PSAs are blends or interpenetrating networks (IPNs) composed of a tackifying MQ resin cured in a cross-linked poly(siloxane) network. The synthesis and structure of MQ resins have been described above. The poly(siloxane) network is traditionally derived by free-radical cross-linking of a high molecular weight PDMS polymer or gum using a peroxide catalyst, such as benzoyl peroxide or 2,4-dichlorobenzoyl peroxide. The curing reaction is performed immediately after the PSA has been coated onto a tape substrate, such as PET, PTFE, or Kapton. Uncured PSAs are supplied as a solution in an organic solvent. Some silicone PSAs also incorporate phenyl groups in the gum portion of the adhesive to increase the application temperature.

Another important aspect of the chemistry of silicone PSAs is the molecular interaction between the tackifying MQ resin and the PDMS network. For optimal adhesive properties it is important that some covalent bonding exists between the resin and the PDMS. This bonding is usually achieved by promoting a silanol condensation reaction between residual OH groups on the resin and on the end caps of the PDMS. The condensation reaction can occur either during blending of the PSA components or during processing of the tape. Studies of the viscoelastic properties of cured silicone PSAs indicate that these materials are microphase-separated (517,531,532). The adhesive properties of PSAs are a function of the unique rheological properties of the MQ resin/PDMS blends.

The key adhesive properties of a silicone PSA are tack, peel adhesion, and cohesive strength (lap shear). The required balance of these properties is controlled by several factors. A PSA composition rich in MQ resin usually favors low tack and high peel adhesion and cohesive strength values. A high cross-link density or a larger number of covalent bonds between the MQ resin and the PDMS network favors high cohesive strength at the expense of tack and peel adhesion. Low peel adhesion is observed when uncured cyclic or linear silicones are present. Other PSA properties important to the tape manufacturer, ie,

viscosity, solvent content, cure time, and temperature, are typically controlled by varying the type and amount of organic solvent and peroxide cure catalyst. Primers are also frequently used to promote adhesion of the PSA to the tape backing.

One advance in silicone PSA chemistry is the use of Pt-catalyzed hydrosilylation reactions as the method of cure (549,550). Advantages of hydrosilylation-cured silicone PSAs include lowering the level of solvent, lowering cure temperatures, increasing line speeds, and the ability to be used with a broader range of tape backings. In this technology, lower molecular weight polymers containing hydrosilylation-reactive SiH and SiVi groups are substituted for the traditional OH-end-capped PDMS gum. A Pt catalyst and inhibitor are used instead of a peroxide (549,550).

There are several important, specialized applications for silicone PSA tapes. Platers tape mask selected areas of parts during etching or plating operations. Masking tapes are also used as protective coatings against high temperatures, radiation, harsh chemical environments, or moisture. These tapes are used frequently in the manufacture of printed circuit boards (551). Splicing tapes are used to join plastic films. Silicone PSAs are often used to splice low surface energy materials or to provide high cohesive strengths at extreme temperatures. Plasma or flame spray tapes are used to protect selected metal surfaces during sandblasting or flame spraying operations. Silicone PSAs are particularly useful as the adhesive for electrical insulating tapes. A common application is as a wire wrap in motor coils. Silicone PSAs are also used in medical applications, notably as an adhesive for bandages and transdermal drug delivery systems (552).

6.6. Paper Release Coatings.   Paper release coatings are a fast-growing segment of silicone technology. These materials are used in label systems in which the silicone coating is part of the disposable paper liner. The role of the silicone is to provide a low surface energy interface between the liner and PSAs. Silicone release coated substrates provide both protection for the adhesive during coating, handling, and storage, and subsequent easy release of the substrate from the adhesive surface immediately prior to use (553). The process of converting paper to a release liner involves in-line coating in which cross-linkable silicone polymers are applied to the substrate and then cured either thermally or via radiation. The dominant product form is a thermally cured solventless paper release coating comprised of a vinyl-terminated PDMS, an SiH-containing cross-linker, a Pt hydrosilylation catalyst, and a cure inhibitor. Vinyl-terminated polymer chains are more reactive than D−vinyl groups, resulting in faster cure (554). Hydrosilylation inhibitors are used to insure that the siloxane formulation does not cure prior to deposition, thereby providing a bath-life sufficient for industrial processes. Typical hydrosilylation inhibitors are alkynols or alkyl maleates. Control release additives are frequently used in paper release coatings to increase the force required to remove the liner from the adhesive label (555). These additives are usually MQ resins that function by changing the viscoelastic properties of the coating. It is also preferred that these resins contain reactive Si−vinyl groups that cross-link into the silicone network. Ideal curing conditions involve temperatures of 150°C or lower and line speeds up to 460 m/min. Key properties for release coatings are cure speed, integrity of cure, and stable release values.

The need for faster line speeds, which result in increased productivity, and lower temperatures for thermally sensitive substrates is driving the technology of silicone paper release coatings. Advances include faster thermal curing and radiation-curable paper coatings. Substitution of 5Y-hexenyl groups for vinyl groups has been reported to increase the cure rate of thermal paper release coatings (556,557). However, the industry is rapidly evolving toward the use of uv-curable products. These coatings use silicone polymers and control release resin additives that are substituted with functional groups that can be cross-linked using photoinitiated catalysts (epoxides) or groups that can be directly photocured (acrylates, vinyl ethers) (277,558,559). An alternative to uv light for curing silicone release coatings is electron beam (EB) processing, although the initial capital investment for this technology is higher (297).

Typical substrates for silicone release coatings are supercalendered kraft paper, glassines, and thermally sensitive films such as polyethylene and polypropylene. Paper is currently the most widely used substrate, although thermally sensitive films are a growing market segment. One challenge with films is adhesion of the cured silicone to the substrate. Typically, an adhesion promotor is required in addition to the cross-linkable silicone polymers to insure anchorage of the cured silicone to the substrate.

6.7. Fiber Finishing Applications.   Because of their unique properties, silicones have been used in both textile and hair care applications for decades. For textiles, early interest focused on water repellency (560−563), but now they used in a wide variety of applications on fabrics derived from both natural and synthetic fibers, woven and nonwoven (562,564). For example, due to their low surface energy and extreme flexibility, silicones are among of the best fabric softeners used in textile finishing. Silicone-treated fabric exhibits lower inter fiber friction (565) that can lead to wrinkling benefits (durable press and wrinkle recovery). Fabric strength (566,567) and abrasion resistance (566,568,569) are other properties improved with some silicone treatments. Fabrics made from wool and other fiber types have been made shrink-resistant with certain silicone treatments (570−572). Silicones functionalized with polyether groups can impart hydrophilicity as well as softness or enhanced crease resistance to polyester and other fabrics (573−576).

Treated textile is typically rated by various ASTM or AATCC methods or by trained panelists. Standard methods exist for assessing tear strength, tensile strength, fiber friction, wettability, wrinkle recover angle, durable press rating, abrasion resistance, etc. (566,577−581). Panelists are often used to evaluate benefits such as softening, antiwrinkling or stain removal.

For textile applications, silicones can be classified as nonreactive, conventional reactive or organoreactive (578,581). Polydimethylsiloxane fluids are typical nonreactive silicones. They can provide useful tactile and physical properties, but not durability. Conventional reactive silicones include SiH or SiOH polymers. These types, often having structures that give rise to 3D networks upon curing, have been widely studied for durable water repellency and softening. Organoreactive silicones are substituted with groups that are capable of reacting directly with fibers. Textile finishes derived from these types of silicones, typical examples of which include silanol endcapped aminosilicones and epoxysilicones, can also provide durable benefits.

Softening is one of the most common target benefits achieved with silicone treatments (562,577,582–588). Softening benefits can be significant with silicone levels of 0.1% by weight on fabric. Aminosilicones are typically among the best softeners, providing the best feel (566,589). Studies have shown that silicone softeners can provide good durability and enhanced wrinkle recovery with a higher retention of mechanical properties when compared with traditional organic cationic softeners (578). Finishes can be hydrophobic or hydrophilic. Epoxy-substituted silicone materials modified with polyether groups, known for many years, can provide durable hydrophilic softening (590). Microemulsion technology has been applied, particularly with amino-functional silicones to improve fabric penetration and overall softening properties (591). Performance achieved with aminosilicones has been compared with that resulting from treatment with silanol polymers in the presence of alkoxy silane cross-linkers on cotton (578).

One recent study evaluated the softening benefits of aminosilicones on cotton as a function of pH and type of amino group (592). It was found that, in terms of softening, there is an optimum degree of polymer substitution as well as extent to which the amino groups should be ionized. Electrostatic interactions between protonated amines and cotton are the primary driving force of attraction, but significant repulsive forces result from a high charge density. Computer simulations suggested that the primary amine contributes much more to the interaction energy than does the secondary amine within aminoethylaminopropyl-substituted polymers.

Wrinkle resistance and recovery are two key benefits for which silicones are widely studied (567). For example, it was found that silk and silk/wool blends exhibited improved wrinkle recovery when treated with a cationic microemulsion of an aminosilicone (580). Silicones are often added to durable press/shrinkage resistance treatments, and have been used in combination with a range of currently available cellulose cross-linking systems to both enhance the overall durable press benefits and counteract the strength loss associated with cross-linking (593,594). Silanol terminated polymers were found to increase the durable press rating with glyoxal treatments (595,596). Treatment with amino-silicone polymers results in better durable press, retention of strength and abrasion resistance when used with dimethyloldihydroxyethyleneurea (DMDHEU) cross-linking systems in some cases (597), although yellowing of white fabric can be a problem (568). Others have described the use of a durable hydrophilic silicone (polyether substituted) finish to impart hydrophilic softness and durable press properties (598,599). Durable press treatments for cellulosic-based textiles have also been patented where the silicone cross-links the cellulose fibers in the presence of an acid or base catalyst (600). It has also been claimed that certain silicone treatments improve wrinkle resistance and reduce the loss of tear strength when used with formaldehyde (601–602). Many other wrinkle reducing compositions including silicone have been patented (584–586,603–608). While covalent bonding between organofunctional silicone and fiber surfaces is often invoked in the literature as a way of explaining durable benefits, it is rarely backed up with unambiguous evidence. An ir method for characterizing ester linkages to cotton has recently been described (609).

Silicone lubricants have also been studied as cotton processing aids (610). One study found an effective lubrication system containing a 1% loading by weight of a cationic silicone emulsion (611).

There are obvious links between silicone treatments for textiles and those for hair. Indeed, silicones have been used extensively in hair care products for 50 years, primarily in shampoos and conditioners (612–616). Aminofunctional silicones make hair feel soft and are thus outstanding for hair conditioning. Aminosilicones are effective because of their high pKa and the fact that untreated hair has an isoelectric point of ∼ pH 3 (617). Polyether substituted silicones impart hydrophilicity and can be useful in compatibilizing different components of a formulation. They are also light conditioners and have antistatic characteristics. Phenyl silicones provide shine and luster. Alkyl substituted silicone give hair volume and manageability. Silicone resins are substantive and also add volume as well as set retention. High molecular weight polydimethylsiloxane provides good dry feel properties and combing. These materials can be used alone or in combination.

6.8. Room Temperature Vulcanizable Silicones. One component, moisture-curable, room temperature vulcanizable (RTV) silicones represent one of the largest volume and commercially most successful silicone technologies. When exposed to atmospheric moisture, RTV silicones undergo hydrolysis and condensation reactions and cure into high strength elastomers. Sealants and adhesives are the chief uses of RTV silicones. The rate of cure of these products is dependent on temperature and humidity. In the uncured state, in the absence of moisture, one-part products have a shelf life of 6 months to several years. The cured elastomers have excellent primerless adhesion to substrates as varied as glass, metals, wood, masonry, and plastics. Additional benefits include excellent weatherability, durability, electrical insulation, chemical resistance, stability at high temperatures, and flexibility at low temperatures. The RTV products having a wide range of viscosities, from low viscosity self-leveling potting compositions to high viscosity thixotropic pastes, are commercially available. One of the few disadvantages of RTV systems is a slow rate of cure, often requiring > 7 days in low humidities to achieve optimum properties. The cure speed can be increased by raising the temperature or by using a two-part formulation that includes water in one of the parts. Water can also be provided by the *in situ* reaction of carbonyl compounds with primary amines in a two-part formulation (618,619). Although two-part sealant formulations are exceedingly simple (silanol polymer, fillers, and alkoxysilane cross-linker; separate cure catalyst) and have long shelf lives, consumer demand has driven the development of more complex, but also more convenient one-part formulations.

