

## AN OVERVIEW OF THE POLYMERIZATION OF CYCLOSILOXANES

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### Introduction

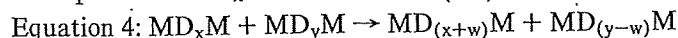
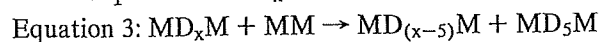
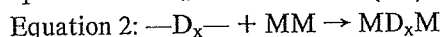
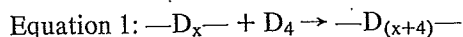
The first syntheses of the major types of the polyalkylsiloxanes were performed by Friedel, Ladenburg, and Crafts in 1865-71 (1-6). However, it was not until the early 1900's that F. S. Kipping and his group proved the siloxane polymeric structure (3). This group prepared a large number of linear and cyclic polymers of type  $(R_2SiO)_N$  and  $HO(R_2SiO)_N H$ , and also crosslinked architectures  $(RSiO_3-NH_3-2N)_M$ . Kipping's studies disclosed for the first time that the Si-O-Si group differs dramatically from the C-O-C group in its reactivity and that the Si-O-Si group could be particularly easily cleaved by acids, bases, or Lewis acids. He was the first to observe the catalytic effect of acids and bases for the now commercially important siloxane redistribution and ring opening polymerization reactions. Following this period, commercial production of siloxane polymers was restrained by the absence of convenient methods for monomer synthesis. In the 1930's, Eugene G. Rochow at General Electric (4,7,8) and R. Müller (nine months later) in Germany apparently independently discovered what is known as the "direct process" (9). This process was essential for the industry since it allowed for the economical manufacture of the family of methylchlorosilanes necessary for siloxane production. Controlled hydrolysis of the various organohalosilanes then provided the cyclic trimers and tetramers which could be used for polymerization.

Although there are a variety of routes presently available for siloxane production, only two are of commercial importance. These include hydrolytic reactions of organohalosilanes or organoalkoxysilanes and redistribution type polymerizations of cyclic monomers. Both of these types of reactions involve a ring-chain equilibrium distribution of products. The principles applicable to the distribution are probably identical in both cases.

The discussion following will deal mainly with the important equilibrations and polymerizations of cyclic siloxanes. For further information concerning these methods and for excellent discussions of other types of siloxane polymerizations, the reader is referred to Voronkov (4), Noll (7), and Meals (10). In addition, Noll (7), Eaborn (11), and Arkles and Peterson (12) offer reviews of the general chemistry of silicon compounds.

### Polymerization of Cyclic Siloxanes

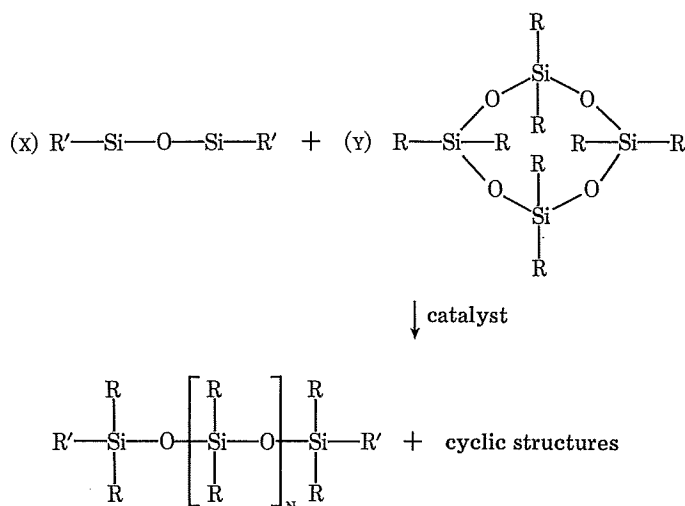
Linear polysiloxane can be synthesized by both the anionic and cationic polymerization of cyclic siloxanes as discussed later in this article. Molecular weight is regulated through the incorporation of controlled amounts of monofunctional endblockers into the system (7,13). As a result of the nature of the configurations of siloxane chains coupled with the similar reactivity of siloxane bonds in the linear as compared to cyclic species, the anionic or cationic catalysts attack both the rings and chains during the polymerization. These so called "redistribution" or "equilibration" polymerizations involved reactions such as those listed in equations 1-4 occurring throughout the process. At thermodynamic equilibrium (at least in the absence of endblocking units) these reactions result in a Gaussian distribution of molecular weights among the chain molecules together with an approximately monotonically decreasing distribution of ring species as ring sizes increases (13-20). Rates of the various processes depend upon factors such as catalyst type and concentration, temperature, pressure, and the use of various types and amounts of promoters and can undoubtedly be controlled to some extent. With the exception of using organolithium catalysts in conjunction with the  $D_3$  monomer (21-22), however, significant amounts of redistribution evidently cannot be avoided.



