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Selective Anionic Ring-Opening Polymerization of Permethyltetrasila-1,4-dioxane, $^2D_2$. Transformation of Poly(silaether) in Polysiloxane and Polysilylene

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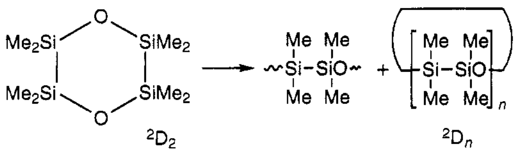
Introduction. Poly[oxymulti(dimethylsilylenes)] of the general formula of the repeating unit $-[(Me_2Si)_mO]-$ are interesting polymers having chains constructed of uniform oligo(dimethylsilylene) sequences linked with each other by oxygen. Thus, they show structural features of poly(dimethylsiloxanes) and poly(dimethylsilylenes), and some of their properties lie between them.[1-5] Regarding the chain skeleton structure, they are silicon analogs of polyethers. These polymers may be obtained only by synthesis from monomers using ring-opening polymerization and polycondensation routes in which bonds between silicon atoms are fully preserved. This condition is met in the cationic ring-opening polymerization initiated by a strong protic acid. The polymerization of this type which has so far been well-studied is that of the fully methylated silicon analog of dioxane, i.e., 2,2,3,3,5,5,6,6-octamethyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane, denoted by the symbol $^2D_2$.[4,5] This polymerization leads to the equilibrium involving linear polymer, cyclic oligomers and macrocycles of the $^2D_2$ series according to eq 1.[4] In a system well isolated from atmospheric oxygen no siloxane unit appears in the polymer or oligomer fraction. The formation of longer dimethylsilylene sequences was not observed either.



(1)

In marked contrast, the anionic polymerization of $^2D_2$ initiated with a strong base was found to occur in a nonselective way.[2] Propagation centers, which are the silanolate ion and the silyl anion, are able to cleave not only the Si–O bond but also the Si–Si bond, thus forming the silaacetal unit and units containing a variable number of silylene groups. The process may eventually lead to poly(dimethylsilylene) and poly(dimethylsiloxane).

Since the anionic polymerization of $^2D_2$ is a unique ring-opening polymerization system known to involve the competition of the Si–Si cleavage and the Si–O cleavage, we thought it would be interesting to study the course of the reaction. So much that the quantitative transformation of the well-defined poly(silaether) structure into two types of well-known polymers, i.e., poly(dimethylsilylene) and poly(dimethylsiloxane), is a very interesting phenomenon from the theoretical point of view.

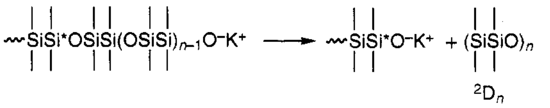
This study revealed that the final equilibrium state of this process in which the polysilylene and polysiloxane are indeed separate and exclusive products is achieved in a very complex way. However, when appropriate conditions are applied, it is possible to attain a high degree of selectivity of this process in its first phase and use the kinetically controlled anionic polymerization of $^2D_2$ as a route to the synthesis of the poly(silaether) of the regular poly(oxymultisilylene) structure. The overall process proceeds in three kinetically distinguished stages. In the first stage the Si–O bond cleavage occurs almost exclusively. The reaction approaches closely the equilibrium state between monomer and poly[oxybis(dimethylsilylenes)], such as that achieved in the cationic polymerization of $^2D_2$. Reactions involving the Si–Si bond cleavage destroying the regular poly(silaether) structure become important in the further phases of the process.

Results and Discussion. The polymerization of $^2D_2$ was performed in the 1:1 (v/v) THF solution in the presence of dipotassium oligo(permethylsiloxanediolate), $KO(SiMe_2O)_{\bar{n}}K$, $\bar{n} = 4$. The concentration of the Me_2SiO unit introduced with the initiator was small enough to be neglected in further discussions. The conversion of monomer and formation of some oligomeric products were followed by gas chromatography (Figure 1).

