

# ON POLYMERIZATION OF ORGANOSILICON CYCLIC COMPOUNDS

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The chemistry of organosilicon cyclic compounds has been vigorously developed. The interest in this field of organosilicon chemistry is due to the exceptionally wide synthetic possibilities and investigations on the structure and properties of cyclic systems. The high reactivity of the cycle in various rearrangements and polymerizations offers unlimited possibilities of synthesizing and investigating the macromolecules of elemento-organic polymers (metalorganic polymers). The polymerization reaction of cyclic organosilicon compounds gains further theoretical and practical interest also for the reason that this is one of the most significant ways for synthesis of oligomers and high molecular compounds with inorganic and organo-inorganic chains in the molecule. It would be impossible for such a report to consider the widespread investigations made in this field of organosilicon chemistry, therefore, I will restrict myself to rearrangements and polymerization reactions exemplified by representatives of two classes of cyclic compounds: organocyclosiloxanes and organocyclosilazanes.

## POLYMERIZATION OF ORGANOCYCLOSILOXANES

A number of papers deal with studies on the polymerization of hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane (OMCTS) in the presence of anionic catalysts.<sup>1-3</sup> In the present report the polymerization of OMCTS with polyfunctional initiators, as well as the polymerization of mixed alkyl(aryl)cyclosiloxanes and polycyclic compounds are discussed.

The anionic polymerization reaction of OMCTS was carried out with mono-, di-, tri-, and tetrafunctional catalysts for polymerization of the general formula  $\text{NaO}[\text{Si}(\text{CH}_3)_2\text{O}]_n\text{Na}$ , where  $n = 2, 4, 8$ ,  $\text{RSi}[\text{OSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{ONa}]_3$ ,  $\text{Si}[\text{OSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{ONa}]_4$  and  $\text{NaOH}$ .

Kinetic studies of polymerization reactions have shown that in all cases the polymerization proceeds as a first order reaction as to the monomer, no matter what the functionality of the initiator taken. This points to the fact that the reaction takes place at every active centre of a polyfunctional initiator independently of other centres. When the polymerization kinetics of OMCTS were studied over the temperature range of 130–160° in the presence of a difunctional initiator with various lengths of disodium salts of the general formula  $\text{NaO}[\text{Si}(\text{CH}_3)_2\text{O}]_n\text{Na}$ , (where  $n = 2, 4, 8$ ), it was found that the rate constants for polymerization are practically the same, which also provides evidence of an independent polymerization at every  $\text{SiONa}$  endgroup present. *Figure 1* shows a plot of  $\text{Lg}K = 1/T$  used in cal-

culating the activation energy values for polymerization of OMCTS in the presence of a difunctional initiator. In all cases the  $E_{act}$ . value was 25.5 kcal/mole.

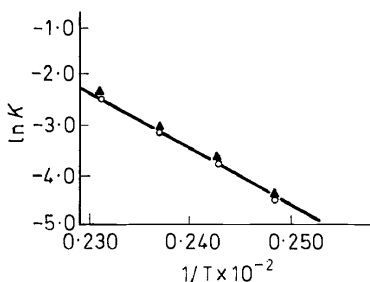
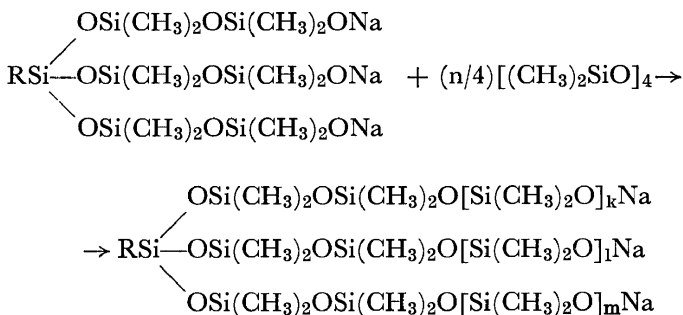


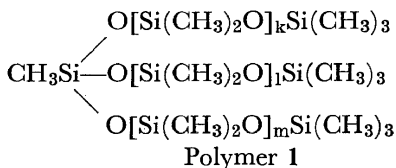
Figure 1. Polymerization of octamethylcyclotetrasiloxane in the presence of  $\text{NaO}[\text{Si}(\text{CH}_3)_2\text{O}]_n\text{Na}$   
 ▲  $n = 2$       ○  $n = 4$

It might be expected that the polymerization of OMCTS in the presence of trifunctional initiators  $\text{RSi}[\text{OSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{ONa}]_3$  would proceed as follows:



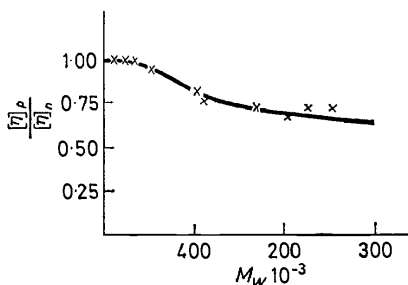
It is obvious from the reaction scheme that the initiator molecule has several active SiONa centres, each of which initiates the growth of a polymeric chain. The polymerization proceeds as a stepwise addition of OMCTS molecules to every SiONa endgroup of the polymeric chains, each of which grows independently. The macromolecules grow in three directions (corresponding to the number of active centres in the initiator molecule). The macromolecules formed in polymerization must have one branching centre.