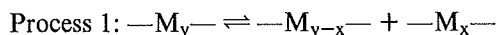
(In silicone nomenclature, "M" denotes a monofunctional siloxane unit whereas "D" refers to a difunctional siloxane unit. "D<sub>4</sub>" therefore represents the cyclic siloxane tetramer while "MM" is the linear dimer. "D" nomenclature is normally associated with dimethylsiloxyl units).

The technique involved in these types of polymerizations is normally quite facile. The general method potentially lends itself well to the laboratory synthesis of di-organofunctional siloxanes through variance of the structures of "R" and "R'" shown in equation 5. The R group is principally methyl, but other groups such as phenyl, vinyl, and trifluoropropyl are also used.

Equation 5



In order to accurately synthesize difunctional siloxanes of varied but controlled molecular weights by this method, an understanding of the mechanisms and ring-chain equilibria must be considered. Jacobson and Stockmayer published their now classic paper (14) in 1950 describing the theory of molecular weight distributions in linear/cyclic equilibrated polymer systems. Up to that time, theories describing molecular weight distributions had not considered the presence of cyclic structures. Jacobson and Stockmayer's theory is based on the premise that the proportion of a macrocyclic species of units in equilibrium with linear components is related to the probability of coincidence of the terminal atoms of the sequence of  $x$  units. In development of this theory, the following processes were considered:

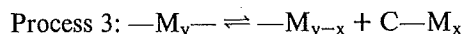


M = monomer unit

C---M = cyclic form of the monomer unit

$x$  and  $y$  = degrees of polymerization

Process 3 denotes the sum of processes 1 and 2.



An equilibrium constant,  $K_x$ , for ring formation (for process 3) was derived from entropy relationships (written in equations 6, 7, and 8 for processes 1, 2, and 3, respectively). "P" in these equations was described by Jacobson and Stockmayer as the probability that a chain would be in an appropriate configuration for ring formation (equation 9). Jacobson and Stockmayer actually set  $\langle \bar{r}_x^2 \rangle$  equal to  $(\nu x b^2)$  which meant implicitly that  $\langle \bar{r}_x^2 \rangle$  was to be set equal to  $\langle \bar{r}_x^2 \rangle_0$ , the mean-square end-to-end distance of the unperturbed chain. " $W_{x(\bar{r}=0)}(\bar{r})$ " in equation 9 denotes the Gaussian distribution function expressing the density of end-to-end vectors,  $\bar{r}$ , in the vicinity of  $\bar{r} = 0$ .

$$\text{Equation 6: } \Delta S_{(1)} = k \ln \left[ \frac{V}{\sigma_A v_s} \right]$$

$$\text{Equation 7: } \Delta S_{(2)} = k \ln \left[ P \frac{\sigma_A}{\sigma_{R_x}} \right]$$

$$\text{Equation 8: } \Delta S_{(3)} = k \ln \left[ \frac{VP}{\sigma_{R_x} v_s} \right]$$

V = Volume of the system.

$\sigma_A$  = Symmetry number for the chain species

( $\sigma_A = 2$  for organosiloxanes).

$\sigma_{R_x}$  = Symmetry number for the ring species of " $x$ " repeating units ( $\sigma_{R_x} = 2x$  for organosiloxanes).

$$\text{Equation 9: } P = \int_0^{v_s} W_x(\bar{r}) d\bar{r} \cong \left[ \frac{\beta^3}{\pi^{3/2}} \right] v_s = \left[ \frac{3}{2\pi\nu x} \right]^{3/2} \frac{v_s}{b^3}$$

$$\nu x b^2 = \langle \bar{r}_x^2 \rangle_0 = \langle \bar{r}_x^2 \rangle$$

$\nu$  = Number of links per repeat unit.

