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# Thermolysis of Poly[oxy(trisdimethylsilylene)] and Poly[oxy(tetrakisdimethylsilylene)]. Evidence for the Transient Formation of Permethyltrisilaoxetane

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The thermal behavior of polymers of formula $Me_3Si-O-[(Me_2Si)_mO]_n-SiMe_3$, $m = 3, 4$, was studied by thermogravimetry, mass spectrometry, and NMR and IR spectroscopies. Polymers heated under an argon atmosphere at temperatures of 200−400 °C undergo decomposition by the chain back-biting process initiated at a random site and terminated at a branching point formed by a competitive cross-linking reaction. The cyclic monomers $(Me_2Si)_3O$ and $(Me_2Si)_4O$ are the main volatile products. Formation of hexamethyltrisilaoxetane was proved by pyrolysis−mass spectrometry with chemical ionization. This very unstable compound was not isolated. Analysis of the decomposition products led to the supposition that the trisilaoxetane undergoes competitive dimerization and decomposition by dimethylsilylene extrusion and by retro (2+2) ring cleavage. Products of these decomposition reactions are inserted into the trisilaoxetane ring. The polymers heated at 400−1000 °C lose most of their organic fragments and are transformed into highly cross-linked Si:C:O materials.

## Introduction

Poly[oxy(oligodimethylsilylene)]s of general formula $-[O(Me_2Si)_m]_n-$ are fully methylated silicon analogues of simple polyethers; thus they are sometimes referred to as polysilaethers.[1,2] They may be obtained either by ring-opening polymerization of cyclic monomers and oligomers of the formula $[O(Me_2Si)_m]_n$[2−5] or by polycondensation of α,ω-functional oligosilanes.[3,5,6] Having the siloxane group, they undergo some reactions characteristic of siloxanes. For example, cationic ring opening polymerization−depolymerization occurs with exclusive cleavage of the silicon−oxygen bond.[2,3] On the other hand, they may be considered as polydimethylsilylenes regularly interrupted with oxygen; thus they undergo reactions with cleavage of the Si−Si bond.[4,6] They are highly crystalline materials; however, in contrast to polydimethylsilylene, poly[oxy(oligodimethylsilylene)]s, at least those having $2 \leq m \leq 6$ silylene units can be melted and are soluble in many organic solvents.[1,6,7]

The interest in the synthesis of these polysilaethers and their copolymers is connected with their potential as radiation-sensitive materials[8−10] and as precursors of ceramic materials.[6] Insertion of polysilaether fragments into chains of other polymers, in particular polysiloxanes, permits the facile catalytic cross-linking of these polymers.[11,12]

The thermal behavior of some polysilaethers of the $-[O-(Me_2Si)_m]_n-$ series has been studied.[6,7,13] The methylated silicon analogue of polyoxyethylene ($m = 2$), polymer **1**, has been the subject of extensive thermal investigations.[7,13] The thermal decomposition of the polymer with $m = 6$ has also been explored.[6] The purpose of this study is to compare the thermolysis, in an atmosphere of an inert gas or in a vacuum, of the polysilaethers with three ($m = 3$, polymer **2**) and four ($m = 4$, polymer **3**) silylene groups in the monomer unit with that of polymer **1**. Thermal studies of these polymers have not yet been published.

The thermal behavior of polymer **2** is of special interest. Polymer **1** was found to undergo thermal depolymerization in the temperature range 200−400 °C, producing the cyclic dimer, octamethyl(1,4-dioxa-2,3,5,6-tetrasilacyclohexane), **4**.[13] No evidence for the formation of the tetramethyldisilaoxirane monomer was found. On the other hand, preliminary studies in our laboratory

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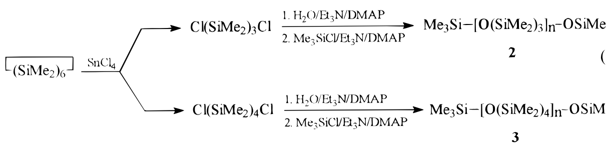
showed that polymer **3** decomposes to the cyclic monomer, octamethyl(1-oxa-2,3,4,5-tetrasilacyclopentane). Thus, it is interesting to see whether the thermolysis of polymer **2** gives only the expected cyclic dimer dodecamethyl(1,5-dioxa-2,3,4,6,7,8-hexasilacyclooctane), **6**, or if the strained ring monomer, so far unknown, hexamethyl(1-oxa-2,3,4-trisilacyclobutane), **7**, is generated as the product of this reaction. Trisilaoxetanes, as well as other 2-silaoxetanes, due to ring strain and the presence of the weakened Si−O bond,[14−16] are unstable. Only those compounds of this class which bear bulky substituents, such as neopentyl[16] or *tert*-butyl,[17,18] have so far been isolated. Trisilaoxetanes have been synthesized by oxidation of some hindered cyclotrisilanes[17−19] and by hydrolytic condensation of 1,3-dichlorohexaorganotrisilanes.[16,20] To our knowledge, permethyltrisilaoxetane, which may be considered as the simplest organic trisilaoxetane, has not been reported so far.

## Results and Discussion

**Polymer Synthesis and Characteristics.** Polymers **2** and **3** were synthesized according to eq 1:



(1)

Selective chlorination of dodecamethylcyclohexasilane was performed according to the method developed by Dręczewski and Wojnowski.[21] Hydrolytic polycondensation of the α,*ω*-dichlorooligosilanes in dioxane, in the presence of an equivalent amount of triethylamine as hydrogen chloride acceptor and of 4-(*N*,*N*-dimethylamino)pyridine (DMAP) as catalyst, gave the respective polymers **2** and **3**. Polymer **1**, $-[(SiMe_2)_2O]-$, was obtained by cationic polymerization of octamethyl-1,4-dioxatetrasilacyclohexane, as described earlier.[2] Any functional group at silicon may strongly affect the thermal behavior of the polymer; thus the hydroxyl end groups in **1**, **2**, and **3** were silylated with a mixture of trimethylchlorosilane, triethylamine, and DMAP. Polymers used for thermal studies also require very careful removal of acidic and basic impurities, which was carried out on a column with silica gel. Cyclic oligomers were removed from the polymers by repetitive precipitation of the polymers from methylene chloride solution with methanol and heating for a long time in a vacuum.