The branched polydimethylsiloxanes with trifunctional (polymer 1) and tetrafunctional (polymer 2) branching centres were synthesized to study the structure of polymers obtained. It may schematically be illustrated as follows:



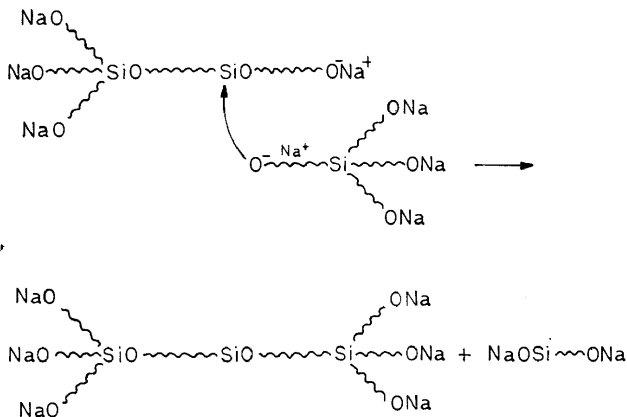


branching centres also indicate that the extent of branching of certain fractions gradually increases with increasing molecular weight and dimensions of macromolecules. The results of calculating the extent of branching of fractions are given in *Figure 3*.



*Figure 3.* Dependence of the branching extent of polymer 2 on molecular weight.

A gradual increase in the extent of branching of macromolecules with their molecular weight is attributable to the occurrence of interchain reactions (chain transfer reactions). Here is the scheme:



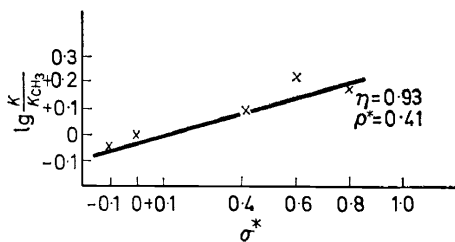
The chain transfer reaction is also corroborated by the formation of an insoluble polymer at high conversions, when OMCTS polymerized in the presence of polyfunctional initiators.

Investigations on polymerization of mixed methyl(aryl)cyclosiloxanes with nucleophilic catalysts has shown that the organic groups framing the cycle affect the polymerization rate. This is associated with the inductive effect of the framing group at the silicon. Electron-donating substituents incorporated slow down the polymerization process, and electron-accepting ones accelerate it (see *Table 1*, *Figure 4*). The relationship between the rate constant of cycle polymerization and the inductive effect of substituents at the silicon is described by the Hammet-Taft equation:  $\lg(k_1/k_0) = \sigma^* \rho^*$ ;  $\rho^*$  (for KOH at 120°) is 0.41. This points to the sensitivity of cycle polymerization to donating and accepting substituents at the silicon atom.

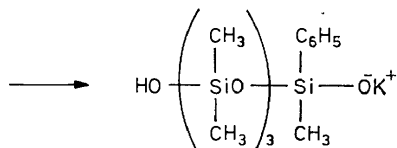
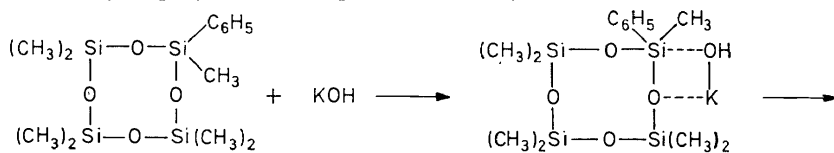
## ON POLYMERIZATION OF ORGANOSILICON CYCLIC COMPOUNDS

 Table 1. Effect of Substituents on Constant  $K$ .

No.	Compound	$K, 10^3$ [min <sup>-1</sup> ]	$\frac{K}{K_{(CH_3)}}$	$\lg \frac{K}{K_{(CH_3)}}$	$\sigma^*$	E kcal. mole
1	$[(CH_3)_2SiO]_4$	4.85	1	0	0	19.6
2	$[(CH_3)_2SiO]_3SiO$   CH <sub>3</sub> C <sub>2</sub> H <sub>5</sub>	4.09	0.89	-0.0491	-0.1	—
3	$[(CH_3)_2SiO]_3SiO$   CH <sub>3</sub> CH=CH <sub>2</sub>	5.55	1.24	0.094	0.4	—
4	$[(CH_3)_2SiO]_3SiO$   CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Cl	6.97	1.52	0.1822	0.8	18.91
5	$[(CH_3)_2SiO]_3SiO$   CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	7.79	1.70	0.9304	0.6	17.85


 Figure 4.  $\lg K$  dependence on the polar constant  $\sigma^*$ .

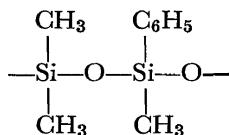
It was found in the polymerization of mixed methyl(aryl)-cyclosiloxanes that the cycle polymerization process not only follows the scheme:



but is also accompanied by a reaction leading to branching of the polymer molecule. The chain transfer reaction with cleavage ascertained for OMCTS

polymerization with polyfunctional initiators could not result in polymer branching; in this case it is consequently connected with a chain transfer reaction of the growing macromolecule differing from the above mentioned.

To clear up the reasons for the occurrence of chain transfer reactions in polymerization of mixed methyl(phenyl)cyclosiloxanes of the  $[(\text{CH}_3)_2\text{SiO}]_n[\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{O}]_{4-n}$  type, an anionic polymerization of cycles (n = 1,2,3) was studied with various catalysts such as  $\text{HO}[\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{O}]_n\text{M}$ , where M = Na, K, Cs,  $\text{N}(\text{CH}_3)_4$ . In all cases at high degrees of cycle polymerization crosslinking of the polymer takes place (see Table 2). A proposal was made that the chain transfer reaction of the growing molecule onto the other is associated with splitting off the phenyl group at the silicon atom. This chain transfer reaction may be caused by the appearance of

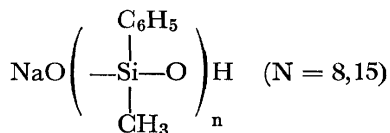


groups in the polymer chain. In such a group a nucleophilic attack on the silicon and a chain transfer with splitting off the phenyl group can take place.