$b$  = Average "effective link length"

$\langle \bar{r}_x^2 \rangle$  = The mean-square end-to-end length averaged over all configurations of chain size  $x$ .

The existence of this function in the entropy term obviously implies to a Gaussian distribution of end-to-end vectors. This point may, in fact, be a poor assumption for the cases of very short chains (which, in turn, form small rings). “ $v_s$ ” was defined as the volume element within which two termini must meet in order to form a bond. It appears in the denominator of Equation 6 due to the fact that the two atoms which formed the bond broken in process 1 were constrained to the volume element  $v_s$  prior to the occurrence of process 1. Since  $\int_0^{\infty} W_x(\bar{r})$  is the probability of the terminal of a molecule meeting in the volume range,  $v_s$ , this factor also appears in the entropy term describing process 2. The enthalpy terms for the first two processes presumably cancel each other with the assumption that the ring formed is not small enough to be sterically strained. This was rationalized by noting that the intramolecular bond formed in process 2 was similar in nature to the one severed in process 1. The equilibrium constant for process 3 (expressed in moles/liter) was derived from equation 8 (equations 10 and 11). The definition of “ $p$ ” in this context (equation 11) differs slightly from its “normal” definition (i.e. extent of reaction). Here, “ $p$ ” is defined as the extent of reaction of the functional endgroups in the chain portion of the system. “ $p$ ” could also be identified as the ratio of the concentrations of acyclic species of sizes  $x$  to  $x - 1$  (12).

$$\text{Equation 10: } K_x = \frac{\left(\frac{3}{2\pi\nu}\right)^{3/2}}{2b^3} N_A^{-1} x^{-5/2} = \frac{\left(\frac{3}{2\pi\nu}\right)^{3/2}}{2\langle\bar{r}_x^2\rangle_0^{3/2} N_A} x^{-1}$$

$$\langle\bar{r}_x^2\rangle_0 = \nu x b^2$$

$$\text{Equation 11: } K_x = \frac{[C-M_x][M_{y-x}]}{[M_y]} = \frac{[C-M_x]}{p^x}$$

The combination of equations 10 and 11 predicted several interesting points:

1. The concentration of  $x$ -mer rings was shown not to be a function of dilution. The number of  $x$ -mer rings was predicted to increase linearly with dilution, thereby making the proportion of rings in the system greater as it is diluted. Upon incrementally adding solvent, this process eventually results in a “critical dilution point” above which only rings are present.
2. The rings formed are small species. As  $p \rightarrow 1$ ,  $K_x \rightarrow [C-M_x]$  and  $[C-M_x]$  approaches proportionality to  $x^{-5/2}$ .

Jacobson and Stockmayer also reasoned that each subset of species (e.g. rings vs. chains) within the overall distributions must be in equilibrium with itself at thermodynamic equilibrium. Therefore, they predicted the normal distribution for the chain species whether or not ring species were formed. Figure 1 (reproduced from their 1950 paper) illustrates the predicted distribution for ring and chain species.

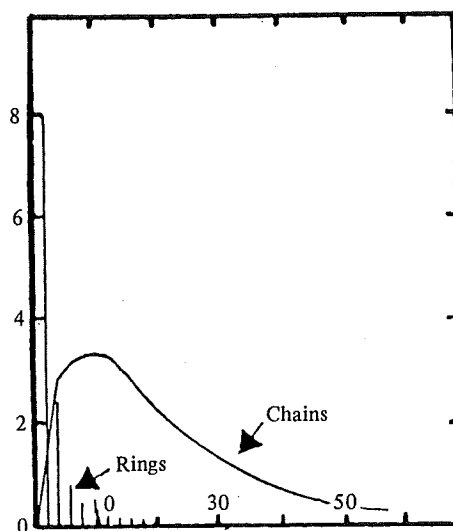


Figure 1: Typical Molecular Distribution for a Ring-Chain Equilibrium Polymer. Weight % is plotted against degree of polymerization (14).