$^{29}$Si NMR and $^1$H NMR indicated a high sequential purity of the structures of polymers **l**, **2**, and **3**. The spectra of polymers **2** and **3** showed only two signals, the one for $Me_2Si$ bonded to two silicons and the other for $Me_2Si$ bonded to oxygen and to one silicon. Only the latter signal is present in the respective spectra of polymer **1**. The SEC analysis of these polymers showed the absence of cyclic oligomers. The number average molecular weights were about (2−3) × $10^4$.

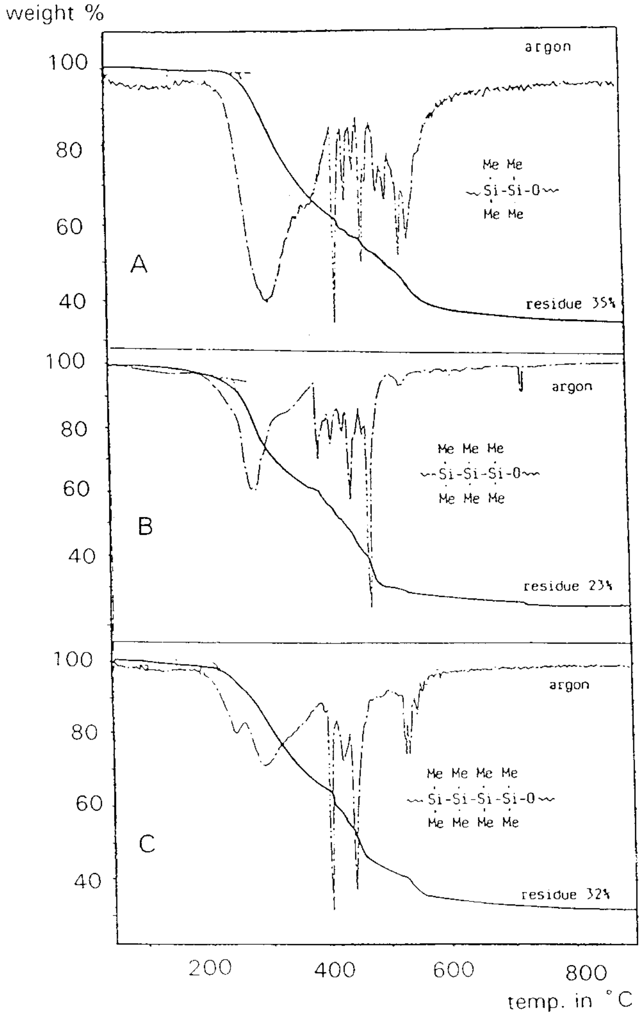


**Figure 1.** Thermogravimetric traces for pyrolysis of polymers: (A) poly[oxy(bisdimethylsilylene)], **l**, (B) poly[oxy (trisdimethylsilylene)], **2**, (C) poly[oxy(tetrakisdimethylsilylene)], **3**. Broken lines represent derivatives. Pyrolysis was performed under argon. Heating rate 20 °C/min.

**Thermogravimetric Studies.** Thermogravimetric investigations were performed in an atmosphere of argon using both temperature-programed and isothermal conditions. Thermograms for polymers **2** and **3** were similar, and both polymers exhibited behavior similar to that of polymer **1** on heating. Thus, the thermograms, taken by using the temperature-programmed method, indicate that the pyrolytic process occurs in two stages, the first one between 200 and 400 °C and the second between 400 and 900 °C (Figure 1A,B,C). Different thermal reactions dominate in these two stages; thus, they should be discussed separately.

In the first stage, the thermogravimetric traces show more regular shapes as compared with the second stage. In all cases, the decomposition, which begins above 200 °C, shows a maximal rate at about 300 °C, and then the rate of the volatilization strongly decreases. It was

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shown for polymer **1**[13] that the formation of cyclic products, mostly the fully methylated tetrasila-1,4-dioxane, was responsible for the loss of weight of the polymer sample heated in this temperature range. The similarity of the thermogravimetric traces in Figure 1A,B,C suggests that an analogous process led to the decomposition of polymers **2**, **3**, and **l**, which was fully confirmed by pyrolysis–mass spectrometry studies of the volatile thermolysis products (see next section).

Since the polymers become insoluble when heated above 200 °C, the formation of cyclic volatile products, classified as depolymerization, is accompanied by another process leading to the cross-linking of the polymer. This competitive cross-linking slows down the depolymerization process and eventually suppresses it, being responsible for a high yield of residue for the overall pyrolysis process.

The thermolysis of polymer **1** under isothermal conditions was shown to conform to eq 2, which approximately describes the kinetics of the depolymerization–cross-linking competition.[13] This equation was derived from the back-biting chain depolymerization (unzipping) initiated at random sites along the chain and terminated in branching points formed at random as a result of the competitive reaction.

$$\frac{W_0}{W} - 1 = \frac{k_\mathrm{i}}{k_\mathrm{B}} \ln \frac{t}{t_0} \qquad (2)$$

$W_0$ and $W$ are the weights of a heated sample after the times of heating $t_0$ and $t$, respectively; $k_\mathrm{i}$ is the rate constant for the initiation of depolymerization; $k_\mathrm{B}$ is the rate constant for the formation of cross-linking points.

