

POLYMERIZATION OF CYCLOSILOXANES  
 MECHANISM OF CROSS-LINKAGE IN THE BASE-CATALYZED POLYMERIZATION OF 2,4,6,8-TETRAMETHYLCYCLOTETRASILOXANE

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The ring-opening polymerization of cyclosiloxanes,  $[(R_1R_2)SiO]_n$ , initiated by carbanions or silanolate anions, is a  $S_N2$  type reaction; the anions attack the silicon and the oxygen departs from the silicon to give polysiloxanolate anions. If "living" polymer<sup>1</sup> is used as a nucleophilic reagent, the characteristic red color of the carbanions disappears and colorless polysiloxanolate anions (leaving groups) are generated as shown below:



where R and R' are alkyl or aryl substituents, M are counter ions and  $n$  is the number of siloxane units in the cyclosiloxane. The polymerization scheme is similar to that of the classical step-wise addition polymerization. Thus, if no side reaction is involved, the reaction should proceed smoothly to give linear high polymers. Typical examples are illustrated in the polymerization of octamethylcyclotetrasiloxane initiated by living polymers<sup>2,3</sup>.

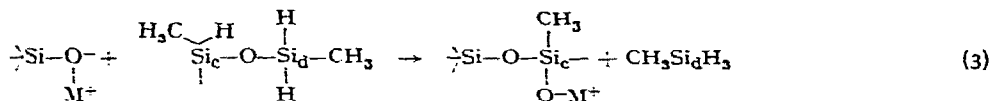
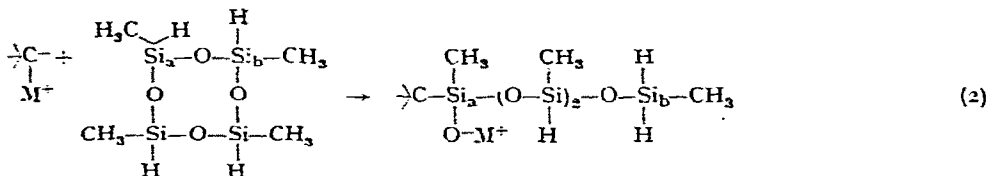
However such a mechanism is not always true if one of the R groups on the silicon is hydrogen. Because of the weakness of the SiH bond, the leaving group in the nucleophilic substitution reaction could be the hydrogen rather than the oxygen. Therefore such a side reaction may compete with the classical ring opening reaction and the resulting polymers could be highly cross-linked. This is demonstrated in the base-catalyzed polymerization of 2,4,6,8-tetramethylcyclotetrasiloxane presented in this paper.

RESULTS AND DISCUSSION

The polymerization of tetramethylcyclotetrasiloxane initiated by living polymers was extremely fast at room temperature. The characteristic color of living polymers disappeared and a gel formed instantly. A vigorous evolution of colorless gas was also observed simultaneously. The reaction was complete within a few seconds. The rate constant of the initiation reaction was estimated to be greater than  $10^4 \text{ l-mol}^{-1}\text{-sec}^{-1}$ , which was about  $10^4$  times faster than that observed in the octamethylcyclotetrasiloxane/living polymer system<sup>2</sup>.

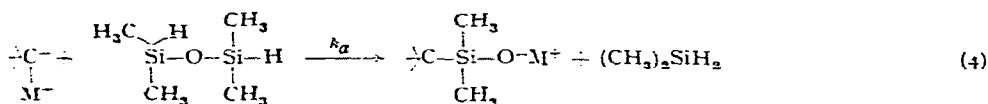
A similar behavior was observed when sodium phenyldimethylsilanolate was used as the catalyst. The reaction was slower when benzene was employed as solvent.

The colorless gas was identified as methylsilane. It was stable at room temperature on exposure to air, but exploded on contact with a hot flame. Intramolecular hydride transfer as shown below was first considered as a mechanism for the formation of methylsilane and gel.

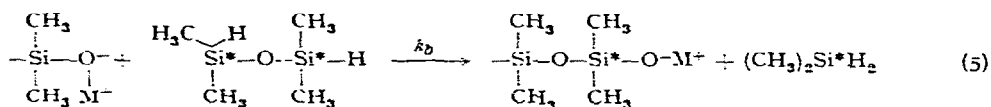


The breaking of a SiH bond is competitive with the rupture of a Si<sub>a</sub>O bond. The hydride simultaneously attacks the Si<sub>b</sub> and cleaves the Si<sub>b</sub>O bond. The consequence of this side reaction is the generation of internal silanolate anions which will eventually lead to cross-linking.