One problem of Jacobson and Stockmayer’s interpretation is observed in the cases of very small but unstrained rings, where much higher concentrations of rings were formed than were predicted. Flory and Semlyen (15) explained this deviation by suggesting that not only did two termini have to meet within a volume “ $v_s$ ” in order to establish a bond, they also had to approach each other from a specified direction. This direction was specified by a solid angle fraction  $\delta\omega/4\pi$ . They explained that this term should appear in the entropy expression for process 1 in the inverse form, i.e.  $4\pi/\delta\omega$ . In process 2, if the chains were sufficiently long, there would be no correlation between the probability

for two termini of a molecule to meet within  $v_s$  and to approach within the solid angle  $\delta\omega$ . In this case, the term  $\delta\omega/4\pi$  would be valid for inclusion into the entropy term for process 2 and, hence, when the entropies for processes 1 and 2 were summed, these terms would cancel (and the equation for  $\Delta S_{(3)}$  from Jacobson and Stockmayer's theory should be valid). However, for short chains, the probability of approach of two termini of one chain within  $v_s$  would depend on bond angles, steric factors, etc., particular to the specific system, and would deviate from  $\delta\omega/4\pi$ . In that case the probability "P" in Jacobson and Stockmayer's theory in the entropy term would be incorrect.

There have been several studies conducted investigating equilibrium distributions of polyorganosiloxanes experimentally. Theoretical and empirical weight fractions of cyclics and their distributions with variances in  $x$  are of particular interest to the synthetic chemist. Equation 10 can be rearranged to give the weight fraction,  $w_r$ , of cyclics (equation 12) for high extents of reaction (the empirical comparisons were all made at  $p \rightarrow 1$ ).

$$\text{Equation 12: } w_r = \left(\frac{3}{\pi}\right)^{3/2} \frac{M_0}{2^4 l^3 N_{AC}} \sum_{x=4}^{\infty} (x C_x)^{-3/2}$$

$c$  = Total siloxane concentration in g/l

$M_0$  = Molecular weight of a repeat unit

$l$  = The length of a siloxane bond.

$$\langle \bar{r}_x^2 \rangle_0 = C_x 2x l^2$$

Contributions from the weight fraction of the stained cyclic trimer, not applicable to the theory, are neglected. Wright and Semlyen compared their own (17) values together with Brown and Slusarczuk's (18) calculated and experimental values of  $K_x$  for polydimethylsiloxane (PDMS). Calculated values were based on calculations of  $\langle \bar{r}_x^2 \rangle_0$  derived from Flory's rotational isomeric state model for PDMS (23). Empirical values came from measurements of the concentrations of  $x$ -meric rings according to Jacobson's and Stockmayer's relationship,  $K_x = [C-M_x]/p^x$ . Brown and Slusarczuk (18) equilibrated PDMS in toluene at 110 degrees centigrade and a concentration of 0.22 g/ml of siloxane. Values from that equilibration and Wright's and Semlyen's bulk equilibration (17) as a function of  $x$  are compared with theoretical values in Figure 2. As predicted, the  $K_x$  values in the range  $x = 11-40$  were experimentally independent of dilution. In direct contrast, the cyclization constants for  $x = 4-10$  increase with dilution (the increase becoming more pronounced with decreases in  $x$ ). Siloxane chains for  $x$  greater than approximately 15 agreed well with theoretical values.

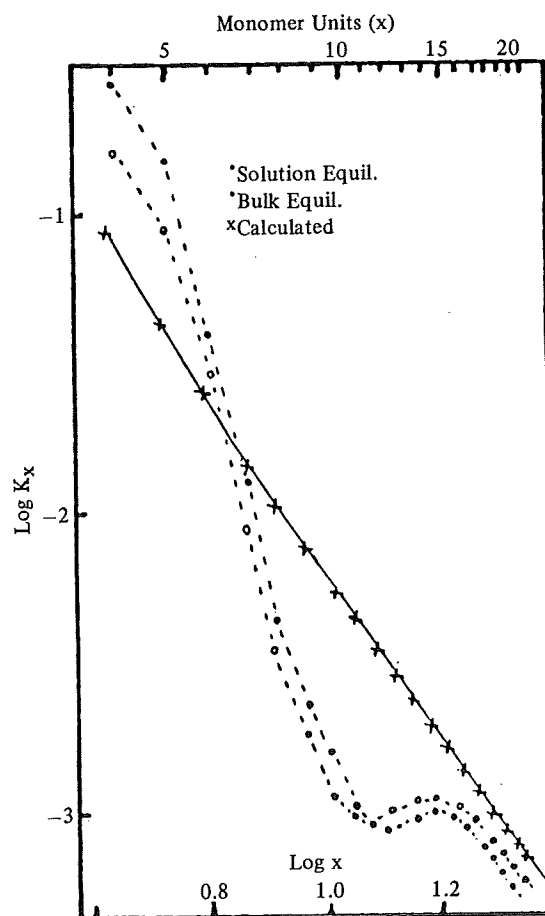


Figure 2. Molar Cyclization Equilibrium Constants of Dimethylsiloxane at 110°C (17).