Table 2. Effect of nature of catalyst on polymerisation.

No.	Monomer	Catalyst, 0.03%	T, °C	Reaction time, min.	Mol. wt. of polymer
1	$[\text{Si}(\text{CH}_3)_2\text{O}]_3-\text{SiO}$ $\begin{array}{c} \text{CH}_3 \quad \text{C}_6\text{H}_5 \\   \quad   \\ \text{---} \end{array}$	$(\text{CH}_3)_4\text{NO}$ $\begin{array}{c} \text{CH}_3 \\   \\ \text{---SiO---} \\   \\ \text{C}_6\text{H}_5 \end{array}_2 \text{N}(\text{CH}_3)_4$	80	7	insoluble
2	$[\text{Si}(\text{CH}_3)_2\text{O}]_3-\text{SiO}$ $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{---} \end{array}$	$(\text{CH}_3)_4\text{NO}$ $\begin{array}{c} \text{CH}_3 \\   \\ \text{---SiO---} \\   \\ \text{C}_6\text{H}_5 \end{array}_2 \text{N}(\text{CH}_3)_4$	80	10	insoluble
3	$[\text{Si}(\text{CH}_3)_2\text{O}]_4$	$\text{HO}[\text{Si}(\text{CH}_3)\text{C}_6\text{H}_5\text{O}]_{26}\text{Cs}$	140	at once	insoluble
4	$[\text{Si}(\text{CH}_3)_2\text{O}]_4$	$\text{HO}[\text{Si}(\text{CH}_3)\text{C}_6\text{H}_5\text{O}]_{26}\text{K}$	140	7	insoluble
5	$[\text{Si}(\text{CH}_3)_2\text{O}]_4$	$\text{HO}[\text{Si}(\text{CH}_3)\text{C}_6\text{H}_5\text{O}]_{26}\text{N}(\text{CH}_3)_4$	140	10	insoluble
6	$[\text{Si}(\text{CH}_3)_2\text{O}]_4$	$\text{HO}[\text{Si}(\text{CH}_3)\text{C}_6\text{H}_5\text{O}]_{26}\text{Na}$	140	120	insoluble

To verify this suggestion, OMCTS was polymerized in the presence of

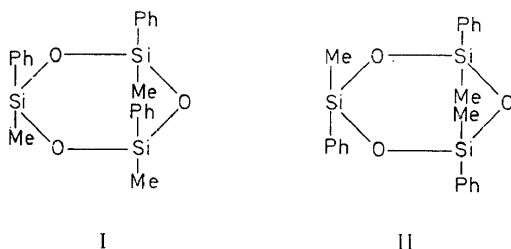




phenylcyclotrisiloxanes were polymerized in the presence of spatially hindered initiators such as  $\alpha,\omega$ -tetramethylammoniumtetramethyldisiloxane  $(\text{CH}_3)_4\text{NO}-[\text{Si}(\text{CH}_3)_2-\text{O}]_2\text{N}(\text{CH}_3)_4$ ,  $\alpha$ -hydroxy- $\omega$ -tetramethylammoniummethylphenylpolysiloxane  $\text{HO}[\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{O}]_8\text{N}(\text{CH}_3)_4$ , and  $\text{KO}(\text{SiCH}_3\text{C}_6\text{H}_5\text{O})_{26}\text{H}$ , it was found that the polymerization of the tetramethyltetraphenylcyclotetrasiloxane with the tetramethylammoniumtetramethyldisiloxane proceeds slowly and reaches an equilibrium state, when the polymer is not yet high-viscous. The polymerization of the mixture of trimethyltriphenylcyclotrisiloxane isomers also proceeds slowly.

Differences in polymerization rates for six- and eight-membered cycles during methylphenyl framing probably arise not only from the strain of these cycles, that being concerned with conformation effects of the framing groups, but also from the steric effect of these groups.

To confirm this consideration, we isolated stereoisomeric forms of the trimethyltriphenylcyclotrisiloxane and studied their polymerization. It has two stereoisomers: *cis*-isomer, m.p.  $99.5^\circ$  (I) and *trans*-isomer, m.p.  $39-40^\circ$  (II).



The two isomers were found to have completely different activity during polymerization. The reaction rate of the *cis*-isomer is higher, and the resulting molecular weight of the polymer is several times as great as that of the *trans*-isomer (see Table 3).

The polymerization of the trimethyltriphenylcyclotrisiloxane *cis*-isomer gives high molecular polymers with intrinsic viscosity of 0.7–0.9, and that of the *trans*-isomers and isomer mixture leads to polymers of low viscosity.

Table 3. Effect of structure on  $[\eta]$

No.	Monomer	Catalyst	$[\eta]$
1	<i>Cis</i> -trimethyltriphenylcyclotrisiloxane	$\text{KO}(\text{SiCH}_3\text{C}_6\text{H}_5\text{O})_{26}\text{H}$	0.73–0.99
2	<i>Trans</i> -trimethyltriphenylcyclotrisiloxane	$\text{KO}(\text{SiCH}_3\text{C}_6\text{H}_5\text{O})_{26}\text{H}$	0.10
3	tetramethyltetraphenylcyclotetrasiloxane	$\text{KO}(\text{SiCH}_3\text{C}_6\text{H}_5\text{O})_{26}\text{H}$	0.12

Similar results were obtained by using other initiators for trimethyltriphenylcyclotrisiloxane polymerization (Table 4).