6.9. RTV Silicone Chemistry. There are two basic cure chemistries operative in RTV silicones: those based on rapidly hydrolyzing groups (acetoxy, ketoxime) and those requiring catalysts to promote hydrolysis (alkoxy based systems) cure systems. Acetoxy-based RTV silicones were first commercialized in the early 1960s (620,621). The general chemical reactions of these first-generation products are shown in Figure 56.

In the first reaction, a multifunctional acetoxysilane cross-linker, such as methyltriacetoxysilane, reacts with a silanol-terminated PDMS, which releases acetic acid and forms a polymer containing multiple, hydrolytically unstable

acetoxysilane end groups. This polymer, plus fillers and other additives are compounded under anhydrous conditions and packaged as a one-part system. When exposed to atmospheric moisture, this functionalized polymer hydrolyzes, releasing more acetic acid and producing diol-functionalized polymer end groups. This intermediate then undergoes self-condensation reactions, resulting in a silicone rubber. Tin(IV)-derived catalysts are frequently used to accelerate the cure of these products. Acetoxy-based RTV silicones have the advantage of having a long shelf life in the uncured state and rapid cure on exposure to moisture; however, their commercial applications are limited by the odor and corrosive nature of acetic acid.

Methoxy-based RTV silicones were introduced commercially in the late 1960s to overcome the deficiencies of their acetoxy predecessors (622). The reactions involved in curing of methoxy-based RTV silicones are similar to their acetoxy analogues.

The principal differences are that methoxy-based cross-linkers such as methyltrimethoxysilane do not spontaneously react with silanol-end-capped PDMS, and methoxysilane-terminated PDMS does not react with atmospheric moisture under neutral pH conditions. Catalysts are thus required for both of these reactions. Amines, Ti and Al complexes, and ammonium carboxylate salts are well-practiced end-capping catalysts (623–626). More recently, novel reagents such as tetralkylammonium fluorides and phosphate esters have been reported (627,628). Tin- and titanium-based catalysts are chiefly used as moisture cure catalysts (623,624,629–635). Unfortunately, these catalysts often promote undesirable siloxane redistribution reactions, which lead to instability of these RTV silicones in the uncured state. Methanol, released during the capping process, also functions in tandem with these cure catalysts in destabilizing compositions via siloxane redistribution reactions (636). Two strategies are used to overcome these side reactions and prepare commercially useful methoxy-based RTV silicones. In the first, an end-capping catalyst based on ammonium formate salts, and Ti- and Sn-based cure catalysts containing specific ligands, are employed. The ligands of interest are typically either hindered branched alkoxides (631–634), β-diketonates (623,630,635,637) or similar functional groups (638,639) that kinetically or thermodynamically stabilize the metal ions against alkoxy exchange reactions. As a result these compounds have been found to be poor siloxane redistribution catalysts, and therefore are useful catalysts in RTV silicones having shelf lives of $\geq$6 months. In the second, one-part RTV silicones with a higher degree of stability are achieved by removing methanol either physically or with methanol scavengers such as hexamethyldisilazane (629) or cyclic alkoxyaminosilanes (640,641). The latter react with methanol *in situ* to form products that also function as adhesion promoters.

6.10. RTV Silicone Compositions, Properties, and Applications. A typical commercial RTV silicone is a blend of a PDMS, end-capped with OH groups or alkoxysilanes. The compositions typically contain excess cross-linking silane, reinforcing fillers, plasticizing oils, adhesion-promoting silanes, a cure catalyst, and other optional additives. The key properties are the tensile strength and adhesion of the cured elastomer, the shelf life and thixotropic behavior of the uncured product, and the cure rate. The tensile strength of an RTV silicone is a function of the cross-link density of the silicone elastomer and the amount and

type of reinforcing filler. Useful fillers include high surface area, silane-treated fumed silica (hexamethyldisilazane or D_4 are often used as treating agents), and calcium carbonate. The latter filler is derived from either natural sources or prepared synthetically (precipitated $CaCO_3$) and commonly treated with organic surface modifiers, such as stearic acid. Plasticizing fluids are usually trimethylsiloxy-end-capped PDMS fluids, which are used to improve thixotropy and adhesion. The outstanding adhesive properties of RTV silicones are affected by almost every ingredient of the composition. Adhesion promoters, typically trialkoxy- or dialkoxy-substituted functional silanes, are frequently used to enhance adhesion to difficult substrates such as glass, metals, and plastics. Examples include γ-aminopropyltrimethoxysilane, β-cyanoethyltriethoxy silane, and γ-glycidoxypropyltrimethoxysilane. Other additives used in RTV silicones are iron and rare earth oxides for improved high temperature stability, platinum for flame retardancy, fungicides for high humidity applications, and a variety of pigments. One-part silicone RTV silicones are sold in three primary markets: household consumer products, construction products, and industrial adhesives. Noncorrosive RTV silicones using methoxy-based cure chemistry are useful as electronic potting compositions. Typical RTV silicon properties are given in Table 11.

7. Economic Aspects

Silicone polymers continue to be an important article of commerce globally. The industry grew at an average annual rate of 6–8% during the 1990s. The total global markets for silicone–silane materials totaled nearly $6.7 billion in 1998. The world capacity for silicones as of 1999 has been estimated at ~1.7 billion ev (642). The silicones industry is a global enterprise with Dow Corning, General Electric, and SKW/Goldschmidt are the major producers of silanes. Table 12 lists the approximate sales of the principal producers for 1991 and 1998 (642). The recent merger of Degussa with SKW/Goldschmidt created a new global player similar in size to Shin-Etsu. This was part of a flurry of consolidation activities in the industry during the latter part of the 1990s. Also, joining forces during the period were GE and Bayer, Witco and Crompton-Knowles, and Hüls and Degussa.

8. Analysis and Testing of Silicones

The unique chemical, physical, and spectroscopic properties of organosilicon compounds are reflected in the analytical methodology used for the detection, quantification, and characterization of these compounds. Several thorough, up-to-date reviews dealing with analytical methods applied to silicones have been published (643–646).

8.1. Chemical Analysis. The presence of silicones in a sample can be ascertained qualitatively by burning a small amount of the sample on the tip of a spatula. Silicones burn with a characteristic sparkly flame and emit a white sooty smoke on combustion. A white ashen residue is often deposited as well. If

this residue dissolves and becomes volatile when heated with hydrofluoric acid, it is most likely a siliceous residue (647). Quantitative measurement of total silicon in a sample is often accomplished indirectly, by converting the species to silica or silicate, followed by determination of the heteropoly blue silicomolybdate, which absorbs at 800 nm, using atomic spectroscopy or uv spectroscopy (648–651). Pyrolysis gc with mass spectroscopic detection of the pyrolysate is a particularly sensitive tool for identifying silicones (652,653). This technique relies on the pyrolytic conversion of silicones to cyclics, predominantly to D_3 [541-05-9], which is readily detected and quantified (Fig. 57).

Functional groups in silicone monomers and polymers are characterized by chemical reactivity. For example, chlorosilanes are hydrolyzed, and the halogen is quantified by titration with alkali or silver nitrate (654). Other types of halogen substitution may require more drastic methods of decomposition. Silicon hydride is assayed by determining the hydrogen evolved after base-catalyzed hydrolysis or alcoholysis (655). Silanol concentration can be calculated by measuring the methane evolved with methyl Grignard reagent.

The structural architecture of silicone polymers, such as the number of D, T, and Q sites and the number and type of cross-link sites, can be determined by a degradative analysis technique in which the polymer is allowed to react with a large excess of a capping agent, such as hexamethyldisiloxane, in the presence of a suitable equilibration catalyst (656). Triflic acid is often used as a catalyst because it promotes the depolymerization process at ambient temperature (Fig. 58).

8.2. Instrumental Methods. A variety of spectroscopic techniques are available for the characterization of silicones. The analysis of bulk samples of silicone oils and related compounds can be accomplished via standard techniques; descriptions of these techniques and literature references relevant to silicone analysis are summarized in Table 12.

However, full characterization of functionalized siloxanes, particularly those containing high degrees of polymerization, can be difficult. Therefore, separation techniques coupled with various detection devices are typically employed. Supercritical fluid chromatography is effective for the separation of silicone oligomers that have molecular weights <3000 Da (689,690). Time-of-flight–secondary ion mass spectrometry (tof–sims) is applicable up to 10,000 Da (661).

A number of techniques have been developed for the trace analysis of silicones in environmental and biological samples. In these analyses, care must be taken to avoid contamination of the samples because of the ubiquitous presence of silicones, particularly in a laboratory environment. Stopcock grease, pump oil, soap, tubing, septa, O-rings, and labels are some just some examples of sources of silicone in the laboratory. Depending on the method of detection, interference from inorganic silicate can also be problematic; hence nonsilica-based vessels are often used in these determinations. Particularly difficult are silicon-specific analyses such as those involving atomic spectrometric techniques where ppb levels of silicon are present.

Silicones have been extracted from environmental samples with solvents such as hexane, diethyl ether, methyl isobutylketone, ethyl acetate, and THF using either sequential or Soxhlet techniques (691–696). Silicones of a wide range of molecular weights and polarities are soluble in THF. This feature,

coupled with its volatility and miscibility with water, makes THF an excellent solvent for the extraction of silicones from wet samples, ie, soils and sediments. Trace levels of silicones extracted from environmental samples have been measured by a number of techniques, including atomic absorption spectroscopy (AA), inductively coupled plasma–atomic emission spectroscopy (ICP–AES), pyrolysis gc–ms, as well as ^{1}H and ^{29}Si nmr spectroscopy (675,685,693,697–701). The use of separation techniques, such as gel permeation and hplc interfaced with sensitive, silicon-specific AA or ICP detectors, has been particularly advantageous for the analysis of silicones in environmental extracts (686,702–705).

8.3. Determination of Physical Properties.   Common properties of silicone polymers, such as refractive index, density, and viscosity, are measured using conventional techniques (706). Molecular weights can be determined by standard methods, provided suitable reference standards are available. Empirical viscosity/molecular weight correlations are also useful as a simple means of obtaining approximate molecular weights (707). End group analysis by suitable spectroscopic or chemical methods can give reliable number-average molecular weight data. Long-chain branching in silicone polymers can be ascertained chemically, by determining the ratio of branch sites to end groups using degradation methods (656,657), or instrumentally, by measuring molecular size–viscosity relationships, eg, using a GPC instrument coupled to a differential viscometry or light-scattering detector (708,709). The level of cross-linking in silicone polymers, quantified in terms of the average molecular weight of strands between cross-links, is often measured by solvent swelling or modulus measurements, which are related to the combined effects of physical and chemical cross-links (710,711). Chemical cross-links can be quantified by nmr techniques or by degradative analysis to determine actual concentrations of T and Q cross-link sites (656).

Thermal stability, highly significant in silicone evaluation, is monitored by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), or dynamic mechanical analysis (DMA). Because environmental factors and chemical neutrality affect performance at high temperatures, oven-aging tests on finished products are frequently required. Measurement of weight loss on heat aging is frequently more sensitive than direct chemical methods for detecting the presence of trace amounts of strong acid or base, which reduce polymer stability.

A great variety of analytical techniques have been applied to silicone processing and quality control. In the early days of commercial production, the composition of chlorosilane intermediate mixtures was determined by analytical distillation and weight determination of fractions, supplemented by wet analysis of hydrolyzable chlorine and specific gravity measurements. These methods have largely been supplanted by gc and gc–ms methods. Gas chromatography is also used to monitor alkoxysilanes, acyloxysilanes, and the lower boiling point linear and cyclic siloxanes. On-line (in-process) monitoring of continuous and semicontinuous processes employs these and other relevant techniques.