If the polymerization was quenched at the moment when the concentration of $^2D_2$ achieved its equilibrium value determined from studies of the cationic polymerization of this monomer,[4] the isolated polymer had a regular structure composed almost exclusively of the oxybis(dimethylsilylene) units. The ^{29}Si NMR (Figure 2A) and ^1H NMR spectra of this polymer were identical with those of the polymer obtained by the cationic polymerization of $^2D_2$. They showed only one signal. The ^{29}Si resonance and the ^1H resonance were observed at 1.14 and 0.155 ppm, respectively, in the accord with the data for the polymer obtained by the cationic polymerization of $^2D_2$.[4] In particular, no silaacetal grouping appeared, giving rise to the ^{29}Si resonance expected at about −22 ppm.[6] Thus, the anionic polymerization may also lead to poly(oxymultisilylene) of a high sequential purity.

Small amounts of only two cyclics containing the silaacetal unit, i.e., $(OSiMe_2)_2O(SiMe_2)_2$ and $OSiMe_2[O(SiMe_2)_2]_2$, appeared in the first stage of the process, but they did not seem to have entered in the polymer. The conversion of monomer approaches the equilibrium concentration of $^2D_2$ according to the first-order kinetics (Figure 3).

The formation of $^2D_3$, next oligomer of the ^2D_n series, was observed (Figure 3), during the monomer conversion, which is proof that expected backbiting depropagation takes place, (eq 2), and the system aims at the equilibrium between $^2D_2$, oligomers, and linear polymer, according to eq 1.



$$\sim SiSi^{*}OSiSi(OSiSi)_{n-1}O^{-}K^{+} \longrightarrow \sim SiSi^{*}O^{-}K^{+} + \underbrace{(SiSiO)_n}_{^2D_n} \quad (2)$$

Thus, the polymerization of $^2D_2$ proceeded in the first stage as an equilibrium first-order reaction involving almost exclusive Si–O bond cleavage in a way similar to the anionic polymerization of cyclic siloxanes.

Starting from the point in which the equilibrium of the Si–O breaking and making was approached, the further consumption of $^2D_2$ proceeded at a much lower rate. The conversion of $^2D_2$ beyond the scope determined by the equilibrium 2 took place at the expense