Of interest were the results obtained by the birefracton method in that the

optical anisotropy of the polymer formed from the *cis*-trimethyltriphenylcyclotrisiloxane considerably differs from that of the *trans*-isomer and the mixed tetramethyltetraphenylcyclotetrasiloxane isomers<sup>4</sup>. The average difference in polarizability of a methylphenylsiloxane chain unit is determined by the part of the side group anisotropy alone, that of the Si—O—Si group being small and the C<sub>6</sub>H<sub>5</sub> group responsible for a negative value.

Table 4. Cyclosiloxane polymerization in the presence of 0.03% of catalyst HO—[Si(C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)O]<sub>n</sub>N(CH<sub>3</sub>)<sub>4</sub> at 80°C

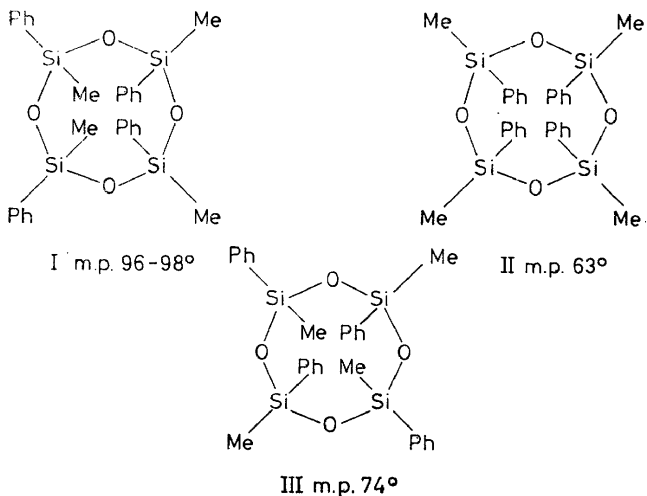
No.	Monomer	<i>n</i> of catalyst	Polymerization time, min	Polymer yield, %	Mol. wt.
1	Trimethyltriphenylcyclotrisiloxane, isomer mixture	15	20	26	62000
2	Trimethyltriphenylcyclotrisiloxane, <i>trans</i> -isomer	8	20	29	49000
3	Trimethyltriphenylcyclotrisiloxane, <i>trans</i> -isomer	11	20	36.8	41980
4	Trimethyltriphenylcyclotrisiloxane, <i>trans</i> -isomer	15	30	31.9	38900
5	Trimethyltriphenylcyclotrisiloxane, <i>cis</i> -isomer	8	20	80	291700
6	Trimethyltriphenylcyclotrisiloxane, <i>cis</i> -isomer	11	20	75.5	185800
7	Trimethyltriphenylcyclotrisiloxane, <i>cis</i> -isomer	15	30	78.5	269200

The negative anisotropy  $\Delta a$  is  $(\alpha_1 - \alpha_2) \cdot 10^{25} = -52$  for the 100 per cent *trans*-polymethylphenylsiloxane in decaline and tetraline, and  $-80.84$  for the *cis*-polymer.

The  $(\alpha_1 - \alpha_2)$  value depends on the stiffness of the backbone and the optical anisotropy of the monomeric units  $(\alpha_1 - \alpha_2) = S\Delta a$ , where  $S$  is the stiffness, and  $\Delta a$  is the monomer property.

Independent  $S$  values were not determined, therefore it would be impossible to explain differing data either by the  $S$  change only or by that of  $\Delta a$  only. But one may very well suggest that changing  $\Delta a$  rather than the chain stiffness  $S$  is of crucial importance, since it is known that the latter would be very slightly affected by the chain stereoregularity as well as by substituting a part of methyl radicals by phenyl ones. The anisotropy of a *cis*-polymer is 1.5 times as large as that of a *trans*-polymer. Thus, it may be concluded that the *cis*-trimethylphenylcyclotrisiloxane polymerization would not give rise to the configuration conversion of the cycle, and the resulting polymer would have a pronounced stereoregularity.

Studies on ionic polymerization of three stereoisomers of the tetramethyltetraphenylcyclotetrasiloxanes in the presence of 0.03 per cent of HO(SiCH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O)<sub>3</sub>K assuring a homogeneous catalysis at 140° reveal a great difference in their reactivities. 2,4,6',8'-tetramethyl-2',4',6,8-tetraphenylcyclotetrasiloxane (I) and 2,4,6,8-tetramethyl-2',4',6',8'-tetraphenylcyclotetrasiloxane(II) were the most active in this reaction under conditions mentioned above (see Table 5, Figure 5).



Under these conditions isomer I converted into the polymer with  $\eta_{sp.} = 0.24$  (Figure 5, curve I) and the molecular weight of 164000.

After 30 minutes polymerization isomer II had  $\eta_{sp.} = 0.21$  (Figure 5, curve 2).