Quality control testing of silicones utilizes a combination of physical and chemical measurements to ensure satisfactory product performance and processibility. For example, in addition to the usual physical properties of

cured elastomers, the plasticity of heat-cured rubber and the extrusion rate of RTV elastomers under standard conditions are important to the customer. Where the silicone application involves surface activity, a use test is frequently the only reliable indicator of performance. For example, the performance of an antifoaming agent can be tested by measuring the foam reduction when the silicone emulsion is added to an agitated standard detergent solution. The product data sheets and technical bulletins from commercial silicone producers can be consulted for more information.

Properties of silicone fluids can be determined by a number of ASTM tests that were developed for the petroleum industry. ASTM D2225 describes methods of testing silicone fluids. ASTM tests typically used for determining standard physical properties are as follows: flash point, D92 and D93; pour point, D97; specific gravity, D1298; viscosity, D445; refractive index, D1807; and volume resistivity, D1169.

9. Health and Environmental Aspects

Few materials of commercial importance possess a range of applications as diverse as silicones. The widespread acceptance of silicones has given rise to remarkable growth of these materials since their first commercial production in the mid-1940s. In 1950, $\sim 10^3$ metric tons of silicones were produced. By 1965, production amounted to 1.4×10^4 metric tons and in 1999, production reached an estimated 3.5×10^5 tons in the United States alone (712). More recently, silicones have found increasing use in personal care products; such as deodorants, shampoos, and cosmetics. As a result of their widespread use and remarkable inertness toward light, heat, and chemical agents, an understanding of the environmental fate and distribution of silicones is important. Several reviews dealing with this subject are available (713–716), including a recently published comprehensive overview of environmental fate and effects of silicones (717).

Some examples of biological applications of silicones are biofouling release coatings, oil spill containment, and vitreous humor substitutes. Silicone elastomer coatings have been developed as nontoxic alternatives to toxic antifouling paints for ship hulls and power plant intakes (718–721). Solutions containing silicone have been developed to encapsulate and solidify oil slicks for easy removal (722,723). Silicone vitreous substitutes are used after retinal attachment surgery (724–726).

Organosilicones have been detected in terrestrial, aquatic, and atmospheric environments (Table 13).

The highest concentrations of environmental silicones are found in the sludges of wastewater treatment plants and upstream of process plants. Much lower levels are found in water or sediment samples except at certain point sources, such as in effluents of dyeing factories and other industries that employ silicones in their processes. In general, levels of organosilicones in sludges and sediments have been found to correlate with the total organic content of these media as determined by pyrolysis weight losses. This implies a migratory aptitude similar to that of other organic pollutants. For example,

analysis of undisturbed, [210] Pb-dated sediment taken from Puget Sound in Washington indicates the presence of organosilicone in a 15-year old sludge but not in a 60-year old sample (732,733). This result suggests that silicones do not migrate appreciably of their own accord but follow sediment movement. Another study of the geochronology of sedimentary siloxanes was conducted in the Ala Wai Canal in Hawaii. The cores, dated using ^{210}Pb and ^{137}Cs measurements, showed the highest concentration of silicone in the most contemporary sediments. The study also found spikes in silicone concentration that could be traced to storm events (734).

Silicones have been detected in water from various rivers and in effluent from wastewater treatment facilities. They are barely detectable in water from municipal treatment facilities. Water solubility (S) of silicones has been found to correlate with the octanol–water partition coefficients (K_{OW}) for a series of trimethylsilyl-capped siloxane oligomers of various molecular weights according to Figure 59 (735).

This expression can be used to predict solubilities from the octanol-water partition coefficients. Solubility and K_{OW} data for four oligomeric siloxanes are listed in Table 14.

The rapid drop in solubility and increase in K_{OW} with increasing molecular weight are evident from these data.

Because of their hydrophobic nature, silicones entering the aquatic environment should be significantly absorbed by sediment or migrate to the air–water interface. Silicones have been measured in the aqueous surface microlayer at two estuarian locations and found to be comparable to levels measured in bulk (735). Volatile surface siloxanes become airborne by evaporation, and higher molecular weight species are dispersed as aerosols.

Silicone contamination has been implicated as a cause of failure in telephone switching systems and other devices that contain relay switch contacts (736). Analysis of airborne particulates near telephone switching stations showed the presence of silicones at these locations. Where the indoor use of silicones is intentionally minimized, outdoor levels were found to be higher than inside concentrations (737). Samples of particulates taken at two New Jersey office buildings revealed silicone levels that were considerably higher indoors than outdoors. In these cases, indoor silicone aerosols are believed to be generated primarily by photocopiers, which use silicone fuser oils.

Airborne organic silicon has been detected in samples collected at Barrow, Alaska (738). Organosilicone levels corresponding to an airborne concentration of 8 ng/m^3 were detected. As a comparison, these samples were determined to hold ~20 ng/m^3 of phthalate-based plasticizers. Two pathways have been proposed for the removal atmospheric organosilicones: degradation resulting from a reaction with OH radicals and wet deposition from the gas phase by incorporation into areosols (739).

Knowledge of the transformation of silicones under various environmental conditions is key to understanding the fate of these materials. Model studies predict that a large fraction of silicones entering the environment through wastewater treatment systems, ie, municipal treatment plants or septic systems, will ultimately be deposited on soils as a result of absorption or of sludge amendment (740,741). The chemistry of silicones on soils is thus an important factor in

assessing the overall environmental impact of these materials. The accumulation of silicone in sediments has been observed in freshwater and marine sites heavily impacted by wastewater discharge. The concentrations ranged from 0.6 ± 0.1 ppm to 78 ± 20 ppm that were still below the "no observable effect concentration" for the sediment organisms (742).

Silicone fluids degrade when exposed to soils (695,743–745). The rate of degradation depends on soil type and moisture content. Degradation is slow but observable on moist soils and becomes quite rapid when the available moisture content of the soil drops below 5% (746). The products of soil-induced abiotic degradation are typically silanol-terminated monomers and oligomers. Dimethylsilanediol, the simplest monomeric unit derived from silicone hydrolysis, is an important degradation product of abiotic silicone degradation. This compound is produced when silicones are exposed to soils and sediments even when the overall extent of polymer degradation is small, indicating a possible kinetic preference for its formation. As a polar, water-soluble species, dimethylsilanediol exhibits environmental distribution properties drastically different from the silicones from which it is derived (747). In organic solvents, dimethylsilanediol undergoes rapid self-condensation producing oligomeric products, whereas in dilute (<400 ppm) aqueous solution (Fig. 60), it is the major constituent among the water-soluble oligomeric silanols (748). Therefore, dimethylsilanediol is expected to be the principal waterborne silicone species found in most environmental samples.

Irradiation of water-soluble silicon species such as dimethylsilanediol with artificial sunlight (xenon arc lamp) in the presence of environmentally significant levels of nitrate led to their rapid disappearance ($t_{1/2}$= 4–9 d) (749). Silicate was determined to be the ultimate photodegradation product. Transformation of the soluble silicones to silicate under these conditions was complete in ∼35 days. Irradiation of an emulsified high molecular weight silicone fluid (degree of polymerization, DP = 50) resulted in negligible (1.7%) conversion to silicate in the same time period. Degradation did not occur in the dark or in the absence of nitrate. Nitrate is thought to act in this system by providing a source of photochemically generated hydroxyl radicals (Fig. 61). Oxidative attack of these reactive species on the silicon–carbon bonds leads eventually to silicate and CO_2.

Water-soluble silanols such as dimethylsilanediol were found to undergo successive oxidative demethylations with tropospheric uv irradiation in the presence of suitable chromophores, such as nitrogen oxides (750). The water-soluble methylated silicones did not promote diatom (Navicula pelliculosa) growth but the demethylated photoproducts did. The sequence of soil-induced degradation of silicones to water-soluble species, followed by light-induced conversion to silicate, suggests a pathway, conceptually at least, for the mineralization of silicones.

Polydimethylsiloxane does not biodegrade at an observable rate under normal conditions of environmental exposure. For example, a ^{14}C-labeled 300-cSt PDMS fluid showed no evidence of biodegradation when exposed to activated sludge over a period of 70 days (751). In a similar microbiological screening study, silicones were found to be inert to all applied cultural conditions (752). However, when ^{14}C-labeled PDMS was applied to soil and allowed to degrade to low molecular weight species, the degradation products were further degraded

to silicate and $^{14}CO_2$, presumably via a biotic pathway (753). This degradation has been observed both in the laboratory and in the field (695,754,755). ^{14}C-dimethylsilanediol is biodegraded on soils at a rate of $\approx 1\%$ per month (756). The rate of $^{14}CO_2$ production can be increased an order of magnitude by the addition of certain carbon sources, such as 2-propanol and methylsulfone, to the medium. Thus, by a combination of abiotic, soil-mediated degradation and biotic or light-induced conversion of the degradation products, silicones can undergo complete mineralization in the environment (757). The rates at which this mineralization occurs depend on the conditions of environmental exposure.

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Table 1. **Silicone Products and Their Uses**

Commercial product		Use
fluids: heat-stable liquids	lubricants, water repellents, defoamers,	release agents, surfactants
filled fluids and gums		valve lubricants, moisture proof sealants for electrical connectors, pressure-sensitive adhesives, personal care products
grease: fluid and carbon black or soap		nonflow lubricants, polishes
resins: cross-linked materials		electrical insulation, lubricant and paint additives, release formulations, water repellents
rubbers: fluids or gums and surface-treated fillers; elastic with good tensile strength		electrical insulation, medical devices, seals, textile coatings, foams

Table 2. **Typical Silicone Fluid Properties**[a]

Property	Value
Physical	
η at 25°C, mm^2/s(=cSt)	50
viscosity–temperature coefficient	0.59
density, g/mL	0.963
refractive index	1.402
pour point, °C	−55
surface tension at 25°C, mN/m (=dyn/cm)	20.8
thermal expansion, cm^3/cm^3/°C	0.00106
max volatiles at 150°C, %	0.5
specific heat	0.36
Electrical	
dielectric strength, V/min	35,000
$\in$ at 60 Hz	2.72
dissipation factor	0.0001
volume resistivity, Ω·cm	1×10^{14}
service temperature, continuous, °C	150
max temperature in air, °C	200
max temperature in N$_2$, °C	300

[a]Refs. 1 and 430

Table 3. **Properties of MD$_x$M and D$_x$[a]**

Compound	Cas Registry Number	MDT formula	Melting point °C	Boiling point °C	Density d^{20} g/mL	Refractive index n_D^{20}	viscosity (n) at 25°C Mm^2	Flash point °C
hexamethyldisiloxane	[107-46-0]	MM	−67	99.5	0.7636	1.3774	0.65	−9
octamethyltrisiloxane	[107-51-7]	MDM	−80	153	0.8200	1.3840	1.04	37
decamethyltetrasiloxane	[141-62-8]	MD$_2$M	−76	194	0.8536	1.3895	1.53	70
dodecamethylpentasiloxane	[141-63-9]	MD$_3$M	−80	229	0.8755	1.3925	2.06	94
tetradecamethylhexasiloxane	[107-52-8]	MD$_4$M	−59	245	0.8910	1.3948	2.63	118
hexadecamethylheptasiloxane	[541-01-5]	MD$_5$M	−78	270	0.9012	1.3965	3.24	133
octadecamethyloctasiloxane	[556-69-4]	MD$_6$M	−63	290	0.9099	1.3970	3.88	144
eicosamethylnonasiloxane	[2652-13-3]	MD$_7$M		307.5	0.9180	1.3980	4.58	159
hexamethylcyclotrisiloxane	[541-05-9]	D$_3$	64.5	134				
octamethylcyclotetrasiloxane	[556-67-2]	D$_4$	17.5	175.8	0.9561	1.3968	2.30	69
decamethylcyclopentasiloxane	[541-02-6]	D$_4$	−44	210	0.9593	1.3982	3.87	
dodecamethylcyclohexasiloxane	[540-97-6]	D$_6$	−3	245	0.9672	1.4015	6.62	
1,3,5,7,11,13-heptaethylcyclo-heptasiloxane	[17909-36-3]	D$_7$	−32	154[b]	0.9730	1.4040	9.57	
hexadecamethylcyclooctasiloxane	[556-68-3]	D$_8$	31.5	290	1.1770[c]	1.4060	13.23	

[a]Ref. 430.
[b]At 2.7 kPa (20 nm Hg).
[c]Crystals.