These same authors (16) also compared experimental  $K_x$  values as a function of  $x$  for a series of bulk equilibrates of the structure  $\text{[R(CH}_3\text{)Si-O]}_x$  wherein R equalled H,  $\text{CH}_3$ ,  $\text{CH}_3\text{CH}_2$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2$ , and  $\text{CF}_3\text{CH}_2\text{CH}_2$  in order to assess the effect of the substituent size on the equilibrium distribution. The  $K_x$  values for the smallest unstrained rings ( $x = 4$  or  $5$ ) were found to increase along the series  $\text{R} = \text{H} < \text{CH}_3 < \text{CH}_3\text{CH}_2 < \text{CH}_3\text{CH}_2\text{CH}_2 < \text{CF}_3\text{CH}_2\text{CH}_2$ . By contrast, the corresponding values for the large cyclics decrease along the same series. The total weight fraction (experimental) of cyclics in these bulk equilibrates are listed in Table 1. The effect of dilution with cyclohexanone

**Table 1 (16)**  
**Cyclic Contents of Undiluted Polysiloxane Equilibrates**

Substituent Group R of Monomeric Unit ( $\text{R(CH}_3\text{)SiO}$ ) <sub>4</sub>	Temperature T(K)	Weight Percent Cyclics in High Molecular Weight Equilibrates ( $p = 1$ )			Total
		$x = 3-5$	$x = 6-18$	$x = 9-\infty^+$	
H	273	4.5	3.4	4.6	12.5
$\text{CH}_3$	383	10.0	3.6	4.7	18.3
$\text{CH}_3\text{CH}_2$	383	17.0	4.9	3.9	25.8
$\text{CH}_3\text{CH}_2\text{CH}_2$	383	27.0	*	—	—
$\text{CF}_3\text{CH}_2\text{CH}_2$	383	71.1	8.9	2.7	82.7

\* 31.0% for  $[\text{CH}_3\text{CH}_2\text{CH}_2(\text{CH}_3)\text{SiO}]_x$  with  $x = 3-8$ .

+ These values have been computed by extrapolation of experimental  $K_{18}$  values assuming that  $K_x$  is proportional to  $x^{-2.5}$ .

in the syntheses of these same polymers is illustrated in Figure 3. In all cases, a critical dilution point was reached as predicted but it was reached at a lower diluent volume than the theoretical value. Molar cyclization equilibrium constants for undiluted poly(methylphenyl)siloxane were later measured (19) and found to be similar to those previously obtained in the case of poly(ethylmethyl)siloxanes.