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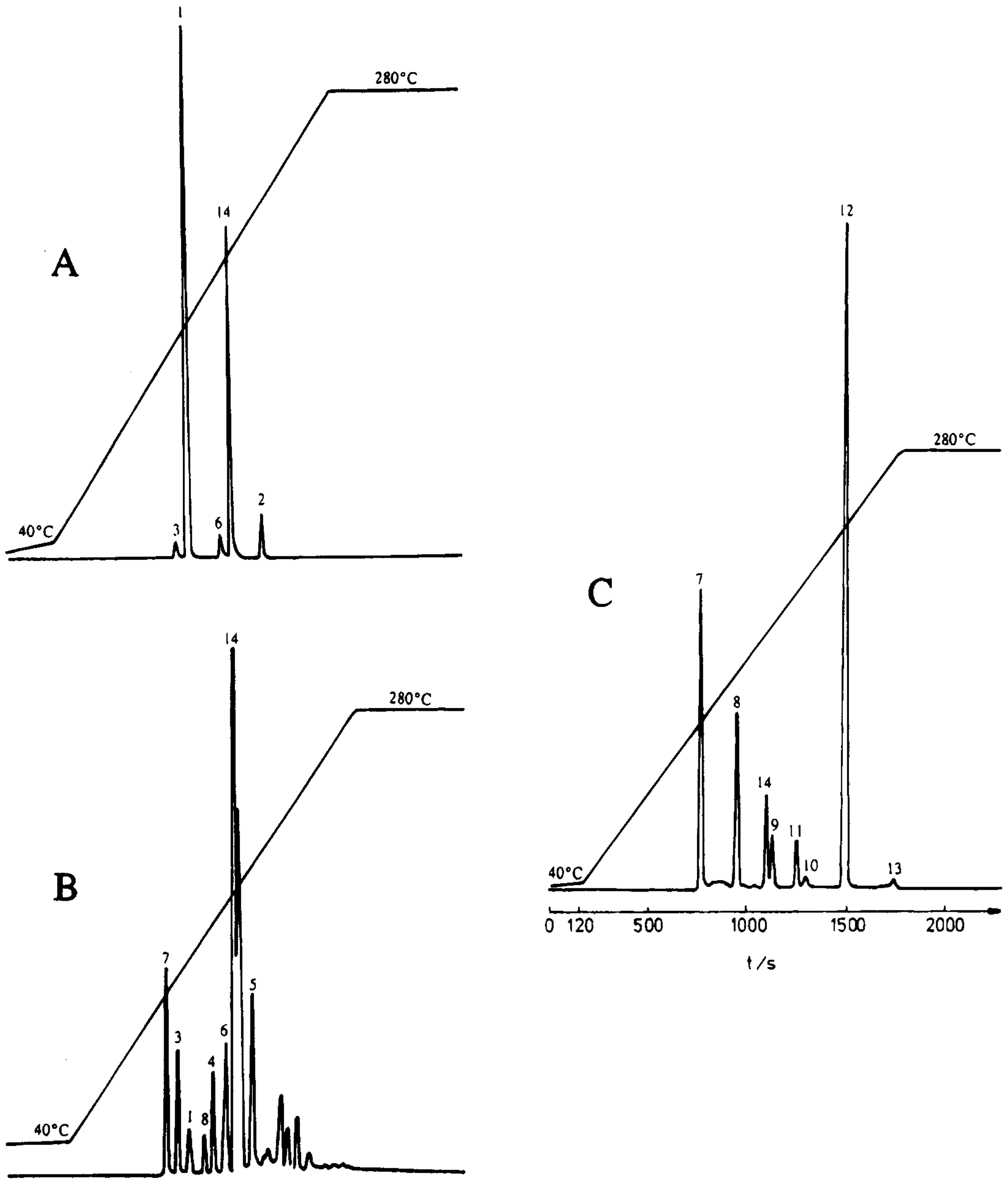
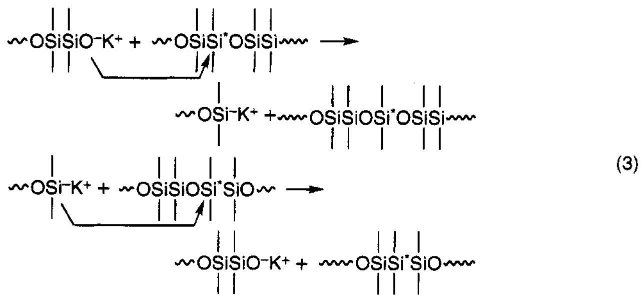


Figure 1. Gas chromatograms of the polymerization system of $^2D_2$ in THF in the presence of potassium oligo(dimethylsiloxanolate), [SiOK] = 10^{-3} mol·dm^{-3}, 25 °C. Peaks of the following cyclics are marked by numbers: $^2D_2$ (1); $^3D_2$ (2); $[(OSiMe_2)_2O(SiMe_2)_2]$ (3); $[(OSiMe_2)_3O(SiMe_2)_2]$ (4); $[(OSiMe_3)_4O(SiMe_2)_2]$ (5); $\{OSiMe_2[O(SiMe_2)_2]_2\}$ (6); $(OSiMe_2)_4$ (7); $(OSiMe_2)_5$ (8); $(OSiMe_2)_6$ (9); $(OSiMe_2)_7$ (10); $(SiMe_2)_5$ (11); $(SiMe_2)_6$ (12); $(SiMe_2)_7$ (13); tridecane (standard) (14). Chromatograms were taken (A) at the end of the first stage when the concentration of $^2D_2$ achieved its equilibrium value for processes of the Si–O bond cleavage and reformation, (B) at the end of the second stage when a considerable part of $^2D_2$ is converted due to the Si–Si bond cleavage, (C) at the end of the third stage when the system is at full equilibrium of processes of the Si–O and Si–Si bonds making and breaking.

of the formation of the silaacetal grouping OSiO and longer polysilylene groupings which appeared in both the cyclic fraction (Figure 1B) and the polymer fraction as it was recorded by ^{29}Si NMR. They could be formed according to the route illustrated by eq 3.