Table 4. **Viscosity of Silicone Oil versus Petroleum Oil**

Temperature, °C	Silicone η, mm^2/s(=cSt)	Petroleum η, mm^2/s(=cSt)
100	40	11
38	100	100
−18	350	11,000
−37	660	230,000
−57	1560	solid

Table 5. **Cure Agents for Silicone Rubber**[a]

Curing agent	Commercial name	Activation Temperature, °C	Application
Active paste[b] composition			
di(2,4-dichloroben-zoyl) peroxide	Cadox TS-50 or Luperco CST	104–132	hot-air vulcanizing
benzoyl peroxide	Cadox BS or Luperco AST	116–138	molding, steam curing
Active powder composition			
dicumyl peroxidec[c]	DI-CUP 40C	154–177	molding thick sections, bonding, steam curing
2,5-di(*t*-butylper-oxy)-2,5-dimethyl-hexane[d]	Varox, Luperco 101 XL, or Luperco 101[e]	166–182	molding thick section, bonding, steam curing

[a]Refs. 460.
[b]50% active paste composition.
[c]40% active powder composition.
[d]50% active powder composition.
[e]100% active liquid.

Table 6. **Properties of Different Classes of Silicone Rubbers**[a]

| Class | Hardness, durometer | Tensile strength, MPa[b] | Elongation % | Compression set[c], % | Useful temperature range, °C | | Tear strength, J/cm,[2d] |
					min	max	
general purpose	40–80	4.8–7.0	100–400	15–50	−60	260	0.9
low compression set	50–80	4.8–7.0	80–400	10–15	−60	260	0.9
extreme low temperature	25–80	5.5–10.3	150–600	20–50	−100	260	3.1
extreme high temperature	40–80	4.8–7.6	200–500	10–40	−60	315	
wire and cable	50–80	4.1–10.3	100–500	20–50	−100	260	
solvent-resistant	50–60	5.8–7.0	170–225	20–30	−68	232	1.3
high strength flame retardant	40–50	9.6–11.0	500–700				2.8–3.8

[a]Refs. 481–483.
[b]To convert MPa to psi, multiply by 145.
[c]At 150°C, 22 h.
[d]

Table 7. **Properties of Silicone Gums**[a]

Type	CAS Registry Number	Density, d^{25} g/cm^3	T/g,°C	ASTM D926 Williams plasticity
$(CH_3)_2SiO$	[9016-00-6]	0.98	−123	95−125
$CH_3(C_6H_5)SiO$	[9005-12-3]	0.98	−113	135−180
$CH_3(CF_3CH_2CH_2)SiO$	[25791-89-3]	1.25	−65	

[a]Refs. 482,485.

Table 8. **Permeability of Silicone Elastomers**[a]

Type	CAS Registry Number	Temperature °C	Gas	Permeability nmol/ (m·s·kPa)[b]
dimethylsilicone	[63148-62-9]	25	CO_2	180
MDnM		25	O_2	35
		25	Air	19.6
		30	butane	0.89
		70	butane	0.76
Fluorosilicones	[63148-56-1]	26	CO_2	35
MDnDn$^{(CH_2CH_2CF_3)}$M		26	O_2	5.8
Nitrilesilicone	[70775-91-6]	31	CO_2	105
MDnDn$^{(CH_2CH_2CN)}$M		31	O_2	17.8

[a]Refs. 486−488.
[b]To convert nmol/(m·s·kPa) to (cm^3·cm)/(s·cm^2·mm Hg), multiply by 3×10^{-8}.

Table 9. **Electrical Properties of Typical Silicone Rubber**[a]

Property	Value
volume resistivity[b], $\Omega \cdot$cm	$1 \times 10^{14} - 1 \times 10^{16}$
electric strength, V/25.4 μm (=V/mil)	400–700
dielectric constant, 60 Hz	2.95–4.00
power factor, 60 Hz	0.001–0.01
surface resistance, Ω	$3.0 \times 10^{13} - 4.5 \times 10^{14}$
dielectric loss factor, tan δ	$5 \times 10^{-4} - 4 \times 10^{-3}$

[a]Ref. 57.
[b]Ref. 81.

Table 10. **Physical and Flammability Properties of Silicone Foam Rubber**[a]

Property	Value
density, kg/m^3	80–240
tensile strength, MPa[b]	0.52
elongation, %	90
thermal conductivity, W/m·K	0.06
operating temperature range, °C	−60 to 205
limiting oxygen index	30
UL-94 flammability (3.2-mm thick)	V−0
flame spread index (ASTM E162)	16
smoke density flaming (ASTM E662)	18
smoke density smoldering (ASTM E662)	9
verticle burn (FAA 25.853)	compliant

[a]Refs 514.
[b]To convert MPa to psi, multiply by 145.

Table 11. **Typical RTV Silicone Properties**

Property	Value
density, g/cm^3	1.07
hardness, Shore A	30−35
tensile strength, MPa[a]	2.55−3.24
elongation, %	375−450
service temperature, continuous, °C	200−260
max temperature, short periods, °C	260−315
dielectric strength, kV/mm	19.7

[a]To convert MPa to kgf/cm^2, multiply by 10.2.

Table 12. **Total Silicone−Silane Sales by Company, 1991 and 1998**

	Sales, $ millions	
Company	1991	1998[a]
Dow Corning	1850	2400
General Electric	750	1215
Shin-Etsu	750	600
Wacker Chemie	675	870
Rhodia	460	400
Degussa/SKW		670
Crompton		400
Others	465	134

[a]From Ref. 642.

Spectroscopic Methods for Analysis of Silicones[a]

Technique	Information provided[b]	References
mass spectrometry	Identification, structural information, molecular weight information, and quantification; information is dependent on the mode of ionization; particularly useful when combined with a chromatographic separation technique, such as in gc-ms, hplc-ms, and pyrolysis gc-ms	652,653, 657–663
ir/uv spectroscopy	Identification, structural information, quantification and functional group identification; can be employed as detectors in chromatographic separations	664–673
NMR[a]	Detailed structural information; molecular weights can be determined by end group analysis; solid-state cp–mas techniques can be used to characterize solid samples and cross-linked elastomers	674–682
atomic spectrometric methods (AA/emission)	Quantitatively detects total silicon in the sample; sensitivities in the ppb range are possible; particularly useful when used in combination with chromatographic separation devices; can be used to detect trace elemental contaminants in silicones	683–688

[a]Of particular interest are ^{1}H, ^{13}C, and ^{29}Si nuclei.

[b]Gas chromatography–mass spectromity = gc–ms, high-performance ligand chromatography–spectromity = hplc–ms, cross-polarization–magic-angle spinning = cp–mass.
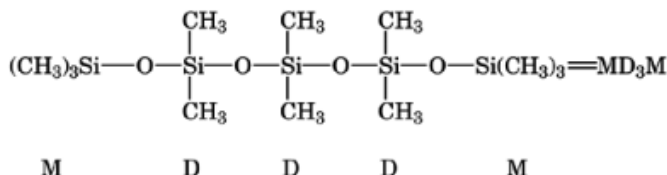
Table 13. **Silicones in Environmental Samples**

Location	Silicone ppm[a]	Organic silicone, pp[b]	References
Nagara River[c] sediment	0.3–5.8	2–54.2	697
dye factory	41–6290	0–1150	
sewage plant sludge	144	10.2	
night soil plant	34.3		
domestic wastewater treatment plant		2.4–4.9	
Blue Plainsd[d] wastewater treatment plant		4	727
sludge	89–104		727,728
filter cake	26–46		727
Potomac River[d]	0.46–3.07		728
Delaware Bay	0.1–1.56	34	728
Chesapeake Bay	0–36.1	30	728,729
Bight[e] wastewater treatment plant	0.48		730
Hudson River[e] sediment	10–350		731

[a]Wt Si/dry wt.
[b]Aquatic samples.
[c]Japan.
[d]Washington, D.C.
[e]New York.

Table 14. **Effect of Siloxane Molecular Weight on Water Solubility and Octanol–Water Partition Coefficient**

Molecular weight	Solubility in H_2O, ppm	log K_{ow}
1,200	1.6	2.86
6,000	0.56	3.26
25,000	0.17	3.83
56,000	0.076	4.25

$$CH_3—Si—O$$

M group

D group

T group

Q group

For example,

$$(CH_3)_3Si—O—Si—O—Si—O—Si—O—Si(CH_3)_3 {=} MD_3M$$

M   D   D   D   M
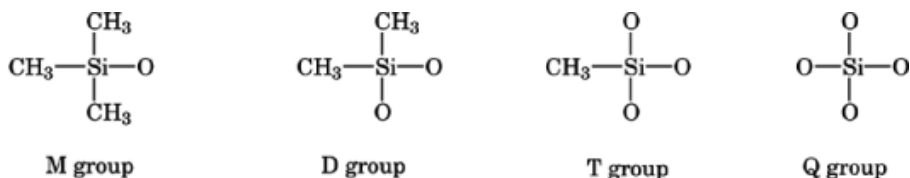
Fig. 1.   Polydimethylsiloxanes.

Cleavage reactions:

$$Cl_2CH_3Si—SiCl(CH_3)_2 + HCl \xrightarrow{(C_4H_9)_3NHCl} Cl_2CH_3SiH + Cl_2Si(CH_3)_2$$

Disproportionation:

$$n\ Cl_2CH_3Si—SiCl(CH_3)_2 \xrightarrow{\text{base catalyst}} n\ CH_3SiCl_3 + {-}(Si)_n{-}$$
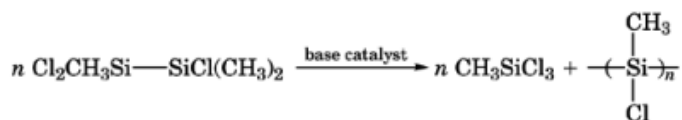
Si–C-bond-forming reactions:

$$Cl_2CH_3Si—SiCl(CH_3)_2 + R—C{\equiv}C—R \xrightarrow{Pt} Cl_2CH_3Si\diagdown_{CR=CR}\diagup SiCl(CH_3)_2$$

$$Cl(CH_3)_2Si—Si(CH_3)_2Cl + CH_2{=}CH_2 \longrightarrow Cl(CH_3)_2SiCH_2CH_2Si(CH_3)_2Cl$$

$$ArCOCl + Cl_2CH_3Si—SiCl(CH_3)_2 \xrightarrow{Pd} ArSiCl(CH_3)_2 + Cl_3SiCH_3\ + CO$$
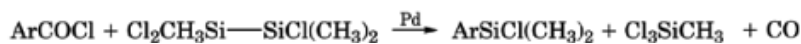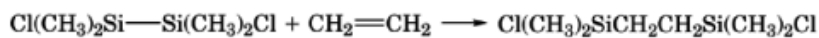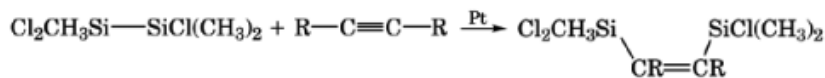
Fig. 2.   Widely accepted abbreviations used for silicone groups.