Table 5. Cyclotetrasiloxane polymerization in the presence of catalyst  $\text{HO}(\text{CH}_3\text{C}_6\text{H}_5\text{SiO})_8\text{K}$

No.	Monomer	Polymerization time, min.	Mol. wt.
1	Tetramethyltetraphenylcyclotetrasiloxane*	30	69180
2	2,4,6',8'-tetramethyl-2',4',6,8-tetra-phenylcyclotetrasiloxane	40	164000
3	2,4,6,8-tetramethyl-2',4',6',8'-tetra-phenylcyclotetrasiloxane	30	—
4	2',4,6',8-tetramethyl-2,4',6,8'-tetra-phenylcyclotetrasiloxane	50	31120

\* The polymerization was carried out in the presence of  $\text{HO}(\text{SiCH}_3\text{C}_6\text{H}_5\text{O})_8\text{N}(\text{CH}_3)_4$

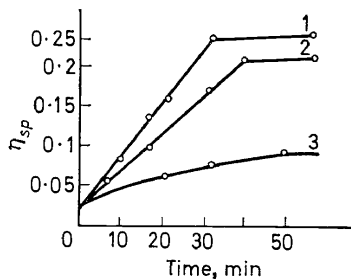


Figure 5. Polymerization of isomers of the tetramethyltetraphenyl-cyclotetrasiloxane:

1. polymer I
2. polymer II
3. polymer III



Table 6. Fractional precipitation of polymethylphenylsiloxane formed from a mixture of tetramethyltetraphenylcyclotetrasiloxane isomers.

No. of fraction	Fraction yield %	$\eta_{sp}$	$[\eta]$ of reprecipitated polymer	Mol. weight (in methylethylketon)
I	2.0	0.48	0.49	529900
II	3.9	0.23	0.23	175400
III	40.0	0.09	0.11	53830
IV	44.3	0.046	0.051	14660

From the above data it is obvious that the polymerization of an isomer mixture yields chiefly polymers of low molecular weight. We succeeded in isolating only 6 per cent of a high molecular fraction of the polymer, the rest (85 per cent) being low molecular.

Table 7 and Figure 7 illustrate the effect of *cis*-to-*trans*-isomer ratio of the triphenylmethylcyclotrisiloxane on the average molecular weight value of the polymer.

Table 7. Co-polymerization of *cis*- and *trans*-trimethyltriphenylcyclotrisiloxanes

Catalyst	Isomer ratio		$\eta_{sp}$ , before precipitation	$\eta_{sp}$ , after precipitation	Mol weight after precipitation
	<i>cis</i>	<i>trans</i>			
HO $\left( \begin{array}{c} \text{CH}_3 \\   \\ \text{—SiO—} \\   \\ \text{C}_6\text{H}_5 \end{array} \right)_{26}$ Na	1	0	0.57	0.73	1148000
	1	0.05	0.51	0.63	976800
	1	0.5	0.12	0.14	95380
	1	1	0.08	0.12	61940
HO $\left( \begin{array}{c} \text{CH}_3 \\   \\ \text{—SiO—} \\   \\ \text{C}_6\text{H}_5 \end{array} \right)_{26}$ N(CH <sub>3</sub> ) <sub>4</sub>	1	0	0.12	0.3	262400
	1	0.5	0.08	0.13	70310
	1	1	0.08	0.11	53830

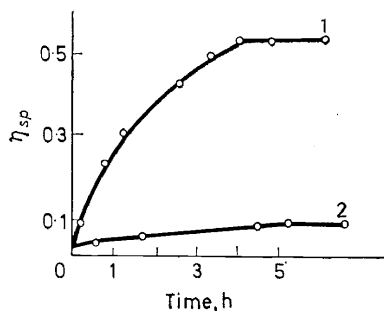


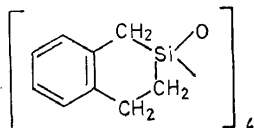
Figure 7. Polymerization of isomers of the trimethyltriphenylcyclotrisiloxane:

1. *cis*-isomer
2. *trans*-isomer

## ON POLYMERIZATION OF ORGANOSILICON CYCLIC COMPOUNDS

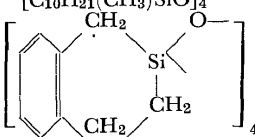
To provide support for the effect of sterically hindered framing groups on the anionic polymerization of organocyclosiloxanes, cyclic compounds of the general formula  $(R,R'SiO)_n$  (where  $n = 3, 4$ ;  $R = CH_3$ ;  $R' = C_6H_{13}, C_8H_{17}, C_9H_{19}, C_{10}H_{21}$ ) were synthesized by using sterically hindered radicals with a flexible chain.

In the presence of KOH at various temperatures up to  $280^\circ$  polymerization experiments with these cyclic compounds did not lead to polymer formation (see Table 8). Six- and eight-membered cyclic compounds used in the polymerization did not markedly change on heating. The following eight-membered cycle also did not polymerize at  $200^\circ$  with 0.15 — 1 per cent of KOH.



The above factors reveal a very large effect of the groups framing the silicon atom, so that the anionic polymerization does not take place in the case of sterically hindered groups.

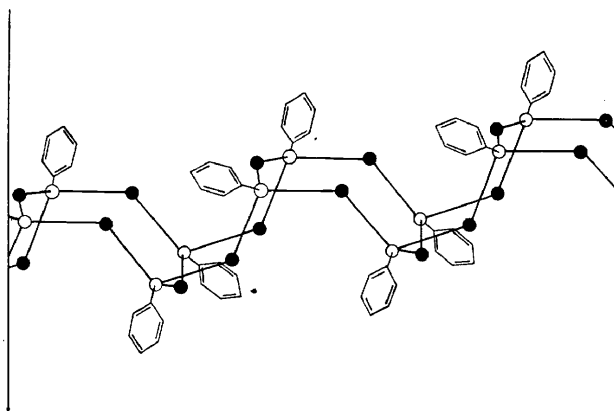
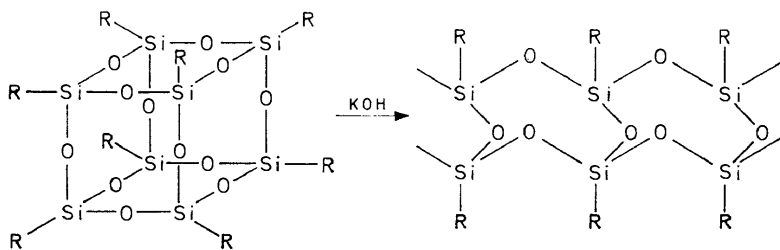
Table 8. Polymerization of higher alkyl(methyl)-cyclosiloxanes.

