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Ring-Opening Polymerization of Octamethyltetrasila-1,4-dioxane, $^2D_2$. 2. Cyclic Oligomer Formation and Mechanism of the Reaction

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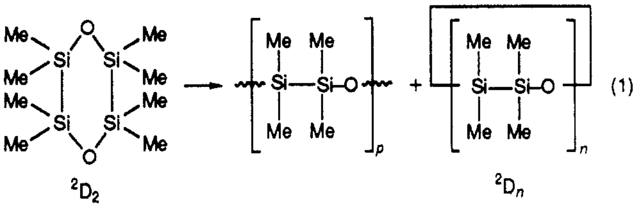
ABSTRACT: The kinetics of the cationic ring-opening polymerization of octamethyl-1,4-dioxatetrasilacyclohexane, $^2D_2$, initiated with trifluoromethanesulfonic acid in methylene chloride were studied. The cyclic oligomer formation, polymer formation, and monomer conversion were simultaneously followed by gas–liquid chromatography. The kinetic results provide evidence of direct interconversion of monomer and lower cyclic oligomers. The correlation of this process with the formation of the polymer fraction may be understood on the assumption that the chain propagation and the cyclic interconversion proceed through the same intermediate. The results are best explained by a mechanism which assumes that tertiary silyloxonium ions of a ring compound are active centers of propagation and at the same time serve as intermediates in the interconversion of cyclics. These cationic centers can undergo ring expansion–ring contraction isomerization which leads to the interconversion of cyclic oligomers. They are mostly formed by an acid activation of reactive end groups. The ester end group itself is unable to propagate the chain, but it may be converted with acid to the oxonium active center.

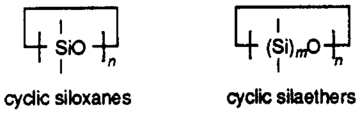
Introduction

It has recently been shown[1] that the cationic ring-opening polymerization of octamethyl-1,4-dioxatetrasilacyclohexane, denoted here by the symbol of $^2D_2$, leads to linear polymer and considerable amounts of cyclic homologs ^2D_n according to eq 1.



The formation of cyclic oligomers occurs in most ring-opening polymerization systems. Knowledge of the mechanism of the cyclization process is important for at least two reasons. First, the quantity of ring oligomers generated in the course of polymerization is often significant, and the yield of high molecular weight polymer is reduced. Thus, avoiding the excessive formation of cyclics is a very important problem in polymer synthesis.[2] Secondly, studies of oligomer formation accompanying the polymerization may give important information on the mechanism of the polymer formation since both processes, the oligomer ring generation and the chain propagation, are closely related to each other and often involve the same intermediate.[3-5] A study of the cyclic oligomer formation in the polymerization of $^2D_2$ seems to be important in both of the above-mentioned aspects. The polymer formed in this process is a material with interesting properties and practical potential. It is easily cross-linked[6-8] and may be transformed into ceramic materials[5] and oxidized to polydimethylsiloxane block copolymer.[5]

On the other hand, the theoretical aspects of reaction 1 deserve special attention. It is generally accepted to differentiate between two classes of the carbon–oxygen monomers, i.e., cyclic acetals and cyclic ethers. It is logical to extend this classification to silicon analogs of these monomers, thus differentiating between cyclic siloxanes (silaacetals) and cyclic silaethers. There is a great deal literature on the cationic ring-opening polymerization of cyclic acetals, cyclic ethers, and cyclic siloxanes, and for a review see refs 4, 9, and 10. Considerable attention has been devoted to the formation of cyclic oligomers in these processes. In contrast, very little is known on analogous reactions leading to polysilaethers. The first kinetic and equilibrium study of these reactions has been performed only recently using $^2D_2$ as the model monomer.[1] We believed that the extention of this study to the kinetics of the oligomer formation would permit us to formulate the mechanism of the cationic ring-opening polymerization of cyclic silaethers, which would broaden the knowledge of the polymerization of cyclic silicon monomers.



Some mechanistic similarities exist between the polymerizations of cyclic ethers and acetals. For example, the tertiary oxonium ion plays a significant role in both these processes.[4,9] In connection with this it is worth noting that the cationic ring-opening polymerization of $^2D_2$ involves Si–O bond opening[1,11] and shows a close similarity to the cationic ring-opening polymerization of certain cyclic siloxanes, in particular to that of octamethylcyclotetrasiloxane (D_4),[12] which is an important route to dimethylsiloxane polymers. Polymerizations of $^2D_2$ and D_4 both lead to equilibrium states containing appreciable amounts of monomer.[1,2] These reactions carried out in methylene chloride solution and initiated with trifluoromethanesulfonic acid show similar kinetic features.[1,12-15] In particular, their behavior on addition of small amounts of initial water is very characteristic and almost identical.[1] These similarities imply that the polymerizations of D_4