Direct chlorination: $CH_3SiCl_3 + Cl_2 \xrightarrow{h\nu} ClCH_2SiCl_3$

Hydrosilylation: $HSiCl_3 + CH_2{=}CHCH_2Cl \xrightarrow{Pt} Cl_3SiCH_2CH_2CH_2Cl$

$HSiCl_3 + HC{\equiv}CH \xrightarrow{Pt} Cl_3SiCHCH_2$

Nucleophilic substitution:

$(CH_3O)_3SiCH_2CH_2CH_2Cl \xrightarrow{H_2NR} (CH_3O)_3SiCH_2CH_2CH_2NHR$

$\xrightarrow[R_3N]{} (CH_3O)_3SiCH_2CH_2CH_2O\text{—}$

$\xrightarrow[R_3N]{H_2S} (CH_3O)_3SiCH_2CH_2CH_2SH$

$\xrightarrow{H_2NCH_2CH_2NH_2} (CH_3O)_3SiCH_2CH_2CH_2NHCH_2CH_2NH_2$

 $\xrightarrow{} (CH_3O)_3SiCH_2CH_2CH_2O\text{—}$

 $\xrightarrow{} (CH_3O)_3SiCH_2CH_2CH_2O\text{—}$
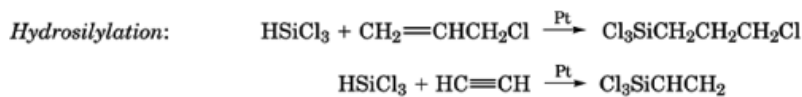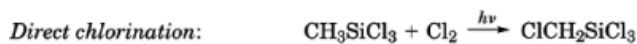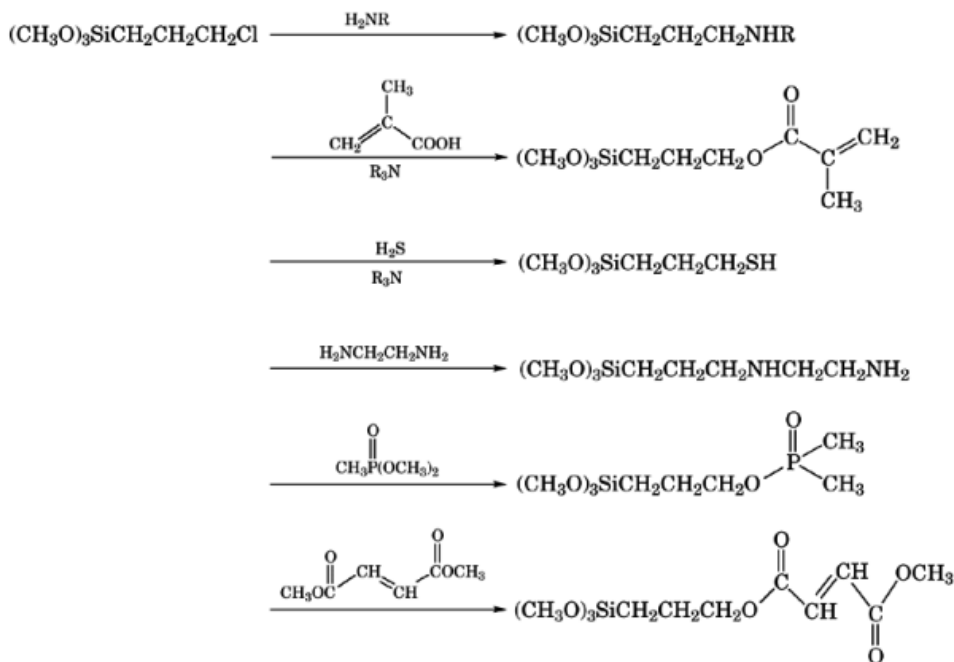
Fig. 3. Silylene species; possible intermediates in the direct process.
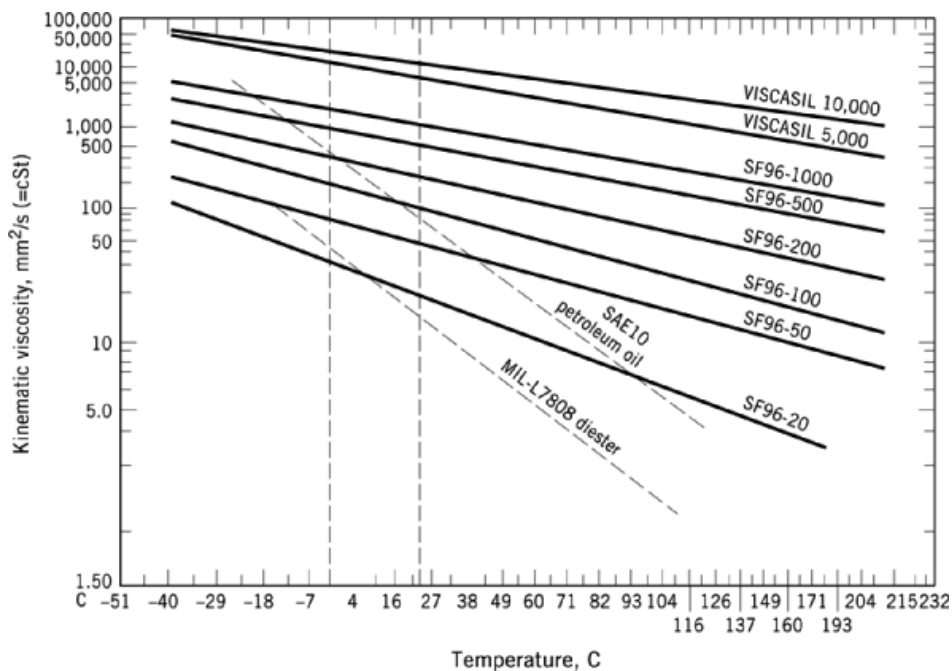
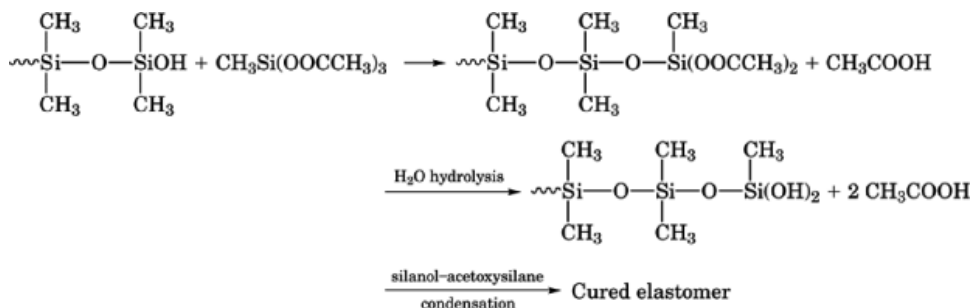**Fig. 4.**   Reaction of methanol with silicon.
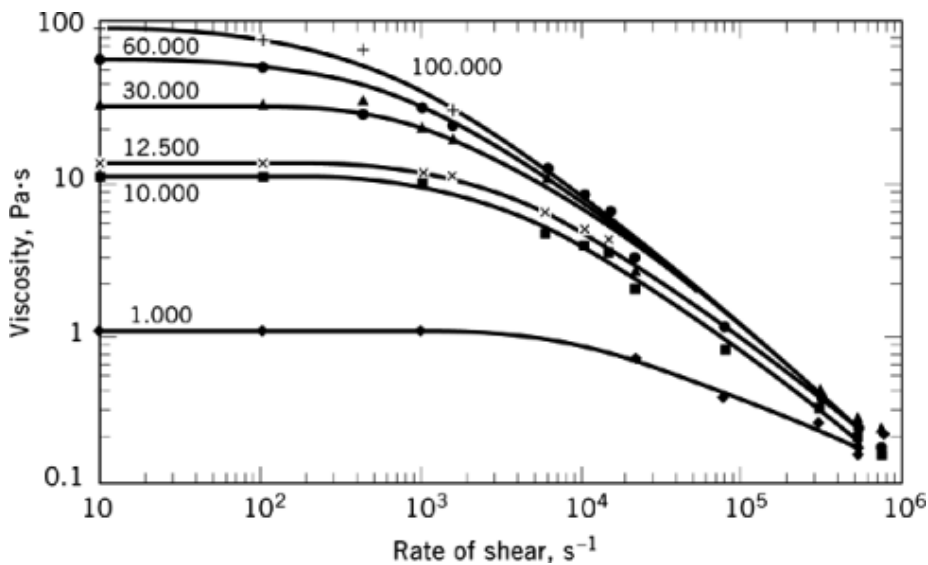
Fig. 5.   Chemistry of direct-process residue methylchlorodisilanes. The reactions are discussed in detail in the following references: (2) (71); (3) (67,68); (4) (72); (5) (73);
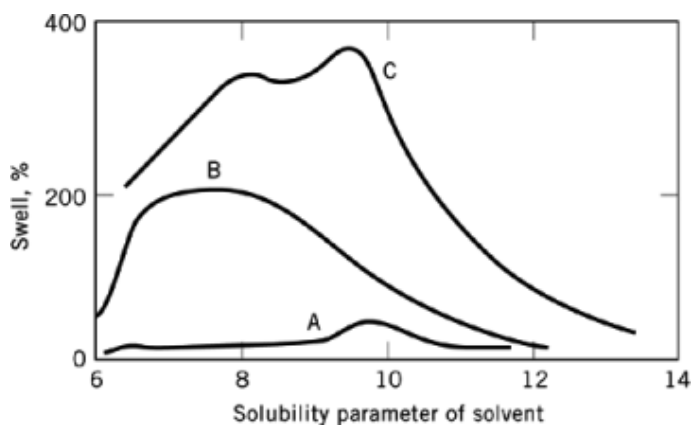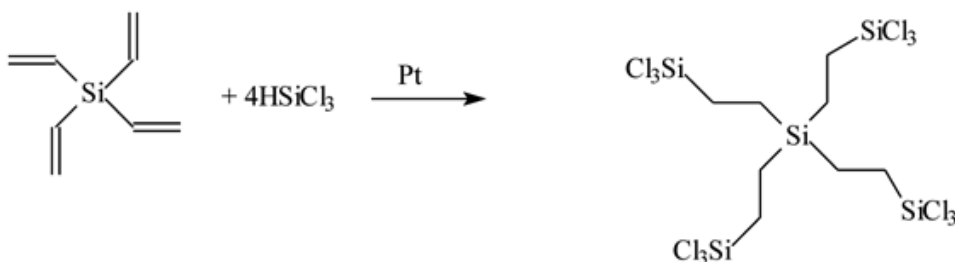
Fig. 6.   Diels-Alder route to aryl-silicon compounds.
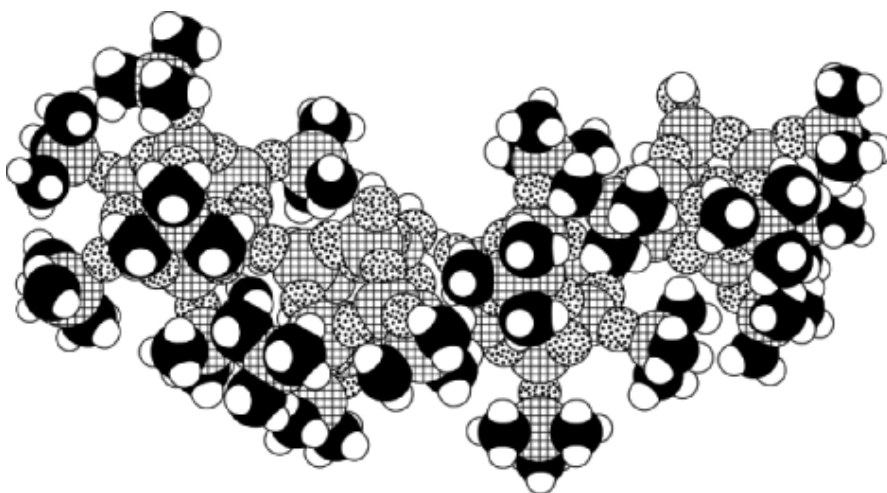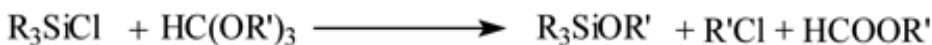

Fig. 7.   Hydrosilylation of olefins.

$$\underset{\overset{|}{CH_3}}{\overset{\overset{|}{CH_3}}{\sim\!\!\sim\!\!Si}}\!\!-\!O\!-\!\underset{\overset{|}{CH_3}}{\overset{\overset{|}{CH_3}}{Si}}OH + CH_3Si(OOCCH_3)_3 \longrightarrow \underset{\overset{|}{CH_3}}{\overset{\overset{|}{CH_3}}{\sim\!\!\sim\!\!Si}}\!\!-\!O\!-\!\underset{\overset{|}{CH_3}}{\overset{\overset{|}{CH_3}}{Si}}\!\!-\!O\!-\!Si(OOCCH_3)_2 + CH_3COOH$$

$$\xrightarrow{\text{H}_2\text{O hydrolysis}} \underset{\overset{|}{CH_3}}{\overset{\overset{|}{CH_3}}{\sim\!\!\sim\!\!Si}}\!\!-\!O\!-\!\underset{\overset{|}{CH_3}}{\overset{\overset{|}{CH_3}}{Si}}\!\!-\!O\!-\!Si(OH)_2 + 2\,CH_3COOH$$

$$\xrightarrow[\text{condensation}]{\text{silanol–acetoxysilane}} \text{Cured elastomer}$$

Fig. 8. Hydrosilylation of phenylacetylene to provide β-vinyl silicones.