If this mechanism is correct, then the reaction between living polymers and tetramethyldisiloxane should give dimethylsilane.



The resulting silanolate reacts further to give polydimethylsiloxanolate and dimethylsilane.



To test this mechanism, 10 ml of living polymer in tetrahydrofuran (THF) was mixed with 8 ml of tetramethyldisiloxane and the evolved gas was analyzed. Gas-liquid chromatography showed that the gas consisted of a single species which boiled at about  $-20^\circ$ . This was shown to be dimethylsilane by infrared and mass spectrometry. Polydimethylsiloxane was also identified by infrared spectroscopy. The same result was also reported by Zichy<sup>4</sup> during the preparation of this paper.

According to this mechanism, the reaction should be first order with respect to tetramethyldisiloxane, in accordance with the equation

$$d[\text{Me}_2\text{SiH}_2]_t/dt = (k_a[\text{S}^-]_0 + k_b([\text{S}^-]_0 - [\text{S}^-]))[(\text{Me}_2\text{HSi})_2\text{O}] \quad (6)$$

where  $k_a$ ,  $k_b$  are the rate constants for reactions (4) and (5) respectively, and  $[\text{S}^-]_0$ , and  $[\text{S}^-]$  are the concentration of living ends initially and at time  $t$  respectively.

In the present case, the first volume reading could not be taken in less than 60 seconds. During this period, essentially all of the living ends were converted to polydimethylsiloxanolate; reaction (4) was complete in a fraction of a second. Thus eqn. (6) can be reduced to

$$d[\text{Me}_2\text{SiH}_2]/dt = k_b[\text{S}^-]_0[\text{Me}_2\text{HSi}_2\text{O}] \quad (7)$$

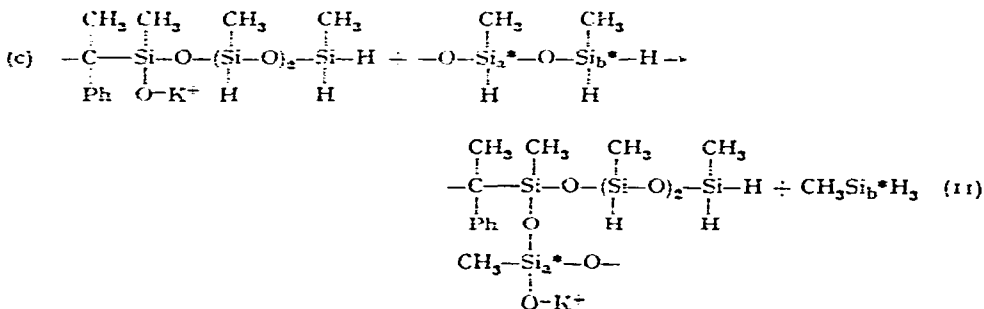
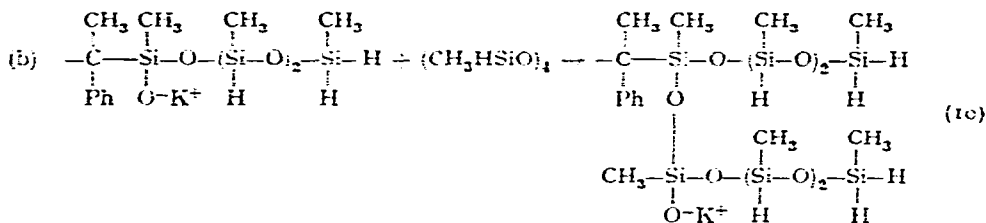
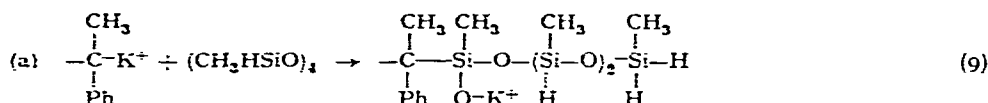
and

$$\ln[(V_\infty - V_0)/(V_\infty - V_t)] = k_b[\text{S}^-]_0 t \quad (8)$$

where  $t$  is reaction time and  $V_0$ ,  $V_t$  and  $V_\infty$  are burette readings at times 0,  $t$  and infinity respectively.