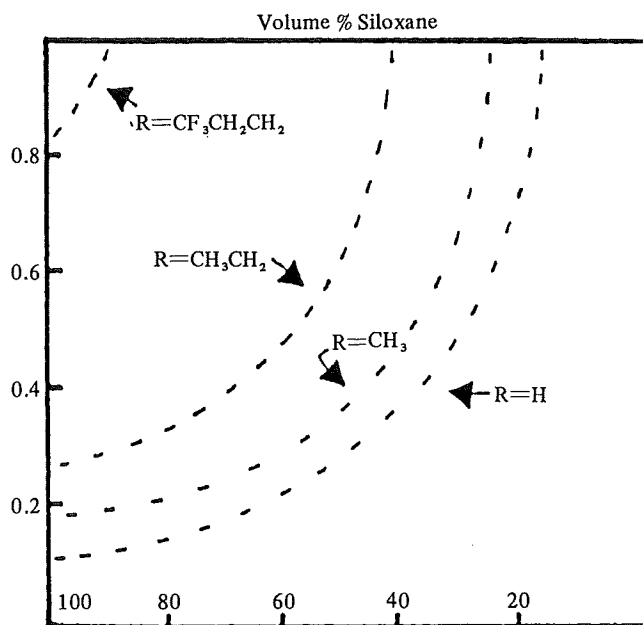


Figure 3: Weight Fractions of Cyclics  $[\text{R(CH}_3\text{)SiO}]_x$  in High Molecular Weight ( $p \approx 1$ ) Polysiloxane Equilibrates at 383K ( $\text{R} = \text{CH}_3, \text{CH}_3\text{CH}_2, \text{CF}_3\text{CH}_2\text{CH}_2$ ) and 273K ( $\text{R} = \text{H}$ ) as a Function of the Volume % Siloxane in Cyclohexanone ( $\text{R} = \text{CF}_3\text{CH}_2\text{CH}_2$ ) and Toluene ( $\text{R} = \text{H}, \text{CH}_3, \text{CH}_3\text{CH}_2$ ) (16).

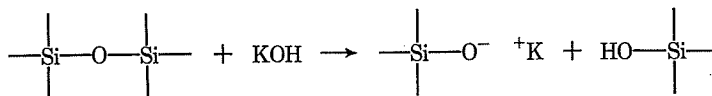
As predicted by theory, the position of the ring/chain equilibrium was found to be independent of the nature of the redistribution catalyst employed (acid or base) (4,13,24-25) and of the specific inert solvent used (26). Russian authors (4,27) equilibrated mixtures of cyclosiloxanes comprised of dimethylsiloxane (75 mole %) and either trifluoropropylmethyl, cyanoethylmethyl, or cyanopropylmethyl siloxane (25 mole %) in acetone at a siloxane repeating unit concentration of 0.833 moles/l. They measured the dipole moments of the respective cyclosiloxanes,  $[(\text{CH}_3)_2\text{SiO}]_3[\text{Si}(\text{CH}_3)\text{RO}]$ , to be 2.76 for  $\text{R} = \text{trifluoropropyl}$ , 3.45 for  $\text{R} = \text{cyanoethyl}$ , and 3.58 in the case of  $\text{R}$

= cyanopropyl. The equilibrium weight fraction of rings, 54.7%, 96.2%, and ~100% respectively, was found to increase with the dipole moment, and, hence, with the polarity of the substituent.

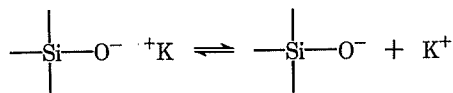
Carmichael et al. performed a series of bulk equilibrations of hexamethyldisiloxane and  $D_4$  using sulfuric acid activated fuller's earth as the catalyst (28-29). These workers varied the molar ratio of endblocker to  $D_4$  so as to obtain calculated molecular weights (on the basis of monomer ratio) of 459, 904, and 1348 g/mole. They found the total weight fractions of cyclics in these polymers to be 4.86%, 7.69%, and 8.92% respectively whereas they had obtained a corresponding value of 12.8% for analogous polymer with  $\langle M_n \rangle = 10^6$  (24). They explained this molecular weight dependence by variances in "p" according to Jacobson's and Stockmayer's equation for cyclization equilibrium constants,  $[C-M_x] = K_x p^x$ , by assuming the equilibrium distribution of linear x-mers to be random (i.e.  $[C_x] = A p^x$  wherein  $[C_x]$  = concentration of linear x-mer (moles/l), A = a normalization constant, and p = fraction of unreacted endgroups in the linear portion of the polymer). Carmichael et al. derived "p" for their polymers from the slopes of plots of  $\ln [C_x]$  vs. x. They used these values together with measured concentrations of cyclics as x was varied to calculate  $K_x$  values. In all cases their values of  $K_x$  derived as explained above agreed well with values of  $K_x$  calculated for a high molecular weight polymer.

The mechanism illustrated in equations 13-15 was proposed by Grubb and Osthoff (30) for the anionic ring opening polymerization. There is, however, considerable question as to whether the ion pair formed in equation 13 also participates as a propagating species (4).

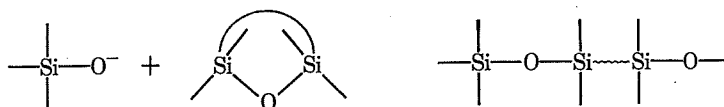
Equation 13



Equation 14



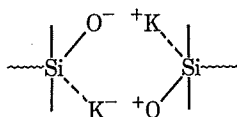
Equation 15



These anionic ring opening polymerizations are usually carried out either in bulk or in solution. A host of catalyst types are active. For synthetic references using specific catalysts, the reader is referred to several excellent sources (4,7,31-32). Representative catalysts include hydroxides, alcoholates, phenolates, silanolates, siloxanates, mercaptides of the alkali metals, organolithium and potassium compounds, and quaternary ammonium and phosphonium bases and their silanolates and siloxanates.