Compound	Reaction temperature $^\circ C$	KOH catalyst %	Reaction product
$[C_6H_{13}(CH_3)SiO]_4$	250–280	0.5–1	no polymerization
$[C_8H_{17}(CH_3)SiO]_4$	250–280	0.5–1	no polymerization
$[C_9H_{19}(CH_3)SiO]_4$	250–280	0.5–1	no polymerization
$[C_{10}H_{21}(CH_3)SiO]_4$	250–280	0.5–1	no polymerization
	250–280	0.5–1	no polymerization

## POLYMERIZATION OF POLYCYCLIC COMPOUNDS, ORGANOCYCLOSILSESQUIOXANES

The product of hydrolysis of the phenyltrichlorosilane was polymerized in the presence of alkali to form a high molecular polyphenylsilsesquioxane<sup>5</sup> with a ladder structure of the molecule. Later a mixed polyphenylhexylsilsesquioxane was obtained<sup>6</sup>. Polymerization of the octaphenylcyclosilsesquioxane  $(C_6H_5SiO_{1.5})_8$  [extracted in Soxhlet with methylene chloride from the hydrolytic product of phenyltrichlorosilane insoluble in benzene and identified from analysis data and by thin layer chromatography from  $Al_2O_3$  (with iodine developer)] showed that the former yields polyphenylsilsesquioxane of high molecular weight<sup>7</sup>. Birefracton investigations in the diffusion or sedimentation stream of the polyphenylsilsesquioxane fractions of molecular weight 20000 to  $2.5 \times 10^6$  give evidence of a large value in the equation  $[\eta] = K \cdot M^a$  ( $a = 0.88$ ), due to the high chain stiffness of

the molecules. The difference in polarizability of a monomeric unit of the polymer proved to be twice as great as the anisotropy of the monomeric unit of linear polyphenylsiloxane corresponding to the two-chain structure of the ladder polymer in the reaction scheme given below (see also *Figure 8*).



*Figure 8.* Chain structure of the polyphenylsilsesquioxane.

A great difference in alkylcyclosilsesquioxane activities during anionic polymerization (1 per cent of KOH in ditolylmethane at 250°) was observed in polymerization of alkylcyclosilsesquioxanes of the general formula  $(R\text{SiO}_{1.5})_8$ , where  $R = \text{C}_4\text{H}_9$ ,  $\text{C}_6\text{H}_{13}$ ,  $\text{C}_9\text{H}_{19}$  and others.

Alkylcyclosilsesquioxanes with  $R = \text{C}_4\text{H}_9$  and  $\text{C}_6\text{H}_5$  polymerize to form polymers with a ladder structure of the molecule, while those with  $R = \text{C}_6\text{H}_{13}$  and *cis*- $\text{C}_9\text{H}_{19}$  do not polymerize under the given conditions.

*Table 9.* Polymerization of higher alkylcyclosilsesquioxanes.

<i>Compound</i>	<i>Polymerization temperature, °C</i>	<i>KOH catalyst %</i>	<i>Reaction products</i>
$(\text{C}_6\text{H}_{13}\text{SiO}_{1.5})_8$	250	0.5-1	no polymerization
$(\text{C}_7\text{H}_{15}\text{SiO}_{1.5})_6$	250	0.5-1	no polymerization
$(\text{C}_8\text{H}_{17}\text{SiO}_{1.5})_6$	250	0.5-1	no polymerization
$(\text{C}_9\text{H}_{19}\text{SiO}_{1.5})_6$	250	0.5-1	no polymerization
$(\text{C}_6\text{H}_5\text{SiO}_{1.5})_8$	250	0.5	polymer with intrinsic viscosity of 1.0

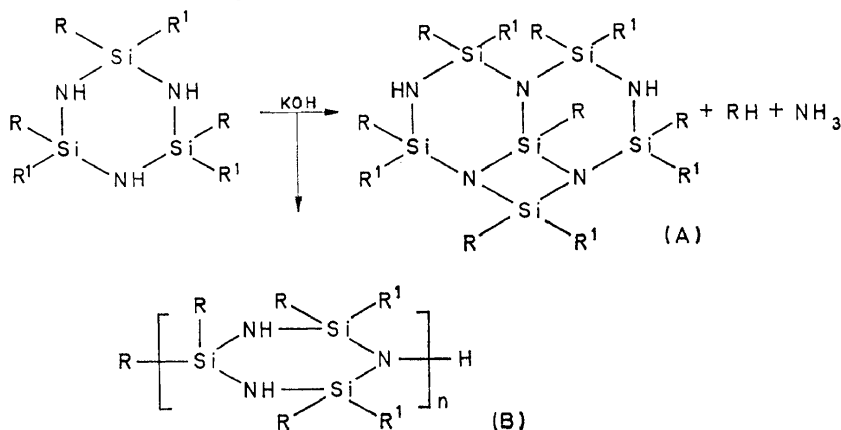
Such a difference in anionic polymerization can probably be explained only by steric hindrances. It is of interest that there is a certain relationship

between the magnitude of the organic radical at the silicon atom and the alkylcyclosilsesquioxane polymerization. The alkylcyclosilsesquioxanes and their activities in anionic polymerization are summarized in *Table 9*.