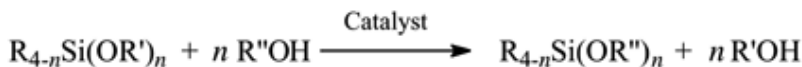**Fig. 9.** Hydrosilylation reactions the synthesis of dendritic siloxanes.

$$RSiCl_3 + 3\,R'OH \longrightarrow RSi(OR')_3 + 3\,HCl$$

Fig. 10. Alcoholysis of Si−Cl bonds to form silyl ether linkage.

$$R_3SiCl + HC(OR')_3 \longrightarrow R_3SiOR' + R'Cl + HCOOR'$$

Fig. 11. Use of alkyl orthoformates as an alternative to form alcohols or metal alkoxides.

$$R_{4-n}SiH_n + n\,R'OH \xrightarrow{\text{Catalyst}} R_{4-n}Si(OR')_n + n\,H_2$$
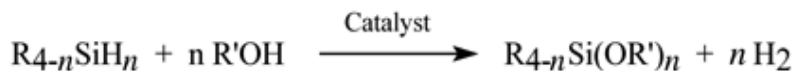
Fig. 12. Alcoholysis of silicon-hydride bonds.

$$R_{4-n}Si(OR')_n + n\,R''OH \xrightarrow{\text{Catalyst}} R_{4-n}Si(OR'')_n + n\,R'OH$$

Fig. 13. Preparation of alkoxylsilanes by exchange of an existing alkoxy group with another one.

$$R_3SiH + R'COOH \xrightarrow{\text{Catalyst}} R_3Si-O-\underset{\underset{O}{\|}}{C}-R' + H_2$$
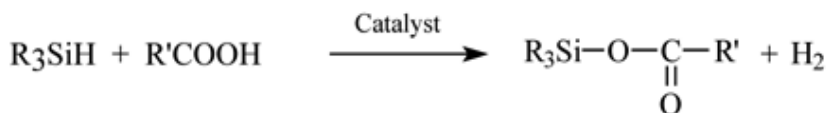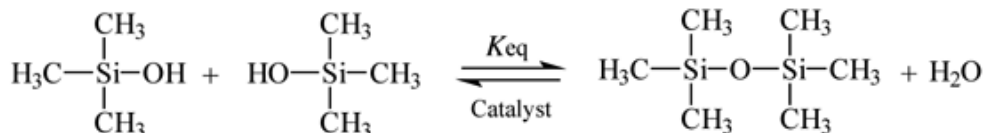
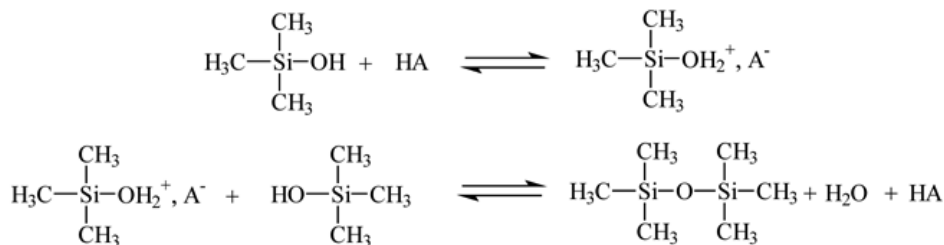**Fig. 14.** Synthesis of acyloxysilanes by reacting triorganohydridosilanes with carboxylic acids.
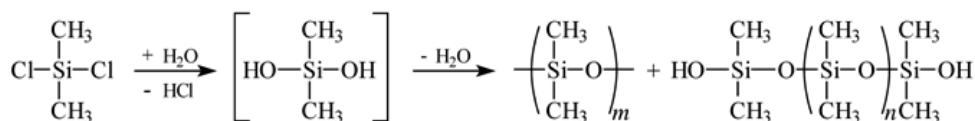
Fig. 15. Hydrolyses of chlorosilanes obtained from the divert process yield a mixture of cyclic and silanol-stopped oligomers.
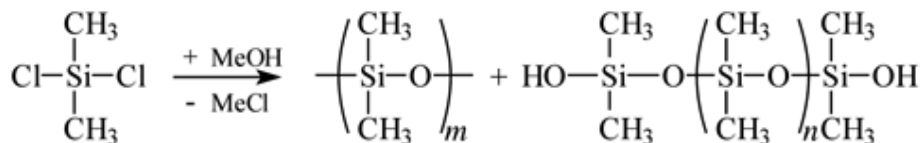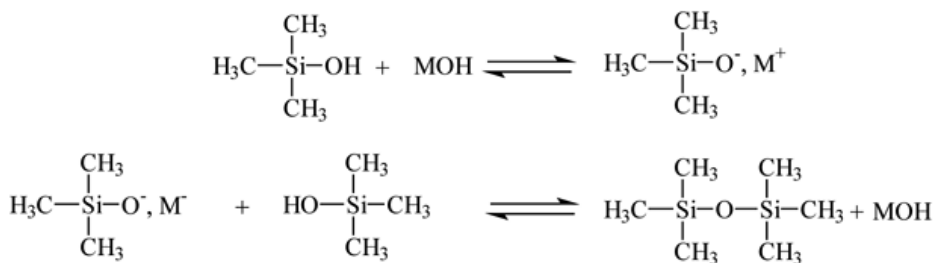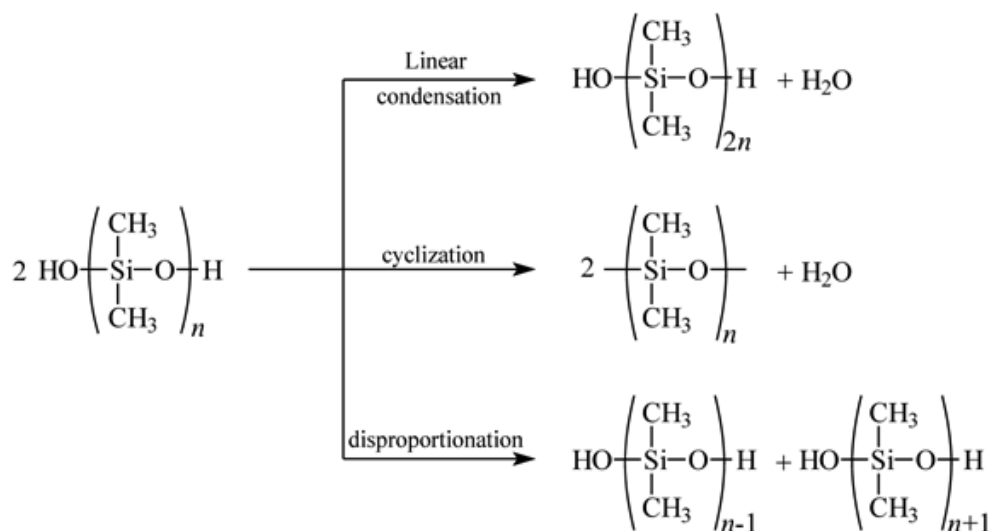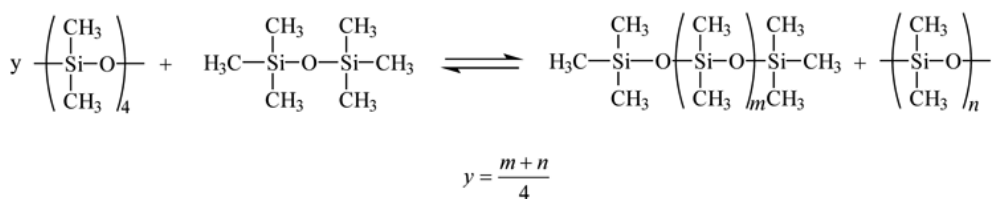
Fig. 16. Dichlorodimethylsilane converted into siloxane silanol-stopped oligomers by a methanolysis process.

**Fig. 17.** Polycondensation.

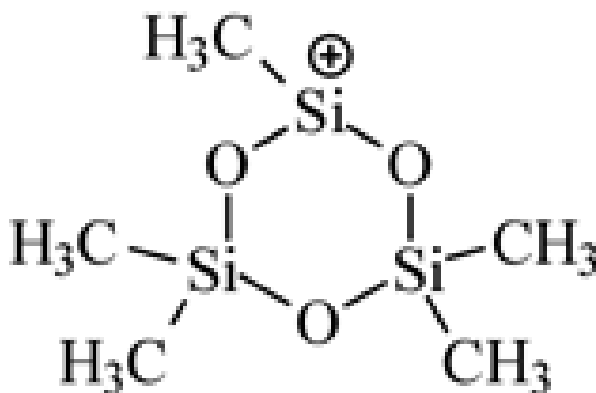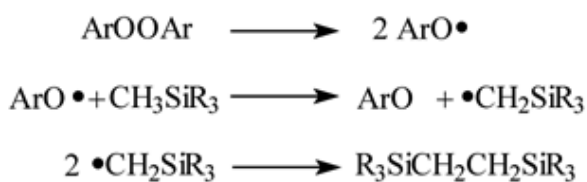**Fig. 18.** Acid-catalyzed condensation.

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-OH \;+\; MOH \; \rightleftharpoons \; H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O^-, M^+$$

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O^-, M^- \;+\; HO-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_3 \; \rightleftharpoons \; H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_3 + MOH$$

Fig. 19. Base catalyzed condensation.

$$2\; HO{\left(\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\!\right)}_{n} H$$

Linear condensation $\longrightarrow$ $HO{\left(\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\!\right)}_{2n} H \; + H_2O$

cyclization $\longrightarrow$ $2\; {\left(\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\!\right)}_{n} \; + H_2O$

disproportionation $\longrightarrow$ $HO{\left(\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\!\right)}_{n-1} H \; + HO{\left(\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\!\right)}_{n+1} H$

Fig. 20. In the presence of strong protic acids, three processes are considered.

$$y\;{\left(\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\!\right)}_{4} \;+\; H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_3 \; \rightleftharpoons \; H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O{\left(\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\!\right)}_{m}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_3 \;+\; {\left(\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\!\right)}_{n}$$

$$y = \frac{m+n}{4}$$

Fig. 21. Equilibration polymerization of D_4.
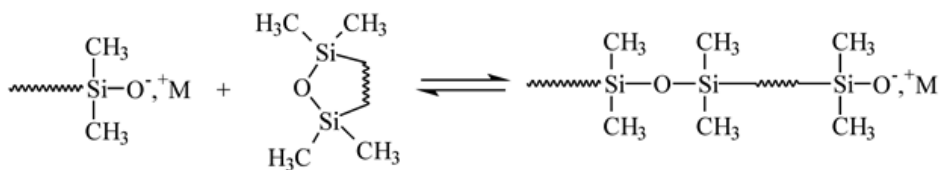
Fig. 22.   Anionic ring-opening polymerization.

Fig. 23.   A silylenium cation.

$$ArOOAr \longrightarrow 2\ ArO\bullet$$

$$ArO\bullet + CH_3SiR_3 \longrightarrow ArO\ + \bullet CH_2SiR_3$$

$$2\ \bullet CH_2SiR_3 \longrightarrow R_3SiCH_2CH_2SiR_3$$

Fig. 24.   Peroxide induced crosslinking.