The activities of the often used hydroxides and siloxanates decreases in the order Cs > Rb > K > Na (33). At equal molar concentrations, the rates using the hydroxide or siloxanolate of the same metal have been found to be similar (30). Tetramethylammonium siloxanates reportedly exhibit activities close to the cesium siloxanates (33). Tetramethylammonium hydroxide, silanolate, and siloxanolate decompose above 130°C yielding methanol, methoxy trimethylsilane, or methoxysiloxane respectively and trimethylamine (34-35). In the cases of the first two compounds listed above, the catalyst breakdown products are fugitive at the decomposition temperature. Thus, the usual need for catalyst neutralization and removal following polymerization is eliminated.

At low catalyst concentrations, the degree of polymerization is approximately inversely related to the catalyst concentration (36). Russian authors (4) have noted a deviation in the linearity of the  $1/X_n$  vs. catalyst concentration function at high catalyst loadings. It was suggested that this deviation could be attributed to the presence of stable associated structures similar to **1** being formed.



Practically, polymerization temperatures are selected on the basis of the activities of the catalyst, cyclosiloxane, and endblocker used with the aim of arriving at thermodynamic equilibrium within an acceptable time period. In the bulk polymerization of  $D_4$ , temperature changes reportedly do not affect the final equilibrium number average molecular weight of the polymers (37).

Rates of anionic polymerization are influenced by the number of siloxane units present in the monomer rings. Due to ring strain in the three unit rings, all of the cyclotrisiloxanes polymerize faster than the cyclotetrasiloxanes. In the dimethylsiloxanes,  $D_3$  reportedly polymerizes approximately 50 times faster than  $D_4$  (4).

Several investigations have been performed concerning the relative reactivity of cyclic tetramers substituted with varying amounts of phenyl and methyl groups (38–42). Andrianov et al. (42) studied anionic copolymerizations of  $D_4$  with varying amounts of octaphenylcyclotetrasiloxane (10–70 mole percent). They found that the rate of copolymer formation, the viscosity of the resulting copolymers, and the equilibrium yield of linear species all decreased regularly as the mole percent of phenyl tetramer was increased in the reaction mixture. They also noted that in the early stages of conversion, although both monomers had become incorporated in the linear portion to some extent, the polymers formed were enriched with diphenyl units. On the basis of electronic factors, it was reasoned that in the diphenyl substituted tetramer, the silicon atoms would be more susceptible to nucleophilic attack. Conversely, the phenyl substituted siloxanolate anion, once formed, would be less reactive than the methyl substituted analog. These same authors (42) also studied the structure of the cyclics as equilibration proceeded. Redistribution type steps had evidently occurred even in the initial stages since mixed cyclics (diphenyl and dimethyl units in the same cyclic molecules) were observed soon after the beginning of the reaction.

In equilibration reactions, hexaorganyl disiloxane or low molecular weight siloxanes terminated with triorganylsiloxy groups in the reaction mixture can regulate molecular weight by acting as chain transfer agents or "end-blockers". The efficiency of these agents depends on the relative amount of positive charge on their silicon atoms. Results of viscosity measurements as a function of time using hexamethyldisiloxane endblocker,  $D_4$ , and tetramethylammonium hydroxide catalyst (13) are shown in Figure 4. The initial large viscosity increase was found to be a result of the faster reaction of  $D_4$  as compared to hexamethyldisiloxane under these conditions. Contrasted with the above results was the analogous reaction with the exception that a sulfuric acid catalyst instead of tetramethylammonium hydroxide (see Figure 5) was used (13). The shape of the curve in Figure 5 represents approximately equal reactivity of  $D_4$  and hexamethyldisiloxane towards an acid catalyst.