### POLYMERIZATION OF ORGANOCYCLOSILAZANES

Organocyclosilazane reactions with nucleophilic compounds are exemplified by dimethylcyclosilazanes<sup>8</sup> and methylphenylcyclosilazanes<sup>9</sup>. It is accompanied by the formation of methane or benzene depending on the initial cycle and of high melting polymers with a cyclic structure. Consistent patterns of these reactions were studied on a dialkylcyclosilazane series of the general formula  $(R'R''SiNH)_n$ , (where  $n = 3, 4$ ;  $R = CH_3, C_2H_5$ ;  $R' = C_2H_5, C_4H_9, C_6H_{13}, C_9H_{19}$ ), in order to follow the effect of the magnitude of the organic radical on the reactivity of these compounds and the properties of the products obtained.

The study showed that methylethyl-, methylbutyl-, methylhexyl-, and diethylcyclosilazanes react with KOH or  $C_2H_5ONa$  at a relatively high temperature. With dimethylcyclosilazanes, methane and ammonia evolution begins at about  $100^\circ C$ , while the other compounds mentioned evolve the same products at  $250^\circ C$  and higher, the reaction subsiding after 10–15 hours. Raising the temperature to  $300^\circ C$  and more does not result in any appreciable evolution of gaseous products. Compounds of the formula  $R_6R'_5Si_6N_3(NH)_2$  were isolated from the reaction mixture ( $R = CH_3, C_6H_5$ ;  $R' = C_6H_5, C_4H_9, C_6H_{13}$ ); product properties are listed in *Table 10*, the reaction scheme being as follows:



*Table 10.* Properties of organocyclosilazanes.

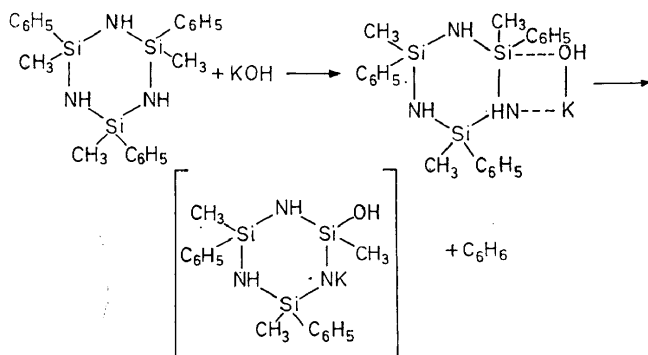
Compound	b.p. °C/min	m.p. °C	$\eta_D^{20}$	$d_4^{20}$	MR		Yield %
					calcul.	found	
$(C_2H_5)_6(CH_3)_5Si_6N_3(NH)_2$	150–152/1	—	1.4869	1.0044	140.67	140.27	52.5
$(C_4H_9)_6(CH_3)_5Si_6N_3(NH)_2$	219–224/1	—	1.4786	0.9586	194.23	194.57	46
$(C_6H_{13})_6(CH_3)_5Si_6N_3(NH)_2$	249–254/1	—	1.4790	0.9441	249.79	248.26	47.5
$(C_6H_5)_6(C_2H_5)_5Si_6N_3(NH)_2$	191–191.5/1	41.5– 42.5	—	—	—	—	28

Apparently, in this case, as with dimethyl cycles<sup>8</sup>, a transition complex with the alkali is formed, which dissociates into a hydrocarbon and a negative ion. This ion then attacks the neutral molecule of the cycle rupturing the Si—N bond with subsequent cyclization into product A. As a result, a molecule of ammonia is evolved and a molecule of alkali regenerated. The total quantity of ammonia collected corresponds to that which would be expected in this reaction (*Table 11*); the quantity of methane formed, however, considerably exceeds that calculated from this equation. Therefore, it may be suggested that the polymerization takes place breaking the cycle simultaneously with the formation of higher molecular oligomers (product B). The chemical inertness of the pure product A when treated with catalytic quantities of alkali shows that oligomers are not formed via this product, but according to the mechanism suggested earlier.<sup>8,9</sup>

*Table 11.* Polymerisation of alkylcyclotrisilazanes.

Starting substance	Hydrocarbon quantity evolved in $M_{RH}/M_{\text{start.cycle}}$	Ammonia quantity evolved in $M_{NH_3}/M_{\text{start.cycle}}$	Ammonia quantity evolved in $M_{NH_3}/M_{\text{product A}}$
$(CH_3C_2H_5SiNH)_3$	0.79	0.36	0.96
$(CH_3C_4H_9SiNH)_3$	0.69	0.22	0.97
$(CH_3C_6H_{13}SiNH)_3$	0.52	0.30	1.1
$[(C_2H_5)_2SiNH]_3$	0.53	0.17	1.1

Investigations of anionic polymerization of dimethyl- and phenylmethylcyclosilazanes established a mechanism for the conversion of organocyclosilazanes into polymers in the reaction with nucleophilic reagents other than in organocyclosiloxanes. The polymer formation in the reaction of catalytic quantities of alkali with cyclosilazanes was found to proceed without breaking the cycle. A hydroxyl coordination with the silicon atom is likely according to the scheme:



Due to a new distribution of electron density, one of the silicon bonds of the transition complex weakens, namely the Si—N bond, rather than the Si—C bond, as a result of which the benzene splits off and an anion forms.

## ON POLYMERIZATION OF ORGANOSILICON CYCLIC COMPOUNDS

The next stage is a coordination of cyclosilazane ions with the cyclosilazane.