Equation 2 was derived by using simplifying assumptions and may approximate the kinetics of the depolymerization process only in a limited range, excluding its initial period and the period when a higher extent of conversion is achieved. Nevertheless, eq 2 may serve as a diagnostic tool for the assumed mechanism. An example of the isotherm and its transposition to the coordinate system for the linear plot of the dependence are presented in eq 2, as shown in Figure 2. This result is in good agreement with the unzipping mechanism for the formation of cyclic volatile products. Suppressing the depolymerization by the cross-linking process, well-evidenced in the temperature-programmed experiment, implies that the cross-linking proceeds with a higher activation energy. It should be remembered that the activation enthalpy of the initiation step of the depolymerization of polymer **1** was estimated to be about 18 kcal/mol, while that of cross-linking about 30 kcal/mol, which was interpreted by assuming ionic character for the depolymerization and a free radical mechanism for the cross-linking.[13] Since polymers **2** and **3** show a thermal behavior that is very close to that of polymer **l**, it is assumed that the mechanism of their depolymerization also has an ionic character.

**Pyrolysis–Mass Spectrometry Studies.** Samples of polymers **2**, **3**, and **1** were heated with a temperature program under high vacuum in a probe connected to the ionization chamber of a mass spectrometer. The mass spectra of volatile decomposition products of the polymer were recorded at various temperatures up to 360 °C, which was the limit of our instrument. The total ionization current, as well as currents for selected ions, was followed as a function of the temperature, which was raised at the same rate as in the thermogravimetric experiments.

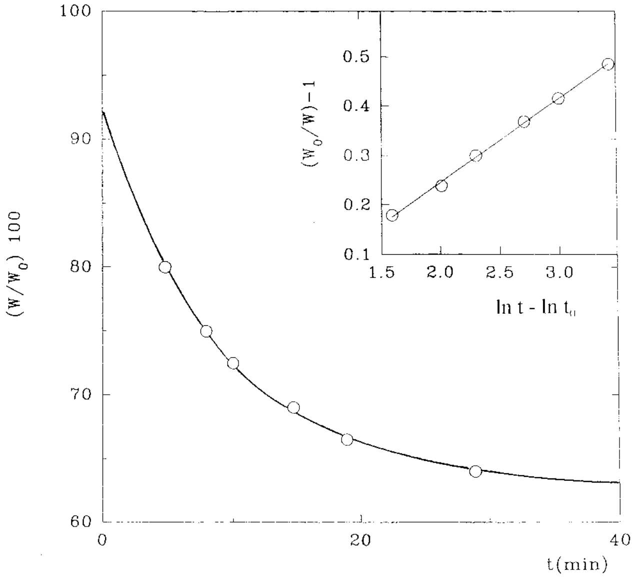
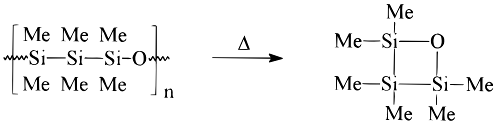


**Figure 2.** Thermogram for the decomposition of polymer **2** under isothermal conditions (240 °C) in argon and its transposition into the depolymerization–cross-linking competition plot (upper right corner).

The total ionization currents and single ion currents indicated that the decomposition of these polysilaethers in a vacuum occurred more or less in the same temperature range as the depolymerization in an argon atmosphere, as studied by thermogravimetry.

The mass spectrum of the thermolysis products of polymer **2** taken at the temperature of its depolymerization (360 °C) using the EI technique showed a peak of considerable intensity at $m/z = 190$ and an about 2 times stronger signal at $m/z = 175$ (see Experimental Section). These signals correspond to the molecular ion of the repeating unit of polymer **2**, thus to monomer **2**, and to its fragment formed by the detachment of a methyl group. The intensities of the respective signals for dimer $[(\mathrm{Me_2Si})_3\mathrm{O}]_2$ (**6**), $m/z = 380$ and $m/z = 365$, were lower almost by 1 order of magnitude compared with those for the monomer. Pure cyclic dimer **6** was synthesized and its fragmentation under electron impact was studied under the same conditions. The intensities of the peaks at $m/z = 190$ and 175 were much lower than those of the respective signals in the spectrum of the decomposition products of polymer **2**; thus they could not arise from fragmentation of the dimer. A similar experiment using cyclic $(\mathrm{Me_2Si})_4\mathrm{O}$ (**5**), which was found to be the third major volatile product of the decomposition of **2**, also excluded the possibility that the peaks at 190 and 175 could originate from the fragmentation of **5**. Thus, the most probable origin of the 190 and 175 signals is the cyclic monomer 2,2,3,3,4,4-hexamethyl-1-oxa-2,3,4-trisilacyclobutane (**7**) (eq 3). It should be remembered that the thermolysis of polymer **1** led to dimeric species as the almost exclusive product, and no indication for the formation of monomer, i.e., tetramethyldisilaoxirane, was found.[13] In contrast, the mass spectrum of the volatile thermolysis product of polymer **3** shows that monomer **5** is generated.


(3)

More clear evidence for the formation of **7** from the direct pyrolysis−mass spectrometry experiments was obtained by using the technique of chemical ionization (CI), exploiting preionized isobutane gas. Ion−molecule reaction leads to ionization by proton transfer with little fragmentation. Thus, a strong (M + 1) signal appears in the CI mass spectrum. A comparison of the spectra for the thermolysis of polymers **l**, **2**, and **3** is made in Figure 3. The spectra show clearly that polymer **2** is depolymerized to the trisilaoxetane **7** and confirm the formation of cyclics **4** and **5** as the main products of the depolymerization of **1** and **3**, respectively. The M + 1 signals of these cyclics dominate in the respective spectra.