The results are shown in Fig. 3. A plot of  $\log [(V_\infty - V_0)/(V_\infty - V_t)]$  vs.  $t$  gives a straight line passing through the origin. Thus, it can be concluded that the reaction is first order with respect to tetramethyldisiloxane.

Based on these data, the experimental results are interpreted in terms of an intramolecular hydride-transfer mechanism. The base-catalyzed polymerization of tetramethylcyclotetrasiloxane in this system was postulated to be proceeding through the following steps:



Reactions (b) and (c) will repeat until most of the active hydrogen is exhausted. According to this mechanism we would expect a heavily cross-linked network polymer having a very low content of SiH bond. This was found to be the case. The gel polymer

contained less than 0.05% active hydrogen. (The theoretical SiH content without side reaction is 1.67%.)

So far we have considered only the intramolecular hydride transfer mechanism. There is, however, also a possibility of intermolecular hydride-transfer reaction. Such an intermolecular mechanism may also give a cross-linked polymer and methylsilane in the base-catalyzed polymerization of tetramethylcyclotetrasiloxane.

Reactions similar to such an intermolecular hydride transfer reaction mentioned above have been reported in some other base-catalyzed reactions. For example, organoalkoxysilicon hydrides such as  $\text{RSiH}(\text{OR})_2$  or  $\text{HSi}(\text{OR})_3$  produce  $\text{RSiH}_3$  or  $\text{SiH}_4$  in the presence of a little sodium alkoxide<sup>5</sup>. With LiH and  $(\text{CH}_3)_2\text{O}$  at  $-96^\circ$ , disilane,  $(\text{SiH}_3)_2\text{O}$ , can be equilibrated to silane as shown below (6):



The equilibration of  $[(\text{CH}_3)_2\text{HSi}]_2\text{O}$  to give  $(\text{CH}_3)_2\text{SiH}_2$  and  $\text{H}(\text{CH}_3)_2\text{SiO}[\text{Si}(\text{CH}_3)_2\text{O}]_x\text{Si}(\text{CH}_3)_2\text{H}$  in the presence of acid clay also has been observed<sup>7</sup>

In the present system, the distinction between an inter- and an intra-molecular mechanism is rather difficult. An attempt to differentiate between them was made by reacting living polymers with a mixture of  $[(\text{CH}_3)_2\text{HSi}]_2\text{O}$  and  $[(\text{CH}_3)_2\text{DSi}]_2\text{O}$  at a 1:1 ratio. The intramolecular mechanism should give  $(\text{CH}_3)_2\text{SiH}_2$  and  $(\text{CH}_3)_2\text{SiD}_2$  at a ratio of 1:1, whereas the intermolecular mechanism should give  $(\text{CH}_3)_2\text{SiH}_2$ ,  $(\text{CH}_3)_2\text{SiHD}$  and  $(\text{CH}_3)_2\text{SiD}_2$  at a ratio of 1:2:1.

Mass spectrometric analyses showed the presence of  $(\text{CH}_3)_2\text{SiHD}$ . The ratio of  $(\text{CH}_3)_2\text{SiH}_2:(\text{CH}_3)_2\text{SiHD}:(\text{CH}_3)_2\text{SiD}_2$  was approximately 1:1:1. This indicates that either both inter- and intramolecular hydride transfer reactions took place concurrently or that a SiD and SiH exchange reaction occurred in the solution.

Although the exchange reaction between SiD and SiH in the presence of a base catalyst had not been reported, it is likely that the exchange may take place since such phenomenon has been observed in the presence of an acid catalyst<sup>8</sup>. It has been reported, however, that the optically active deuteriosilane undergoes deuterium-hydrogen exchange with lithium aluminum hydride<sup>9</sup>. Thus, the use of the deuterated tetramethyldisiloxane does not give a conclusive result in distinguishing between the intra- and intermolecular mechanisms. Further investigation is required.

It has been stated previously in this communication that the hydride transfer mechanism postulated above actually competes with the ring opening reaction ( $S_N2$  mechanism) represented in reaction (1). The relative importance of these two competitive mechanisms depends on the experimental conditions. For example, if *n*-butyllithium in pentane is used as a catalyst, the latter mechanism has been found to be more important than the former since the resulting polymer is only slightly cross-linked and retains most of the SiH bond (about 90%)<sup>10</sup>. If silanolate or  $\alpha$ -methylstyrene living polymer in THF is used, the former mechanism overshadows the latter and a heavily cross-linked polymer is obtained.