$$\sim OSiSiO^-K^+ + \sim OSiSi^*OSiSi\sim \longrightarrow \sim OSi^-K^+ + \sim OSiSiOSi^*OSiSi\sim$$
$$\sim OSi^-K^+ + \sim OSiSiOSi^*SiO\sim \longrightarrow \sim OSiSiO^-K^+ + \sim OSiSi^*SiO\sim \qquad (3)$$

Although the course of the polymerization in the first stage was well reproducible, the reproducibility of the rate of the reaction in its second stage was very poor. In some cases the reaction seemed to be stopped, and the addition of a new portion of the silanolate was necessary to observe the further conversion of $^2D_2$. However, after a longer time interval the overall process suddenly and spontaneously underwent a strong acceleration. The remains of the monomer and the oligomers of the $^2D_2$ series disappeared rapidly. Eventually the process became so fast as a clear exothermal effects was observed. This was the third stage of the process in which the system was fully converted to poly(dimethylsiloxane) and poly(dimethylsilylene). The solution gained a yellow color, indicating that substantial amounts of active propagation centers appeared as silyl anions. This rapid transformation was also accompa-

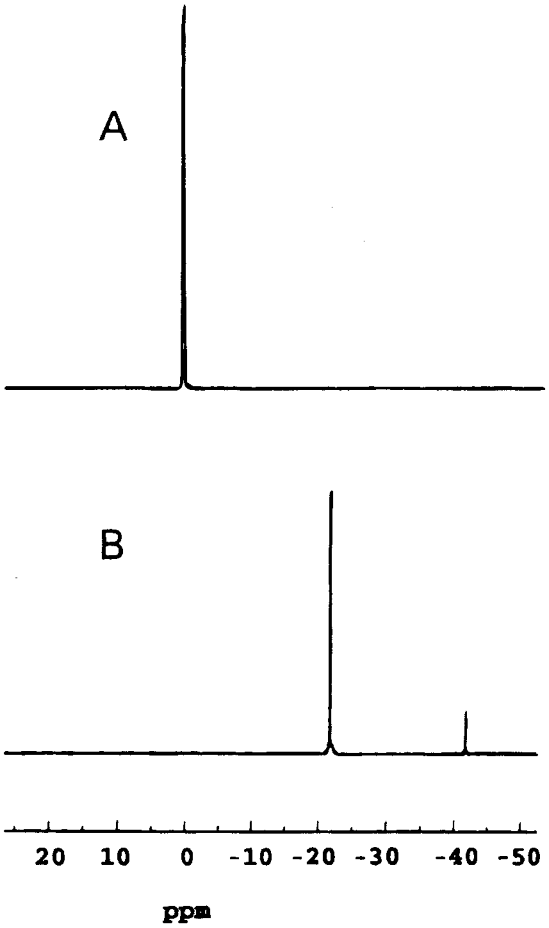


Figure 2. ^{29}Si NMR spectra (solution in $CDCl_3$) of the polymer fraction isolated from the system of the polymerization of $^2D_2$ in the presence of dipotassium oligo(dimethylsiloxanediolate); $[^2D_2]_0$ = 1.54 mol·dm^{-3}, [SiOK] = 1 × 10^{-3} mol·dm^{-3}, 25 °C. (A) Spectrum taken when $^2D_2$ achieved its equilibrium concentration in Si–O making and breaking processes. (B) Spectrum taken at the end of the overall transformation.

nied by a decrease of the viscosity of the system.

When the overall process was finished, the gas chromatogram of oligomers in the system showed the existence of only two series of oligohomologs: cyclic poly(dimethylsiloxanes) and cyclic poly(dimethylsilylenes) (Figure 1C). No cyclics of mixed siloxane–silylene structure appeared, nor was any residue of cyclic silaethers observed. The polymer fraction of these products was pure poly(dimethylsiloxane) showing the ^{29}Si NMR resonance at −21.32 ppm (Figure 2B). A weak signal at −41.83 ppm originated from the resonance of cyclic $(Me_2Si)_6$, a small part of which came to the polymer fraction in the procedure of its isolation by precipitation of the polymer with methanol from the postpolymerization mixture. No resonance of silicon linking oxygen with a polysilylene sequence, i.e., that of the triad SiSiO, occurring in the range of 0–9 ppm was observed. No linear poly(dimethylsilylene) was formed; however, in some experiments made in other conditions the formation of white precipitate of poly(dimethylsilylene) was observed in the last stage of the process.