In an attempt to collect trisilaoxetane **7** or products of its further reactions directly in an NMR tube cooled in liquid nitrogen, we performed a preparative scale experiment of the thermolysis of polymer **2** at 360° C under vacuum. The trapped thermolysate was allowed to warm to −70 °C, at which point the products were analyzed by $^{29}$Si NMR, and after further warming to the room temperature they were studied by gas chromatography−mass spectrometry by using the CI technique. No$^{29}$Si NMR signal was observed at very low field, where the resonance of the oxetane ring silicon atom bonded to oxygen was expected to occur.[22] Trisilaoxetane, **7**, proved to be very unstable under the conditions of this experiment, and only products of its reactions were identified. The main volatile products (contribution to the areas of the peaks in the chromatogram given in parentheses) were identified as follows: **5** (17%); **6** and its isomer **6a** (30%); [$(Me_2Si)_3O(Me_2Si)_2O$] + [$(Me_2Si)_4OMe_2SiO$], **10** + **l0a** (16%); [$(Me_2Si)_3OMe_2SiO$], **13** (9%); [$(Me_2Si)_5O$], **14** (6%).

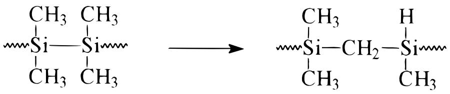
The formation of the thermolysis products can be explained by reactions presented in Scheme 1. According to this scheme, the transformation of **7** takes place along three pathways. Besides dimerization, two decomposition reactions occur, generating highly reactive intermediates, which are supposed to be inserted into the trisilaoxetane, **7**. The main route is presumably extrusion of dimethylsilylene (**8**) with ring contraction to 2,2,3,3-tetramethyl-2,3-disilaoxirane (**9**). Intermediates **8** and **9** would be then rapidly inserted into **7**, giving cycles **5** and **10** + **10a**, respectively. It is worth mentioning that the photochemical decomposition of perneopentyltrisilaoxetane has been postulated to occur via the corresponding silylene and disilaoxirane.[16] The second proposed pathway involves retro [2+2] ring cleavage with transient formation of dimethylsilanone **11** and tetramethyldisilene **12**. Both of these species would undergo insertion to trisilaoxetane, giving cycles **13** and **14**, respectively. However, the formation of the silanone **11** by the decomposition of disilaoxirane **9** and generation of the disilene **12** as a result of dimerization of **8** (Scheme 1) should also be considered.

M + 1 peaks of most products of the decomposition of **7** and intermediates **9** and **12** appear in the CI mass spectrum of the volatile thermolysis products of polymer **2**. It is possible that the decomposition of **7** proceeds already in the mass spectrometer. However, the presence of the M + 1 peaks for most of these products could be also explained by their direct formation in the back-biting process if it involves Si−Si bond breaking in addition to the dominating Si−O cleavage. Similar cleavage of Si−Si bonds has recently been observed in the back-biting thermal decomposition of polyoxyhexakisdimethylsilylene.[6]

The participation of processes involving Si−Si bond cleavage in the back-biting thermal depolymerization of polysilaethers suggests the anionic nature of the active depropagation centers in this depolymerization, as the cationic species are known to cleave selectively the Si−O bond.[2−4]

On the other hand the formation of isomers **10** + **10a** and isomers of **6**, found in the preparative experiments, is better understood on the basis of Scheme 1. The ring opening of disilaoxirane and trisilaoxetane followed by their insertion into trisilaoxetane may occur by the Si−Si scission. Of the Si−Si bonds in the species discussed above, the weakest bond will be found in the disilaoxirane. The Si−Si bond cleavage in this compound has already been reported.[24]

**Thermolysis at 400-l000 °C.** The thermogravimetric traces in the second stage of thermolysis, i.e., above 400 °C, shown in Figure 1, adopt a very irregular shape, thus reflecting more complex decomposition processes. The comparison of the IR spectra of polymer **2**[25] taken before and after heating in an argon atmosphere, presented in Figure 4, permits us to conclude that the main skeleton and most of the methyl substituents are preserved when the polymers are heated below 300 °C. In contrast, the heating at 500 °C causes major transformations of the polymer skeletal structure. A strong band appearing at 2100 cm$^{-1}$ indicates the presence of the Si−H bond, which is formed by the Kumada rearrangement[26] according to eq 4.


(4)

$$\sim Si(CH_3)_2-Si(CH_3)_2\sim \longrightarrow \sim Si(CH_3)_2-CH_2-SiH(CH_3)\sim \qquad (4)$$

The formation of the $-SiCH_2Si-$ linkage is manifested by a strong band at 1030 cm$^{-1}$ which is superimposed on the SiOSi stretching vibration bands, by a strong band at 800 cm$^{-1}$ which is superimposed on the $Si-CH_3$ bands at 830 and 750 cm$^{-1}$, and finally by a weak band at 1350 cm$^{-1}$.[27−30] Heating polymers **2** and **3** at l000 °C results in their transformation into a silicon oxycarbide ceramic material. The polymers lose many of their organic groups, although the IR spectra, taken after 2 h of heating, still show distinct bands at 1260 and 2960 cm$^{-1}$, indicating the presence of some residual

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(22) Strong deshielding is expected for silicon bonded to oxygen in the four-membered oxetane ring. Thus, various 2-silaoxetanes obtained by Brook et al.[23] showed $^{29}$Si resonance in the range of 42−56 ppm. Chemical shifts between 20 and 35 ppm were observed for 2-Si of some 2,3-disilaoxetanes.[24] Finally, the signal for 2-Si in perneopentyltrisilaoxetane appears at +29.4 ppm.[16]

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(25) Polymer **3** showed very similar respective IR spectra.