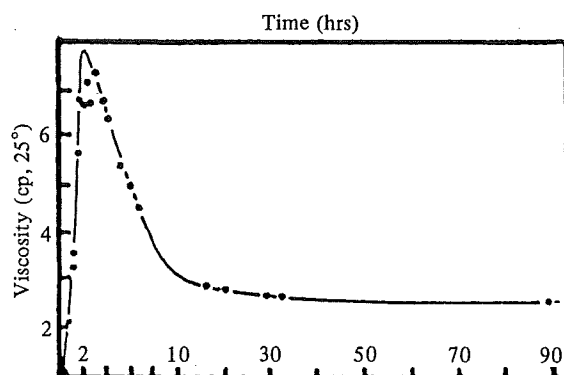


Figure 4: Viscosity vs. Time for Equilibration of One Mole of Hexamethyldisiloxane and One Mole  $D_4$  with 0.1%  $(CH_3)_4NOH$  at  $80^\circ C$  (13).

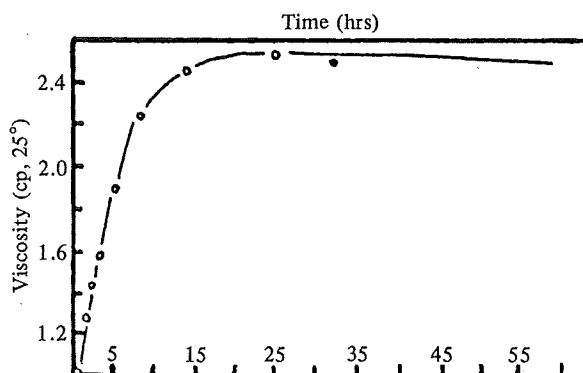


Figure 5: Viscosity vs. Time of Reaction for Equilibration of One Mole Hexamethyldisiloxane and One Mole of  $D_4$  with 4%  $H_2SO_4$  at Room Temperature (13).

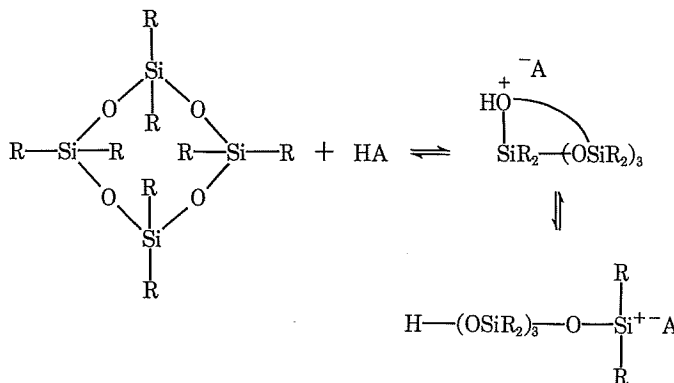
Many compounds with an electron donor character are reported to have an accelerating effect on the anionic polymerizations. Representative "promoters" reported included tetrahydrofuran(43-45), dimethylformamide (46), and sulfoxides (47-48).

Cationic polymerization of cyclosiloxanes is well known but used much less frequently than anionic reactions. The most frequently used catalysts include sulfuric acid and its derivatives (4,49-52). Trifluoroacetic acid has also been used to bulk polymerize  $D_4$  at reflux (53) temperature.

The mechanism of acid catalyzed polymerization is postulated to be that schematically illustrated in equations 16 and 17. According to Odian (54), there is no evidence for the rearrangement of the siliconium ion shown in these equations. It is possible that the tertiary oxonium ion is the propagating species.

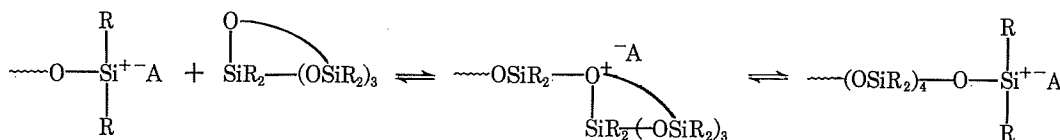
Equation 16 (54)

Initiation:



Equation 17 (54)

Propagation:



McGrath and coworkers (55-58) have recently been concerned with the polymerization of  $D_4$  and of combinations of  $D_4D''_4$  (octaphenylcyclotetrasiloxane) in the presence of organofunctional endblockers used as molecular weight regulators. They have been successful in obtaining aminopropyl, glycidoxypropyl, carboxypropyl, hydroxybutyl, and hydroxyphenylpropyl terminated siloxane oligomers of controlled molecular weights by these methods.

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