## EXPERIMENTAL

### Reagents

(1). *2,4,6,8-Tetramethylcyclotetrasiloxane and 1,1,3,3-Tetramethyldisiloxane*. Both

the 2,4,6,8-tetramethylcyclotetrasiloxane,  $(\text{CH}_3\text{HSiO})_4$ , and 1,1,3,3-tetramethyldisiloxane,  $[(\text{CH}_3)_2\text{HSi}]_2\text{O}$ , used in this study showed only a single peak on gas-liquid chromatography. All samples were dried over calcium hydride in vacuo overnight and the required amount of the sample was distilled in high vacuum prior to use.

(2). *1,1,3,3-Tetramethyl-1,3-dideuterodisiloxane*. Deuterated tetramethyldisiloxane,  $\{[(\text{CH}_3)_2\text{D}]_2\text{Si}\}_2\text{O}$  was prepared by adding a solution of 1,1,3,3-tetramethyl-1,3-dichlorodisiloxane,  $[(\text{CH}_3)_2\text{Cl}]_2\text{SiO}$ , in anisole to lithium aluminum deuteride in anisole. After the reaction was complete, the solution was filtered and distilled. The product was isolated by preparatory gas-liquid chromatography. The infrared spectrum showed an absorption peak at 6.5 microns due to SiD stretching. No peak was observed at 4.7 microns indicating the absence of any appreciable SiH.

(3). *Polymerization catalysts*. Two base catalysts were employed,  $\alpha$ -methylstyrene living polymer and sodium phenyldimethylsilanolate. The former was prepared in THF at room temperature using sodium/potassium alloy as an electron donor. The D.P. of the living polymer was about 3. The sodium phenyldimethylsilanolate was prepared by reacting phenyldimethylsilanol with sodium metal in THF at room temperature. The product was recrystallized twice from THF.

### Polymerization

The tetramethylcyclotetrasiloxane was polymerized in THF at room temperature. Ten ml of catalyst solution was placed in an ampoule A and 8 ml of monomer in ampoule B in the apparatus shown in Fig. 1. The apparatus was evacuated to  $10^{-5}$  mm

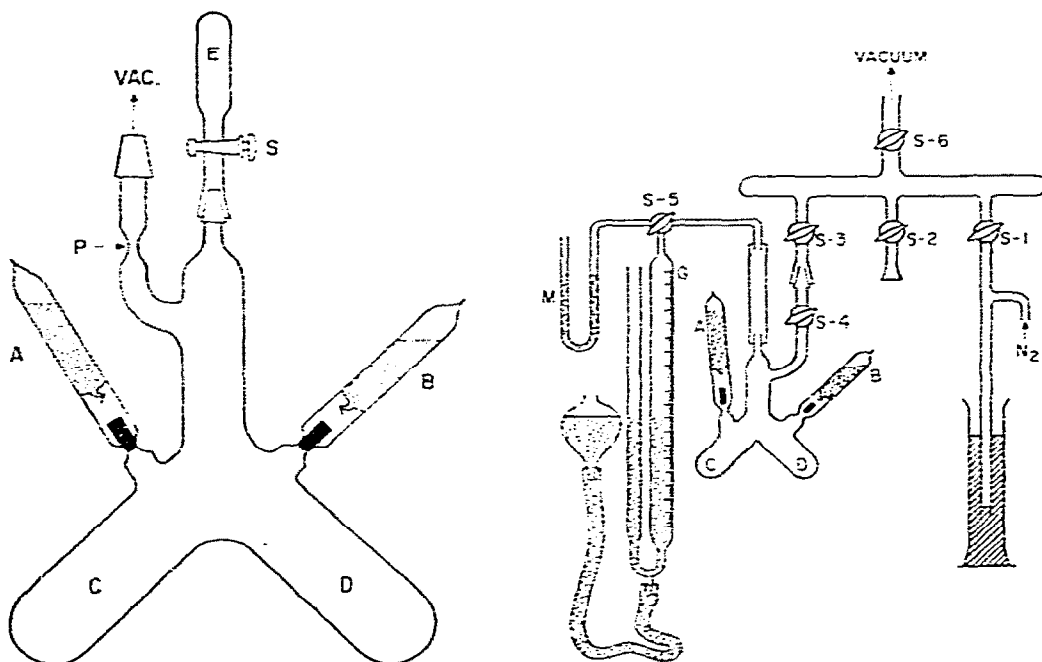


Fig. 1. Apparatus for the polymerization of  $(\text{MeHSiO})_4$ .