(26) Shiina, K.; Kumada, H. *J. Org. Chem.* **1958**, *23*, 139.

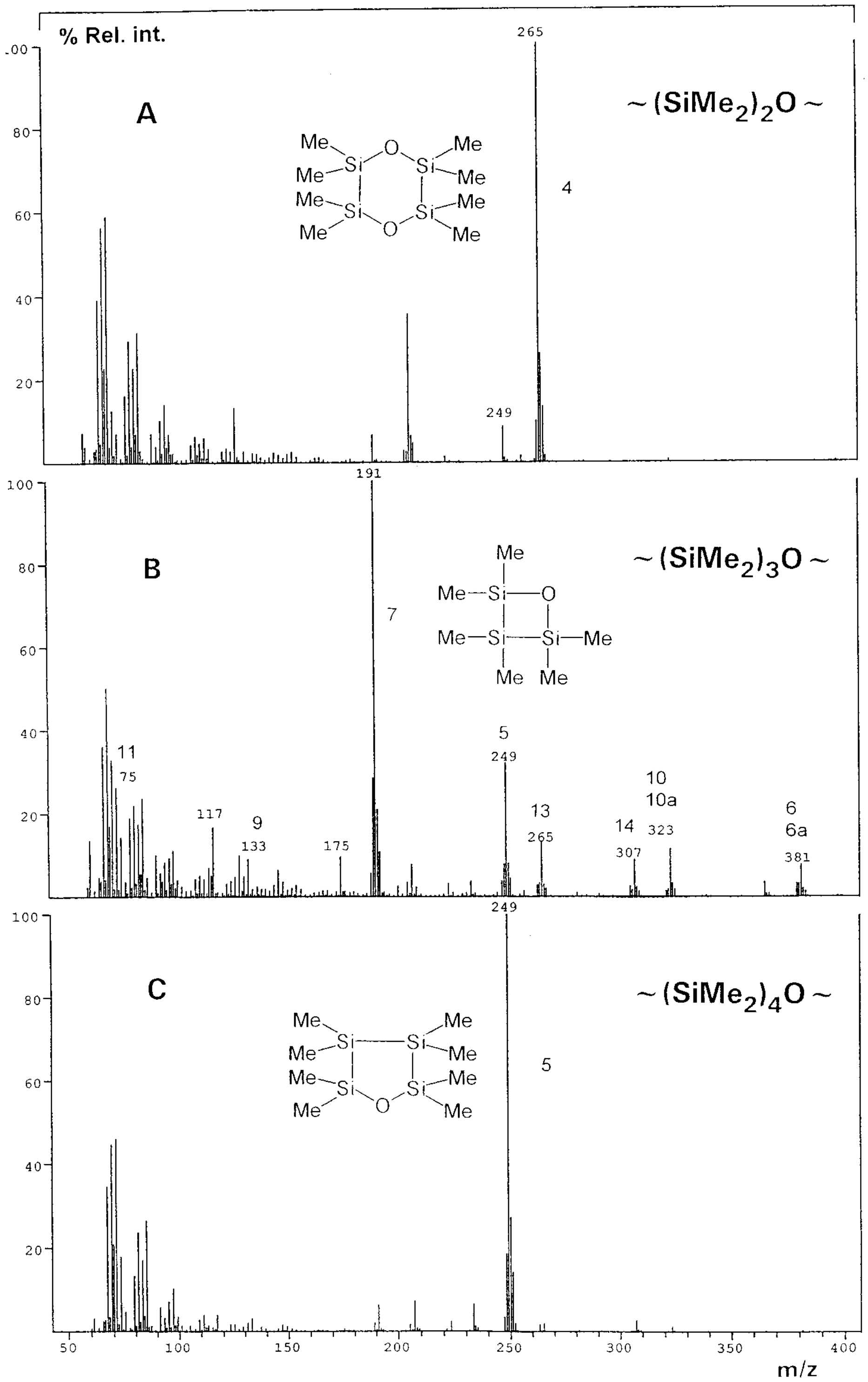

**Figure 3.** Chemical ionization mass spectra of volatile products of the thermolysis of polymers: (A) **1**, (B) **2**, (C) **3**, taken by pyrolysis–spectroscopy technique at 360 °C. Samples were heated with the temperature program 20°/min. Marked are peaks M + 1 by numbers of corresponding compounds.

$CH_3$ groups. There are also some residual Si–H bonds in this material. On the other hand, a strong, very broad band with a maximum at about 800 $cm^{-1}$ can be interpreted as partly belonging to the SiC carbidic units,[31,32] although it may include other SiC vibration bands. A strong band, attributed to $SiCH_2Si$, at 1020 $cm^{-1}$, over a weaker SiOSi band, is also observed.

The above interpretation of the IR spectra is supported by the $^{29}$Si MAS NMR spectra, Figure 5. The highest intensity of absorption is observed in the region of $SiC_4$ and $SiOC_3$ resonance.[33–35] The material must

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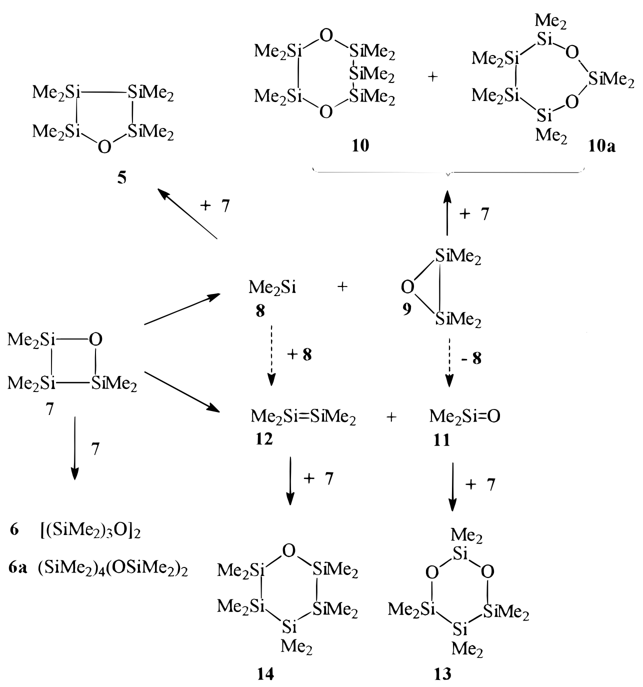
(32) Bhusari, D. M.; Kshirsagar, S. T. *J. Appl. Phys.* **1993**, *73*, 1743.