Fig. 25.   Network formation via hydrosilylation.

$$R_3SiH \quad + \quad R'_3SiCH{=}CH_2 \quad \rightleftharpoons \quad R'_3SiH \quad + \quad R_3SiCH{=}CH_2$$

Fig. 26.   Vinyl silane-hydride exchange.
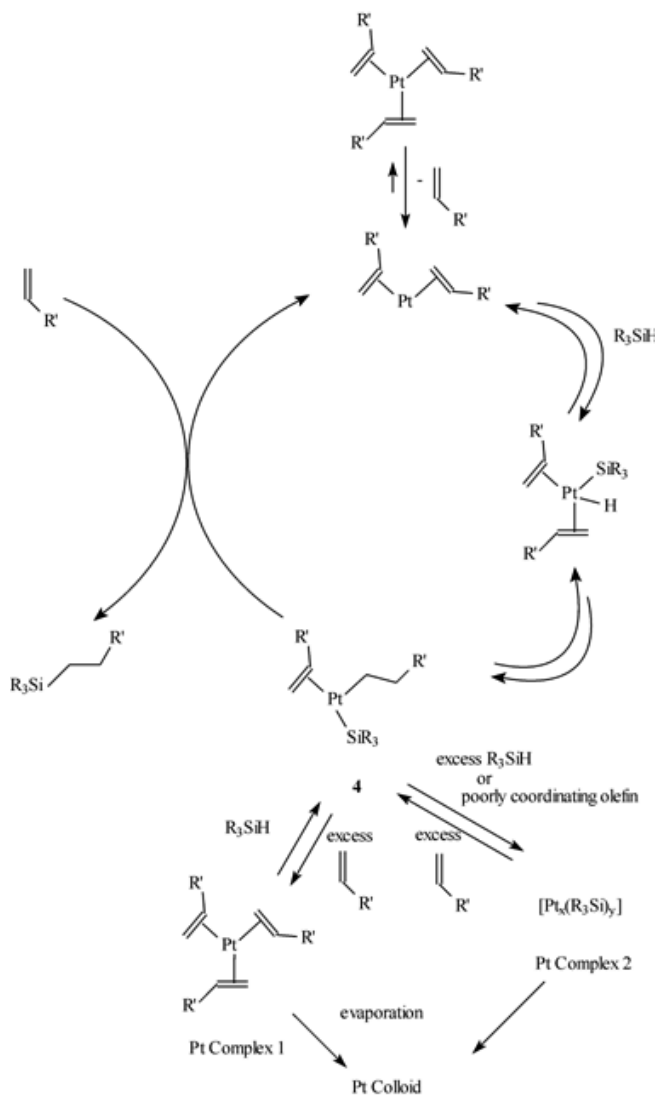
Fig. 27. Hydrosilylation catalytic cycle.

$$PtL_n + xI = PtL_{n-x}I_x + x L_n$$

Fig. 28. A mechanism of inhibition.

$$R_3SiOH + R'_3SiOH \longrightarrow R_3SiOSiR'_3 + H_2O$$

Fig. 29. Condensation of silanol groups to form siloxanes.

Fig. 30. Silanol-alkoxysilane condensation.

$$R_3SiOH + R'_3Si(OCH_3) \longrightarrow R_3SiOSiR'_3 + CH_3OH$$

$$R_3SiOH + R'_3Si(OOCCH_3) \longrightarrow R_3SiOSiR'_3 + CH_3COOH$$

Fig. 31. Silanol acyloxysilane condensation.

$$R_3SiOH + R'_3SiH \longrightarrow R_3SiOSiR'_3 + H_2$$

Fig. 32. Silanol-silylhydride condensation.

$$R_3SiOH + R'_3Si(ON{=}\overset{\underset{\textstyle|}{CH_3}}{C}{-}CH_2CH_3) \longrightarrow R_3SiOSiR'_3 + HO{=}N{-}\overset{\underset{\textstyle|}{CH_3}}{C}{-}CH_2CH_3$$
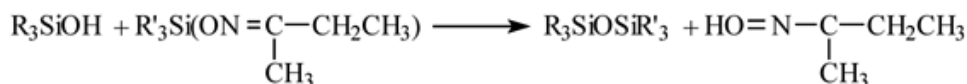
Fig. 33. Silanol-silyloxime condensation.

$$R_2Sn(OCOR')_2 + H_2O \longrightarrow R_2Sn(OCOR')OH + R'COOH$$

Fig. 34. Hydrolysis of dialkyltin esters.

$$R_2Sn(OCOR')OH + Si(OR')_4 \longrightarrow R_2Sn(OCOR')(OSiR')_3 + R'OH$$
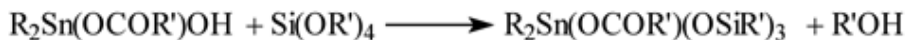
Fig. 35. Generation of a tin-silanolate intermediate.

$$R'_3Si(OR) + H_2O \longrightarrow R'_3SiOH + ROH$$

Fig. 36. Hydrolysis of alkoxy silanes.

$$R_3SiOH + R'_3SiOH \longrightarrow R_3SiOSiR'_3 + H_2O$$

Fig. 37.   Silanol-silanol condensation.

$$R'_3Si(OR) + R''_3SiOH \longrightarrow R'_3SiOSiR''_3 + ROH$$

Fig. 38.   Silanol-alkoxysilane condensation.
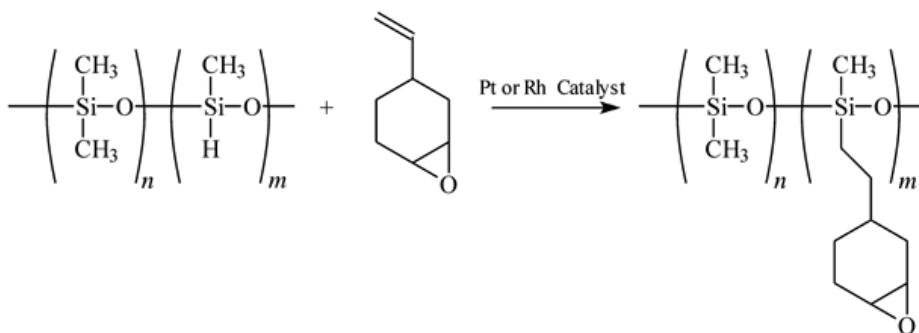
Fig. 39.   Preparation of epoxy-functional silicones.

$$\log(\text{viscosity}) = 1.00 + 0.0123\,(M_n)^{1/2}$$

Fig. 40.   Relationship of M_n to bulk viscosity.

$$[\eta] = 2 \times 10^{-4}\,(M_n)^{0.66} \quad [\eta] = 8 \times 10^{-4}\,(M_n)^{0.5}$$

toluene   methyl ethyl ketone

Fig. 41.   Relationship of M_n to intrinsic viscosity.

$$\log(\eta + b) = a \log T + c$$

$$VTC = \eta_{38c} - \eta_{99c}$$

Fig. 42.   Viscosity-temperature relationship.
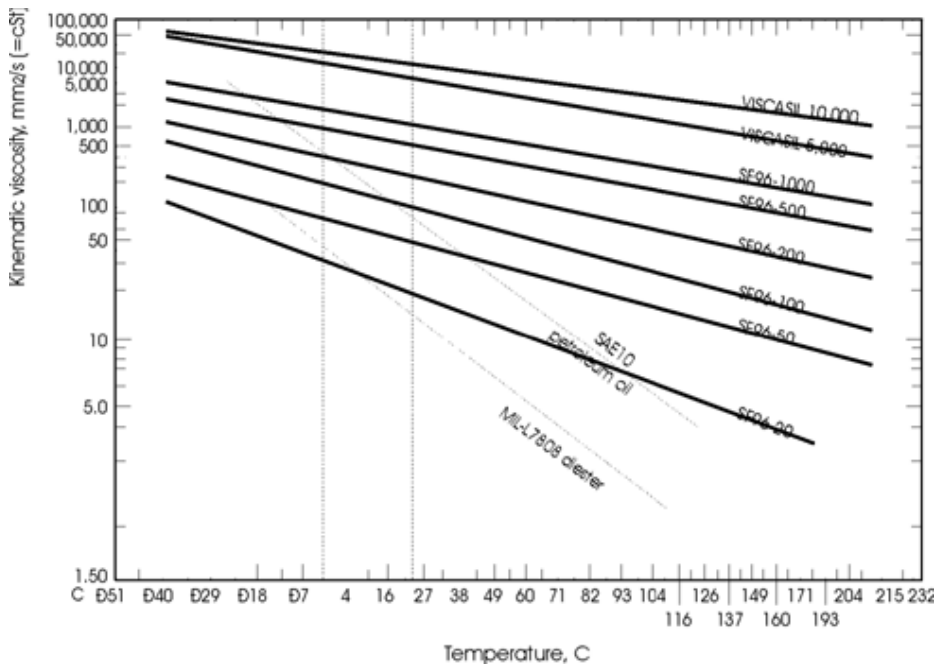
Fig. 43.   Kinematic viscosity-temperature relationship of dimethylsilicone fluids.
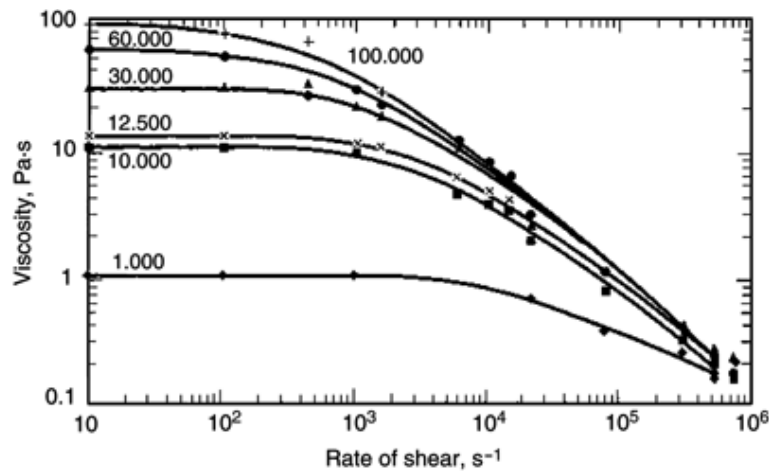
Fig. 44.   Shear rate versus viscosity for PDMS. Numbers on curves indicate molecular weights. To convert Pa.s to poise (P), multiply by 10.
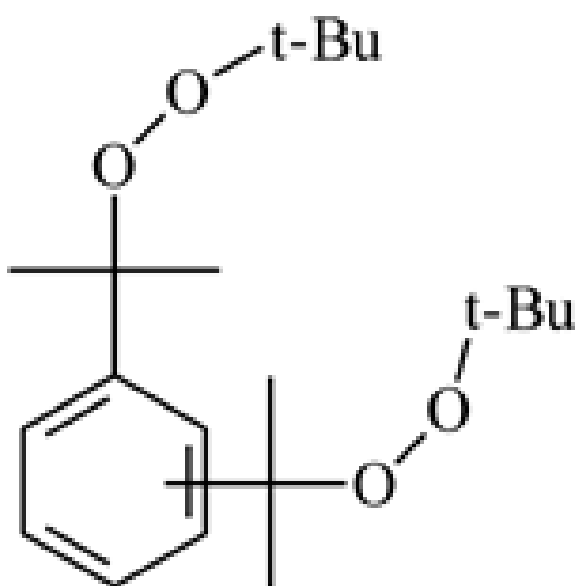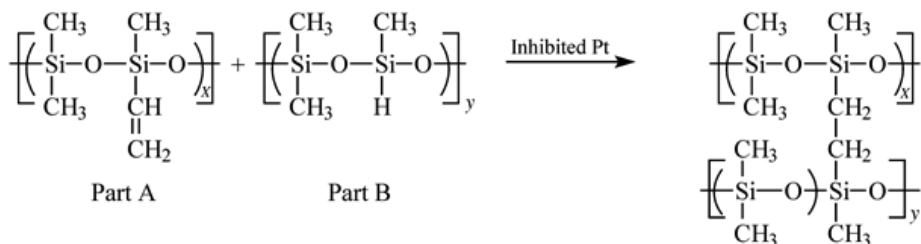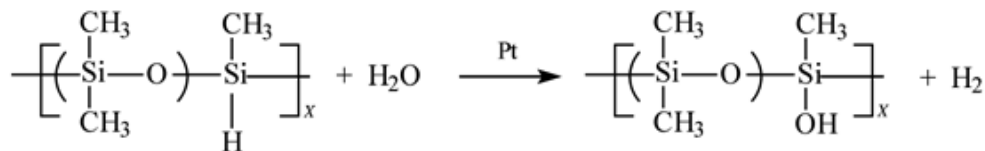
Fig. 45. Bis-peroxide curing agent.
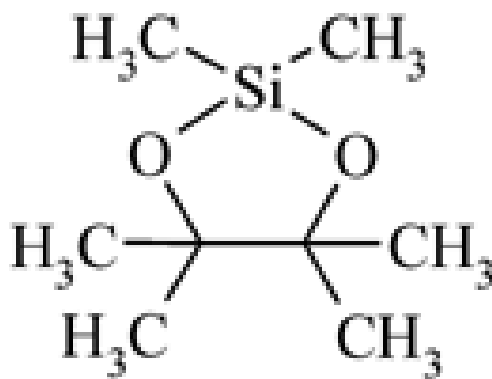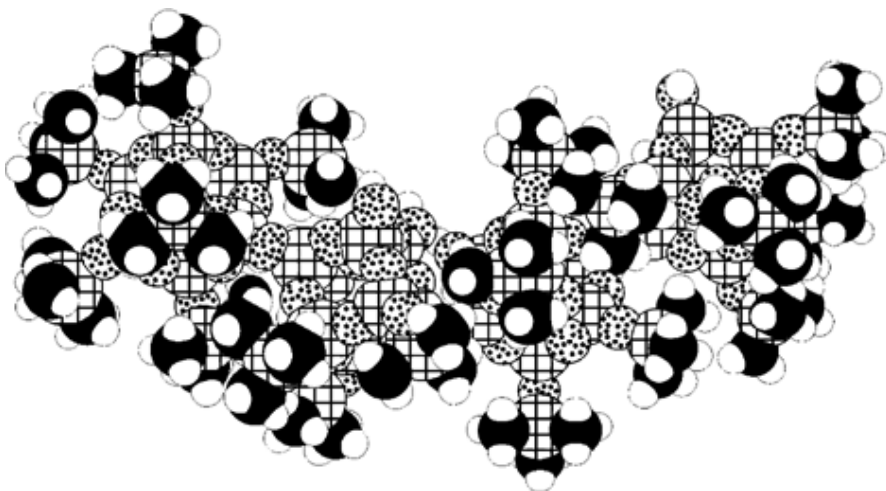