Initial concentrations of $^2D_2$ used here were high enough to ensure the concentration of poly(dimethylsiloxane) finally formed in this transformation to be well above the threshold concentration for the linear polymer formation in the equilibrated poly(dimethylsiloxane).[7,8] The equilibrium constants for the formation of cyclics

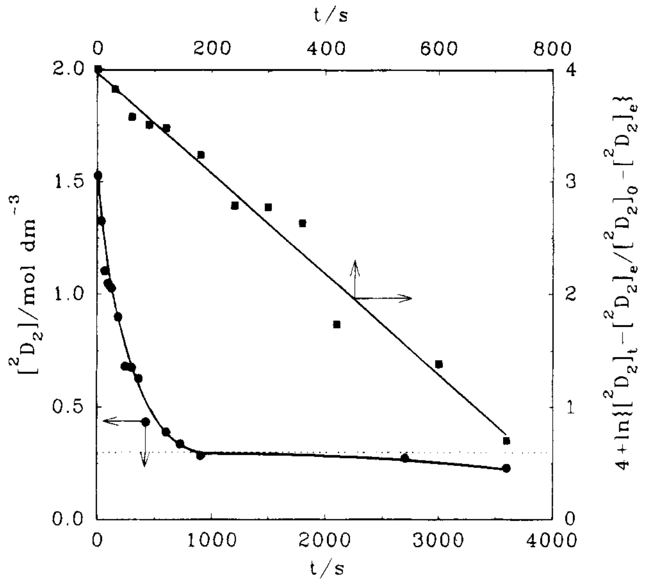


Figure 3. Monomer conversion–time dependence and its transposition to the first-order plot for the polymerization of $^2D_2$ in THF in the presence of potassium oligo(dimethylsiloxanolate); [SiOK] = 8 × 10^{-4} mol·dm^{-3}, 25 °C. The dashed line shows the concentration of $^2D_2$ at equilibrium of the Si–O bond cleavage and re-formation processes.

Table 1. Comparison of Concentrations of Cyclic Oligo(dimethylsiloxanes) $(Me_2SiO)_n$, n = 4–7, Found in the Reaction System after Full Anionic Transformation of $^2D_2$ in THF in the Presence of Potassium Dimethylsilanolate with Known Equilibrium Concentrations of These Oligomers in Poly(dimethylsiloxane) Equilibrated in Bulk and in an Ether Solution

	$-Me_2SiMe_2SiO-$ ($^2D_2$) 536 g·dm^{-3},[a] THF, 25 °C		$-Me_2SiO-$[b] 898 g·dm^{-3}, bulk, 110 °C		$-Me_2SiO-$[b] 212 g·dm^{-3}, diglyme, 60 °C	
n	$[(Me_2SiO)_n]$ (mol·dm^{-3})	w^c	$[(Me_2SiO)_n]_e = K_{Cn}$ (mol·dm^{-3})	w^c	$[(Me_2SiO)_n]_e = K_{Cn}$ (mol·dm^{-3})	w^c
4	0.192	0.52	0.19	0.52	0.21	0.48
5	0.098	0.33	0.09	0.31	0.13	0.37
6	0.028	0.12	0.03	0.13	0.036	0.12
7	0.006	0.03	0.09	0.04	0.0085	0.03

[a] Corresponds to 300 g·dm^{-3} of the Me_2SiO unit. [b] Data taken from ref 8. [c] Weight fraction of cyclic siloxanes, n = 4–7.

in equilibrated poly(dimethylsiloxane), K_{Cn}, above the threshold concentration could be approximated by equilibrium concentrations of these cyclics (eq 4).

$$K_{Cn} \approx [(SiMe_2O)_n]_e \tag{4}$$

The K_{Cn} value for $n > 3$ is known to be almost independent of temperature[7] and rather little modified by a solvent.[8] Thus, if we had indeed the full transformation of the silaether into poly(dimethylsiloxane) equilibrated independently of poly(dimethylsilylene) formed as the other product, then the concentrations of the cyclic siloxanes in this system should be approximately equal to the corresponding values of K_{Cn} reported in the literature. The comparison made in Table 1 fully confirmed that this was the case.