**Scheme 1**



have a strongly cross-linked structure with a considerable contribution from carbidic Si−C units. $SiC_3O$ and $SiC_2O_2$ units are also present.

## Conclusions

The thermolysis of poly[oxy(trisdimethylsilylene)], **2**, and poly[oxy(tetrakisdimethylsilylene)], **3**, from 200 to 900 °C is divided in two stages. Depolymerization occurs in the range 200−400 °C in competition with a cross-linking process. The cross-linking strongly affects the depolymerization and eventually suppresses it. Above 400 °C, the polymer loses most of its organic groups, and its skeleton is transformed by incorporating considerable amounts of carbon.

The depolymerization reaction proceeds according to the back-biting mechanism with predominant cleavage of the Si−O bond, thus producing cyclic monomers together with some larger oligomers. $(Me_2Si)_3O$, **7**, and $(Me_2Si)_4O$, **5**, are formed from polymers **2** and **3**, respectively. Polymer **2** also gives some cyclic products resulting from cleavage of the Si−Si bond in the back-biting process. Monomer **7**, hexamethyltrisilaoxetane, is very unstable. It reacts immediately, presumably by dimerization, or decomposes tentatively by dimethylsilylene extrusion and retro [2+2] cleavage followed by insertion of the formed intermediates into the monomer **7**.

## Experimental Section

**Basic Chemicals.** The monomers α,*ω*-dichloropermethylpolysilanes, 1,3-dichlorohexamethyltrisilane and 1,4- dichlorooctamethyltetrasilane, were obtained by chlorination of dodecamethylcyclohexasilane with $SnCl_4$ according to ref 21. These monomers were purified by distillation over a ca. 20 theoretical plates column, collecting 1,3-dichlorohexamethyltrisilane at 97° C/20 mmHg ($^{29}$Si NMR in $CDCl_3$ $\delta$ **Si**Cl 26.0 ppm, **Si**$(Si)_2$ −42.7 ppm) and 1,4-dichlorooctamethyltetrasilane at 56° C/0.08 mmHg ($^{29}$Si NMR in $CDCl_3$ $\delta$ **Si**Cl 24.74 ppm, **Si**$(Si_2)$ −43.74 ppm). Their purity was checked by gas chromatography. All the monomers are of purity higher than 98%.

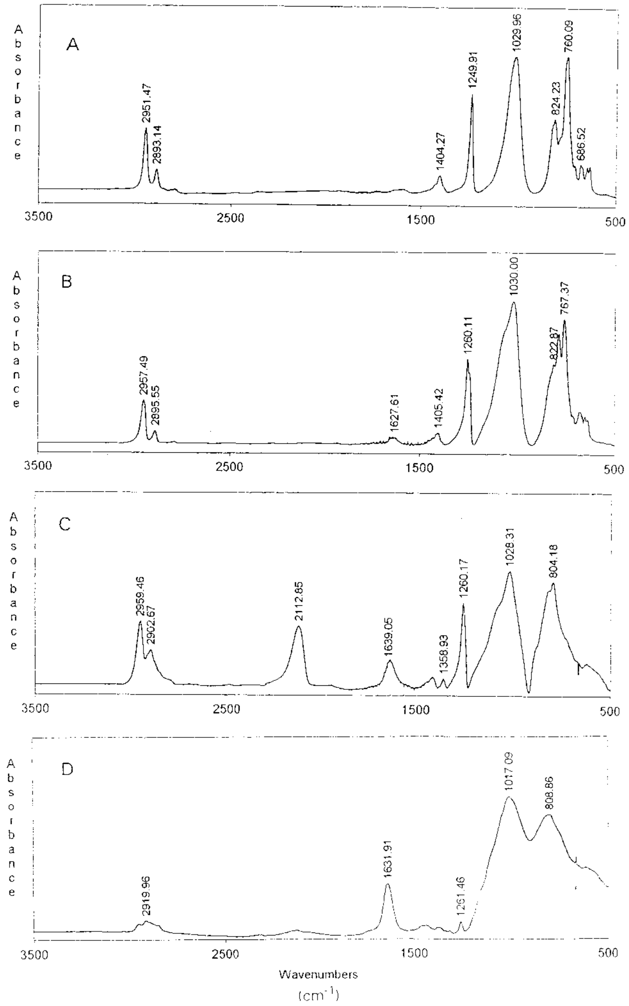


**Figure 4.** IR spectra of polymer **2**: (A) before heating, (B) after heating 2 h at 270 °C, (C) after heating 2 h at 500 °C, (D) after heating 2 h at 1000 °C.

2,2,3,3,4,4,5,5-Octamethyl-1-oxa-2,3,4,5-tetrasilacyclopentane ($^4D_1$), **5**, and 2,2,3,3,5,5,6,6-octamethyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane ($^2D_2$), **4**, were prepared according to the method described earlier.[3,36] They were purified by crystallization from ethanol, mp 45 °C for both **4** and **5**. 2,2,3,3,4,4,6,6,-7,7,8,8-Dodecamethyl-1,5-dioxa-2,3,4,6,7,8-hexasilacyclooctane ($^3D_2$), **6**, was obtained by the method described by Kumada et al.[26] and purified by distillation, b.p 98-l00 °C/2 mmHg: $^{29}$Si NMR $\delta$ **Si**O 7.8 ppm, **Si**$(Si_2)$ −53.6 ppm.