Fig. 2. Apparatus for kinetic runs.

Hg and sealed off at P. Stopcock S was then closed. The solutions were introduced into C and D respectively and then mixed by shaking. A gel formed immediately with vigorous evolution of gas. The evolved gas was collected in tube G and analyzed by gas chromatography, infrared and mass spectrometry.

#### Determination of the order of reaction

The order of reactions between  $\alpha$ -methylstyrene living polymer and 1,1,3,3-tetramethyldisiloxane was determined as follows: Ampoule A and ampoule B, containing 8 ml of  $\alpha$ -methylstyrene living polymer in THF (conc.  $4.5 \times 10^{-3}$  mole/l) and 20 ml of 25% solution of the disiloxane in THF, respectively, were connected to the Y-shaped tube as shown in Fig. 2. The system was evacuated to  $10^{-5}$  mm Hg and then filled with prepurified nitrogen through S-1. The level of the mercury in the gas burette, G, was brought to a maximum height when the pressure was equilibrated to atmospheric pressure.

Solutions A and B were introduced into tubes C and D respectively. The initial reading of the burette gave the initial  $V_0$ . Stopcock S-4, was then closed and the Y-shaped tube was removed from the vacuum system. The run was started by mixing these two solutions and the amount of gas evolved was determined periodically. The

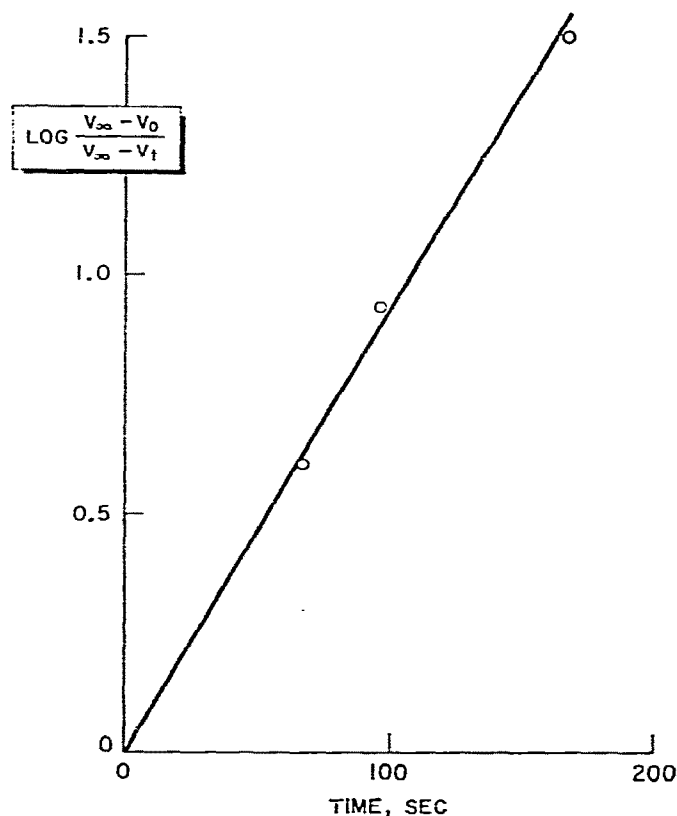


Fig. 3.  $\alpha$ -Methylstyrene living polymer plus  $(\text{Me}_2\text{HSi})_2\text{O}$  in THF at  $25^\circ$ .

timing was done with two electric clocks, alternatively. The error in the burette reading was about 0.05 ml and the timing error about 0.2 sec.

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#### SUMMARY

2,4,6,8-Tetramethylcyclotetrasiloxane,  $(\text{CH}_3\text{HSiO})_4$ , was polymerized using base catalysts. The reaction was very fast. A gel formed rapidly and a vigorous evolution of methylsilane was observed. Such a phenomenon was found to be a general one for the base-catalyzed polymerization of  $(\text{CH}_3\text{HSiO})_4$ . A hydride-transfer mechanism has been proposed to account for the cross-linkage and the formation of methylsilane. Both inter- and intramolecular hydride-transfer mechanisms are found to be possible.

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