Similar reasoning could be applied to the equilibrated poly(dimethylsilylene) product. However, the concentration of the poly(dimethylsilylene) formed in this system is lower than the threshold concentration for the presence of the linear polymer fraction in the equilibrium with the cyclic fraction. Nevertheless, the conclusion about the independent equilibration of poly(dimethylsilylene) in the system studied is confirmed by the observation that relative yields of cyclics of the poly(dimethylsilylene) series $(Me_2Si)_m$, $(m = 5):(m = 6):(m = 7)$, were 0.06:0.92:0.002, respectively, similar to that found by Brough and West in the equilibrated system of cyclic dimethylsilylene oligomers in the same solvent.[9] Thus, the final product of the anionic polymerization of $^2D_2$ is the mixture of independently equilibrated poly(dimethylsiloxane) and poly(dimethylsilylene), both playing only the role of a diluent for each other. The poly(silaether) polymer has the thermodynamic tendency to be transformed according to eq 5.

$$[-Me_2SiMe_2SiO-]_n \rightarrow [-Me_2Si-]_n + [-Me_2SiO-]_n \quad (5)$$

There are two reasons for which the poly(silaether) structure is thermodynamically unstable as compared with the corresponding mixture of poly(silaacetal) (polysiloxane) and polysilylene. Both, polysilylene and polysiloxane, are strongly stabilized by resonance. In polysilylene the σ(Si$-$Si) orbital electron delocalization along the polysilylene chain has a strong impact on spectral properties of these polymers[10] and must considerably increase its thermodynamic stability. The effectiveness of this stabilization increases with the elongation of the polysilylene chain. Considerable red shift of the $\sigma \rightarrow \sigma^*$ (Si$-$Si) transition band is observed with an increase of the size of linear silylene olgiomers, thus giving evidence of increasing electron delocalization. Since oxygen atoms separating oligosilylene sequences in the poly(silaether) chain interrupt the transmission of the σ delocalization, the stabilization of the polymer structure is enhanced when the silylene sequences become larger. On the other hand, the silaacetal structure is additionally stabilized by negative hyperconjugation resulting from the interaction of the lone electron pair orbital of oxygen with the empty σ^* orbital of the neighboring Si$-$O bond.[11,12] This $p_\pi(O)-\sigma^*_\pi(Si-O)$ delocalization must strongly stabilize the polysiloxane chain relative to the poly(silaether) structure where there is no electronegative atom geminal to oxygen at silicon to give the effective p$-\sigma^*$ orbital interaction.

The transformation of poly(silaether) to polysilylene and polysiloxanes under conditions in which both types of skeletal bond, Si$-$O as well as Si$-$Si, may be broken and reformed could thus be an expected process.

The question arises whether carbon analogs, i.e., polyethers, would undergo analogous transformation giving corresponding polyacetals and a hydrocarbon polymer, e.g., 6, if conditions were applied in which all

$$(-CH_2CH_2O-)_n \rightarrow (-CH_2-)_n + (-CH_2O-)_n \quad (6)$$

skeletal bonds of the C$-$O and C$-$C types were cleaved and reformed.

Although the σ delocalization is of lower significance in the carbon catenate chain than in the silicon catenate,[10,13] however, the negative hyperconjugation is stronger in the polyacetal chain than in its silicon analog—polysiloxane.[11,12] Thus, the transformation according to eq 6 could be anticipated. The verification of this hypothesis by the analogous experiment to that with poly(silaether) is, however, difficult as there is no catalyst which would selectively cleave and reform the skeletal C$-$C and C$-$O bonds without affecting other bonds in the polymer.

The understanding of the unusual selective three-step course of the anionic polymerization of $^2D_2$ requires more investigations. Studies are continued.

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