**Synthesis of the Polymers.** Poly[oxy(trisdimethylsilylene)], **2**, and poly[oxy(tetrakisdimethylsilylene)], **3**, were obtained according to the following procedure. A 500 mL glass reactor fitted with reflux condenser, thermometer, mechanical stirrer, and dropping funnel was charged with 80 mL of dioxane, 0.1 mol of α,*ω*-dichloropermethyltrisilane, 0.2 mol of $Et_3N$, and 0.01 mol of 4-(*N*,*N*-dimethylamino)pyridine (DMAP). The mixture was vigorously stirred at 0−5 °C, while 0.05 mol of water in 20 mL of dioxane was added dropwise. Then the

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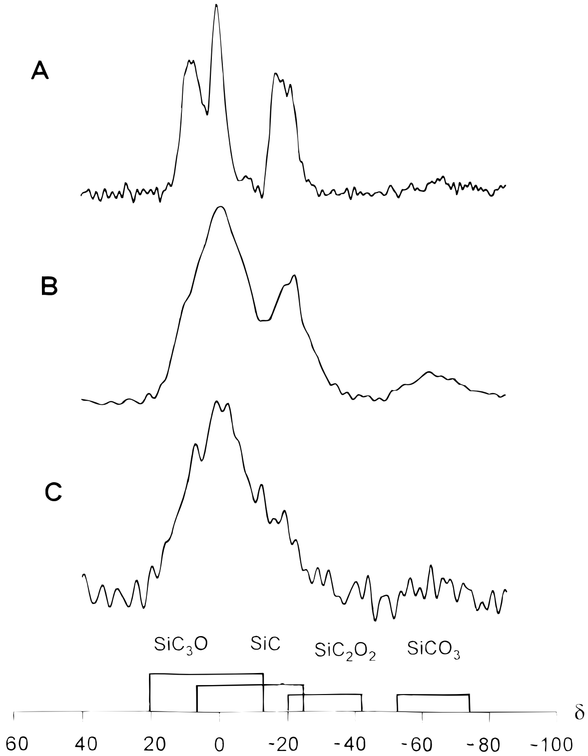

**Figure 5.** $^{29}$Si MAS NMR spectra of polymers: (A) **2** after heating 2 h at 500 °C, (B) **2** after heating 2 h at 1000 °C, (C) **3** after heating 2 h at 1000 °C.

mixture was allowed to reach room temperature, and 20 mL of water was introduced to dissolve the $Et_3N{\cdot}HCl$ formed during the reaction. The organic layer was separated and dried over $CaCl_2$. After filtration, the solution was treated with an excess of a mixture of 1:1:0.1 mol/mol of $Me_3SiCl$, $Et_3N$, and DMAP (1 g of $Me_3SiCl$) to silylate the silanol end groups. The solution was thoroughly rinsed with water and dried over $CaCl_2$, after which it was passed several times through a column filled with Merck silica gel 60, particle size 0.063−0.1 mm, to remove traces of amines. The polymers were precipitated with methanol and heated on a vacuum line at 100 °C/$10^{-4}$ mmHg for 24 h. Yields of polymers **2** and **3** were 67% and 68%, respectively. Polymers were characterized by $^{29}$Si and $^{1}$H NMR and by size exclusion chromatography (SEC).

$^{1}$H NMR ($CDCl_3$ solution): **2**, $\delta$ **$CH_3$**SiO 0.19 ppm (12H), **$CH_3$**Si(Si)$_2$ 0.08 ppm (6H), **3**, $\delta$ **$CH_3$**SiO 0.19 ppm (12H), **$CH_3$**Si(Si)$_2$ 0.12 ppm (12H).

$^{29}$Si NMR ($CDCl_3$ solution): **2**, $\delta$ **Si**O 8.3 ppm (2Si), **Si**(Si)$_2$ −53.5 ppm (1 Si); **3**, $\delta$ **Si**O 8.9 ppm (2Si), **Si**(Si)$_2$ −48.1 ppm (2Si).

$^{13}$C NMR ($CDCl_3$ solution): **2**, $\delta$ **$CH_3$**SiO 3.3 ppm (4C), **$CH_3$**Si(Si)$_2$ − 7.4 ppm (2C): **3**, $\delta$ **$CH_3$**SiO 3.6 ppm (4C), **$CH_3$**Si(Si)$_2$ −6.0 ppm (4C).

SEC: **2**, $\bar{M}_n = 2.8 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.5$; **3**, $\bar{M}_n = 1.7 \times 10^4$, $\bar{M}_w/\bar{M}_n = 2.8$.

Poly[oxy(bisdimethylsilylene)], **1**, was obtained by ring-opening polymerization of $^{2}D_2$ according to the description in ref 3. $\bar{M}_n = 3.1 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.9$.

**Thermogravimetric Studies.** Thermogravimetric analyses were performed using a Perkin-Elmer 7 Series Thermal Analysis System instrument. Samples of 1−5 mg were subjected to thermolysis under an atmosphere of argon, either in the range 50−900 °C at a heating rate of 20 °C/min or under isothermal conditions at 240 or 270 °C. In the isothermal experiment, the temperature was rapidly raised to the required temperature.