Fig. 46. Dimethylpinacoloxysilane.
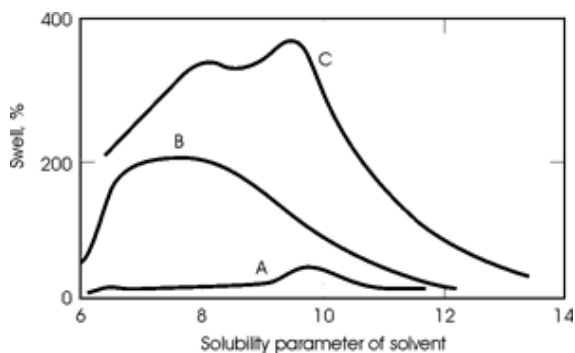
Fig. 47. Swelling of silicone rubber by solvents (497). A = fluorosilicones (methyl tri-fluoropropyl silicones). B = dimethylsilicone: C = methyl(phenyl)silicone.
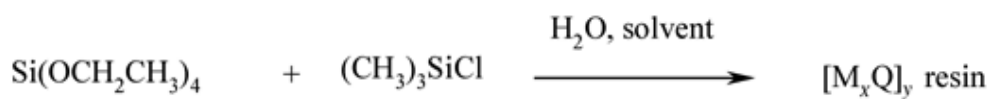

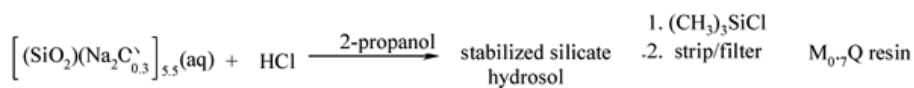**Fig. 48.** Latent addition-curing system.

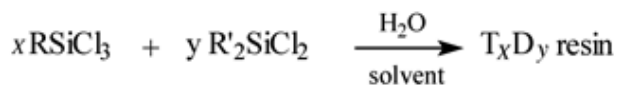**Fig. 49.** Silicone foaming reaction.

Fig. 50. Molecular structure of a typical MQ resin, $[M_{0.62}Q^{OH}_{0.17}Q_{0.83}]_{32}$, where ⊕ = H, ⊕ = C, ⊛ = Si, and ⊕ = ⊕

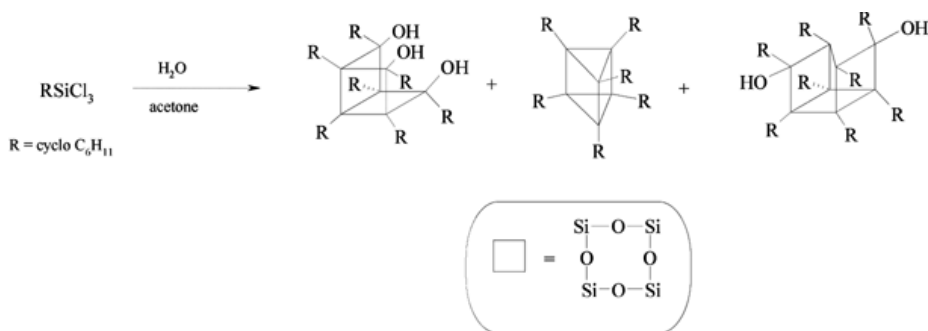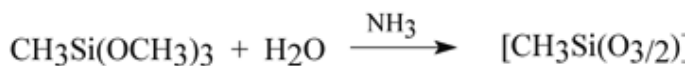$$Si(OCH_2CH_3)_4 \quad + \quad (CH_3)_3SiCl \quad \xrightarrow{\text{H}_2\text{O, solvent}} \quad [M_xQ]_y \text{ resin}$$

Fig. 51. MQ resins from ethyl silicate.

$$\left[(SiO_2)(Na_2C_{0.3})\right]_{5.5}(aq) \; + \; HCl \; \xrightarrow{\text{2-propanol}} \; \begin{array}{c} \text{stabilized silicate} \\ \text{hydrosol} \end{array} \; \xrightarrow[\text{.2. strip/filter}]{\text{1. }(CH_3)_3SiCl} \; M_{0.7}Q \text{ resin}$$

Fig. 52. MQ resins from sodium silicate.

$$x \, RSiCl_3 \quad + \quad y \, R'_2SiCl_2 \quad \xrightarrow[\text{solvent}]{\text{H}_2\text{O}} \quad T_xD_y \text{ resin}$$

Fig. 53. TD resin preparation.

Fig. 54.   Preparation of silsesquioxanes.

Fig. 55.   Synthesis of an amorphous T resin.
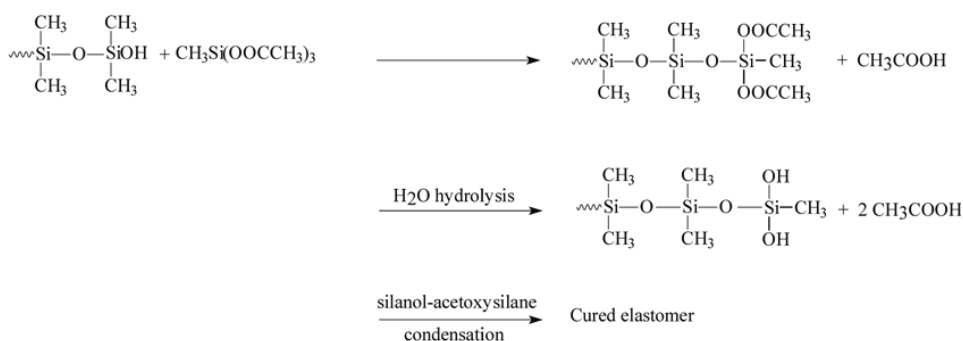
Fig. 56.   Basic chemistry of acetoxy-based RTV silicones. The reactions for curing methoxy-based RTV silicones are the same; in that case, the methoxy group (OCH_3) replaces acetoxy ($OOCCH_3$), and methanol (CH_3OH), rather than acetic acid ($CH3COOH$), is formed.
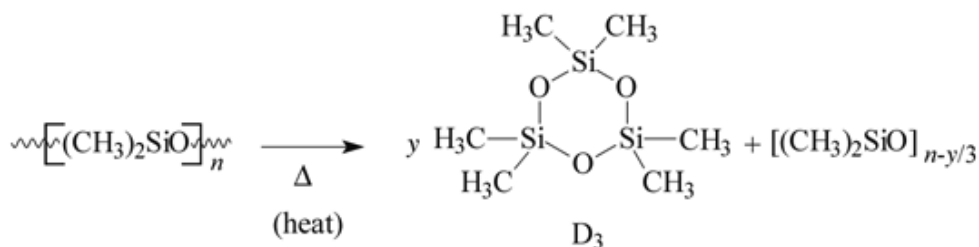
Fig. 57.   Pyrolytic conversion of silicones to cyclics, mainly D_3.

[(CH$_3$)$_3$SiO] $_m$ [(CH$_3$)$_2$SiO$_2$] $_n$ [CH$_3$SiO$_3$] $_o$ [SiO$_4$] $_p$ + (CH$_3$)$_3$SiOSi(CH$_3$)$_3$ $\longrightarrow$

   M   D   T   Q

n (CH$_3$)$_2$Si [OSi(CH$_3$)$_3$]$_2$ + o CH$_3$Si [OSi(CH$_3$)$_3$]$_3$ + p Si [OSi(CH$_3$)$_3$]$_4$

[(CH$_3$)$_3$SiO]m [(CH$_3$)$_2$SiO$_2$]n [CH$_3$SiO$_3$]o [SiO$_4$]p + Si(OC$_2$H$_5$)$_4$ $\xrightarrow{\text{KOH} \atop \text{or KOC}_2\text{H}_5}$

   M   D   T   Q

m (CH$_3$)$_3$SiOC$_2$H$_5$ +n (CH$_3$)$_2$Si(OC$_2$H$_5$)$_2$ + o-CH$_3$Si(OC$_2$H$_5$)$_3$
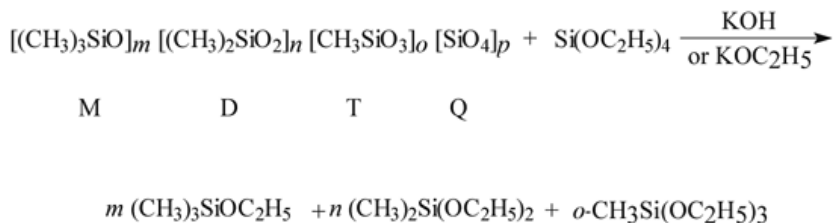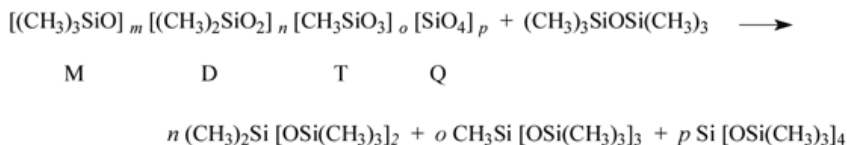
Fig. 58.   Degradative analysis of silicones.

$$\mathrm{Log}\ K_{\mathrm{ow}} = 3.047 - 1.148\ \mathrm{log}\ S \quad (1)$$

Fig. 59.   Correlation of octanol-water partition and water solubility of silicones.

3 HO—Si—OH $\underset{}{\overset{-\mathrm{H_2O}}{\rightleftharpoons}}$ HO—Si—O—Si—OH + HO—Si—OH $\underset{}{\overset{-\mathrm{H_2O}}{\rightleftharpoons}}$ HO—Si—O—Si—O—Si—OH

Fig. 60.   Silanediol equilibria in aqueous solution.

NO$^-$$_3$ + H$_2$O $\longrightarrow$ NO$_2$ + HO$^\bullet$ + HO$^-$

Fig. 61.   Generation of hydroxyl radicals from nitrate ions.