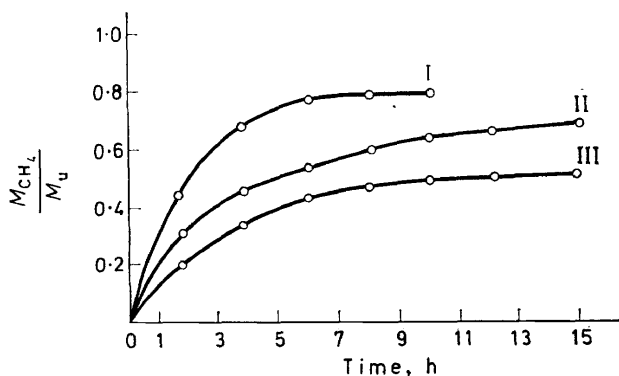
The polymers obtained from trimethyl(phenyl)cyclotrisilazanes have a thread-shaped or branched structure of the molecule. At the beginning of the reaction, that is with a low degree of polymerization, their composition corresponds to the polymer chain unit given in the reaction scheme. Further polymerization raises the glass transition point of the polymer, the structure of which is related directly to the quantity of benzene formed (see *Table 12*).

*Table 12.* Polymerization of trimethyltriphenylcyclotrisilazanes

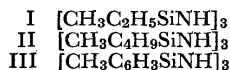
Reaction temperature, °C	Reaction time Hr.	Glass transition point, °C	Benzene quantity formed, moles per mole of initial cycle
2000	2.5	137	1.01
280	0.3	86	0.82
280	2.5	182-185	1.28
280	5.0	285	1.46
400	14.0	400	1.86

With eight-membered cycles the reaction is complicated by the rearrangement of this cycle to six-membered. Thus, 19 per cent of trimethyltriethylcyclotrisilazane, 53 per cent of hexaethylpentamethyltricyclohexasilazane, and 26 per cent of oligomers were formed in the reaction products of tetramethyltetraethylcyclotetrasilazane with KOH.

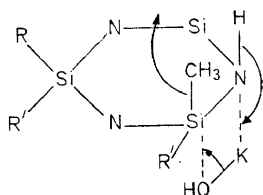
The rate of methane evolution diminishes on passing from methyl-ethyl cycles to methylhexyl cycles at 250°C (see *Figure 9*), and this is probably caused by a steric effect. With trimethyltrinonylcyclotrisilazane the reaction does not take place even at temperatures above 300°C. With hexaethylcyclotrisilazane evolution of the gaseous product starts at an appreciable rate at approximately 300°C. The low reactivity of the compounds investigated compared with dimethylcyclosilazanes can hardly be attributable to



*Figure 9.* Methane evolved in moles per mole of the starting cycle.



spatial screening of the Si—N bond by aliphatic radicals. It is possible that in this case an important role is played by the existence of dialkylcyclosilazanes in different geometrical conformations and their mutual conversion to each other. The structure of the transition complex is also associated with a definite (e.g. flat) conformation of the cyclic part of the molecule, in which the synchronous electron transition leading to breaking certain bonds and to formation of new links is most probable:



The lengthening of the organic radical at the silicon atom will stabilize the conformation of the starting cyclosilazane thus hindering its transition into an activated state. It is this, apparently, that results in such a sharp decline of chemical reactivity, when the methyl group of the hexamethylcyclosilazane is substituted by ethyl, butyl or other groups.

The high reaction temperature of diethyl cycles is also accounted for by increasing the rupture energy of the Si—C bond due to the electron-donating properties of the ethyl group compared to the methyl one.

The infrared spectra of the polymerization products given in *Table 10* were taken to confirm their structure. An absorption band at  $900\text{ cm}^{-1}$  was found, which was absent in the starting cycles and this is probably explained by the Si—N stretching of the four-membered cycle. The intensity of the  $3400\text{ cm}^{-1}$  band characteristic of the N—H stretching is considerably reduced, as should be expected from the resulting structures.

The influence of framing groups at silicon is also associated with the steric effect of the reaction. Voluminous groups such as hexyl, octyl, and nonyl hinder the polymerization process. The data on organocyclosilazane polymerization show that they, unlike organocyclosiloxanes, are more prone to substitution reactions than to addition processes, that is, they display certain properties similar to those of organic aromatic compounds. However, the aromaticity of these compounds bears little resemblance to that of organic systems, and the term itself seems to be conditional. Electron distribution in these molecules includes separate allyl areas, which begin and end on silicon atoms. In these cycles, as in phosphornitrile and borazole rings the delocalization energy in per electron terms increases smoothly with the increasing dimensions of the cycle. This stabilizes the bond and results in a change of the stretching frequencies in the infrared spectra. In the organocyclosilazanes, the Si—N bond stretching frequencies are also shifted by  $10\text{--}15\text{ cm}^{-1}$  towards higher frequencies on passing from six-membered to eight-membered cycles. In the octamethylcyclotetrasilazane the N—H absorption band is shifted towards lower frequencies compared with the hexamethylcyclotrisilazane. In alkylsilsesquiazanes, where the frequency of the Si—N bond stretching is  $960\text{ cm}^{-1}$ , the frequency shift is still greater.

The regular variation in spectra on passing from six-membered to eight-membered cycles and to silsesquiazanes is due to changes in the electron structure of the molecules and agrees with the basic principles of the structure of heteromorphic aromatic systems. Aromatic properties of the organocyclosilazanes are also consistent with their hydrolytic stability, which increases on passing from six- to eight-membered cycles and to silsesquiazanes.

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