**Gas Chromatography−Mass Spectrometry.** Mass spectra were recorded with a GC−MS Finingan MAT 95 instrument using either electron impact ionization (EI) or chemical ionization (CI) techniques. In EI the energy was 70 eV. In CI the reactive gas was isobutane, at a pressure of $10^{-4}$ Torr. The gas chromatograph was fitted with a standard capillary column DB-17, **1** = 30 m, using the temperature program 100 °C (5 min), 100−250 °C at 20°/min, 250 °C (10 min).

**Pyrolysis−Mass Spectrometry.** Direct pyrolysis−MS studies of polymers **1**, **2**, and **3** were made using the Finigan MAT 95 instrument equipped with a heated probe with a temperature limit of 360 °C. The polymer sample was heated according to the temperature program 100−360 °C at 20 °C/min, 360° (2 min). The mass spectra of the volatile products were taken using either the EI (70 eV) technique or the CI (isobutane,$10^{-4}$ Torr) technique. The total ion currents as well as single ion currents were followed.

Mass spectra of volatile products of thermolysis taken at 360 °C with EI showed the following peaks with intensity larger than 1% [tentative fragments, intensity %].

Thermolysis of **2**: 73 [$Me_3Si^+$ 10.27]; 116 [$(Me_2Si)_2^+$ 1.53]; 117 [$Me_2SiMeSiO^+$ 5.30]; 131 [$Me_3SiMe_2Si^+$ 3.48]; 147 [$Me_3SiOMe_2Si^+$ 3.90]; 175 [$(Me_2Si)_2MeSiO^+$ 5.26] (M - 15); 189 [$Me_3Si(Me_2Si)_2^+$ 2.40)]; 190 [$(Me_2Si)_3O^+$ 2.69] (M); 191 [$Me_2SiOMe_2SiMeSiO^+$ 1.87]; 205 [$Me_3SiMe_2SiOMe_2Si^+$ 1.26]; 233 [$(Me_2Si)_3MeSiO^+$ 1.01]; 249 [$Me_2SiO(Me_2Si)_2MeSiO$ 1.56]; 307 [$(Me_2Si)_2O(Me_2Si)_2MeSiO^+$ 0.93]; 365 [$(Me_2Si)_3O(Me_2Si)_2MeSiO^+$ 1.34] ($M_2$ - 15).

Thermolysis of **3**: 73 [$Me_3Si^+$ 26.14]; 116 [$(Me_2Si)_2^+$ 1.79]; 117 [$Me_2SiMeSiO$ 4.63]; 131 [$Me_3Si(Me_2Si)_2$ 1.76]; 147 [$Me_3SiOMe_2Si^+$ 1.39]; 175 [$(Me_2Si)_2MeSiO^+$ 1.69]; 189 [$Me_3Si(Me_2Si)_2^+$ 3.4]; 233 [$(Me_2Si)_3MeSiO^+$ 1.38] (M-15); 248 [$(Me_2Si)_4O^+$ 2.24] (M).

**Preparative Experiment of Thermolysis in a Vacuum.** To trap and identify volatile products, the pyrolysis of **2** was performed in a vacuum ($10^{-3}$ Torr) at 360° C in a glass tube reactor connected with a vacuum line heated at a controlled temperature with an electrical oven. The volatile products were collected in a tube receiver, $d$ = 10 mm, to which 2 mL of $CD_2Cl_2$ had been introduced. The receiver was cooled in liquid nitrogen. After pyrolysis it was cut off the apparatus, heated to −70 °C, and placed in a NMR probe. The $^{29}$Si NMR spectra were taken at −70 and 0 °C. The products were subjected to GC and GC−MS analyses using for the latter a CI technique. From 0.95 g of polymer **2**, 0.59 g (62.1%) of the pyrolysis products was collected. The residue was 0.26 g (27.4%); about 0.1 g (10.3%) of the volatile products was not trapped.

In an analogous preparative experiment argon was streamed through the oven and the receiver to the high-vacuum line. $^{29}$Si NMR spectra were taken subsequently at −100, −75, and +24 °C.

**Preparative Experiments of Thermolysis in Argon.** Polymers **2** and **3** were pyrolyzed at three temperatures: 270 °C, 500 °C in a glass tube reactor, and at 1000 °C in a quartz tube reactor fitted with an inlet and an outlet of argon. The reactor was loaded with 0.5 g of polymer, thoroughly purged with argon, and placed in the electrical oven and heated to the required temperature. After 2 h of heating with the flow of argon, the tube was cooled to room temperature and the residue was analyzed by IR and NMR spectroscopy.

**Instrumental Analysis.** $^{1}$H, $^{13}$C, and $^{29}$Si NMR spectra were taken with a Bruker 300 MSL working at 300, 50.133, and 59.6 MHz for $^{1}$H, $^{13}$C, and $^{29}$Si, respectively.

$^{29}$Si MAS NMR were performed with Bruker 300 MSL at 59.627 MHz.

IR spectra were taken using an ATI MATTSON Infinity Series FTIR. Polymer samples were prepared in KBr.

SEC analyses were performed with LBK 2150-HPLC Pump (RIDK 102) using the following set of chromatographic columns: 2 × 100 Å; 500 Å; 1000 Å and a TSK−GEL 1000 HXL column. THF was the solvent. Calibration was done with polystyrene.

Gas chromatographic analyses were performed with JEOL JGC-1100 chromatogram working with TCD-detector and equipped with Takeda Riken 2215 A integrator: column $l = 2$m, $d = 0.03$ m filled with OV-101 on Varaport 60/80 mesh, carrier gas, hydrogen, 40 mL/min, column temp program 20−200 °C, 15 °C/min.

**Supporting Information Available:** $^{29}$Si NMR of polymers, CI/MS of $-[(Me_2Si)_3O]_2$, (**6**) and GC/MS of thermolysis products. This material is available free of charge via the Internet at http://pubs.acs.org.

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