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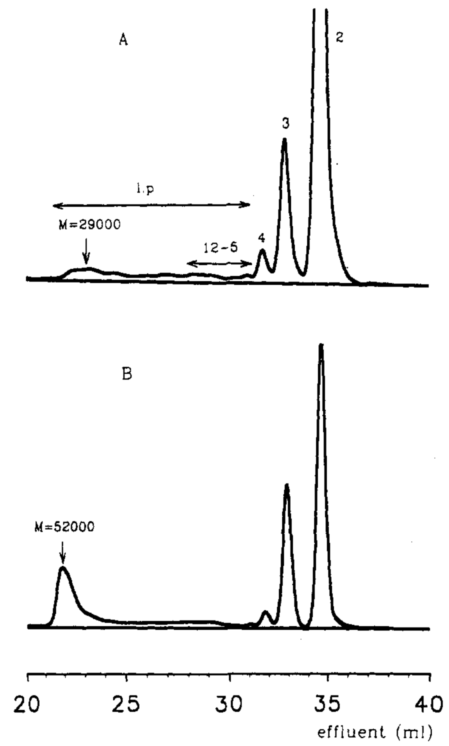


Figure 1. Gel permeation chromatogram of the polymerization system of octamethyl-1,4-dioxatetrasilacyclohexane, $^2D_2$, in methylene chloride, at 25 °C, $[CF_3SO_3H]_0 = 1.82 \times 10^{-3}$ mol·dm^{-3}: A, 25% of the monomer conversion; B, 60% of the monomer conversion. The number of ^2D units in cyclic oligomers, n, are marked at corresponding peaks. $[^2D_2]_0 = 2.2$ mol·dm^{-3}. Waters column for oligomers ($M = 10^2$–10^4) were used.

and $^2D_2$ may also show some similar mechanistic features. The character of the cationic polymerization of D_4 is very complex, and therefore, knowledge of the mechanism of this reaction is limited in spite of many "painful" and time-consuming investigations; for reviews see refs 10 and 14–16. Thus, deeper investigations of the cationic polymerization of $^2D_2$ may afford results important for a better understanding of the polymerization of cyclic siloxanes.

Results and Discussion

Kinetics of the Formation of Cyclic Oligomers: Initial Rates. The polymerization of octamethyl-1,4-dioxatetrasilacyclohexane, $^2D_2$, initiated with a strong protic acid such as CF_3SO_3H leads to the formation of a marked amount of cyclics of the oligohomologue series $(SiMe_2SiMe_2O)_n$, $n > 2$. The true monomer, $^2D_1$, is not formed nor does it appear in products of thermal depolymerization of the linear polymer formed from $^2D_2$.[7] The cyclic oligomers are already formed at the beginning of the polymerization together with the linear polymer. The oligomer fraction is dominated by lower cyclics, mostly $^2D_3$. A considerable amount of $^2D_4$ also appears while higher homologues are generated in much smaller quantities, Figure 1. No noticeable induction period is observed in the generation of the lower cyclic oligomers. The highest rate of their formation is in the beginning of the process. Also, the linear polymer fraction of fairly high molecular weight appears in the first stage of the polymerization of $^2D_2$.

Table 1. Comparison of Initial Rates of the Monomer $^2D_2$ Conversion, R_{02}, and Cyclic Oligomer $^2D_3$ and $^2D_4$ Formation, R_{03} and R_{04}, respectively, at Different Initial Concentrations of the Initiator and Monomer in the Polymerization of $^2D_2$ in Methylene Chloride at 25 °C in the Presence of Trifluoromethanesulfonic acid

no.	$[^2D_2]_0$[a]	$[CF_3SO_3H]_0$[b]	$-R_{02}$[c]	R_{03}[c]	R_{03}/R_{02}	R_{04}[c]	R_{04}/R_{02}
1	2.2	3.81	5.49	2.33	0.42	0.111	0.020
2	2.2	1.82	2.80	1.21	0.43	0.059	0.021
3	2.2	1.57	0.79	0.33	0.42	0.0172	0.022
4	2.2	0.80	0.41	0.180	0.44	0.0094	0.023
5	2.2	0.42	0.097	0.042	0.43	0.0022	0.023
6	1.10	0.80	0.232	0.143	0.62	0.0075	0.032
7	0.49	0.80	0.136	0.125	0.92	0.0053	0.039

[a] In mol·dm^{-3}. [b] In 10^3 mol·dm^{-3}. [c] In 10^3 mol·dm^{-3}·s^{-1}.

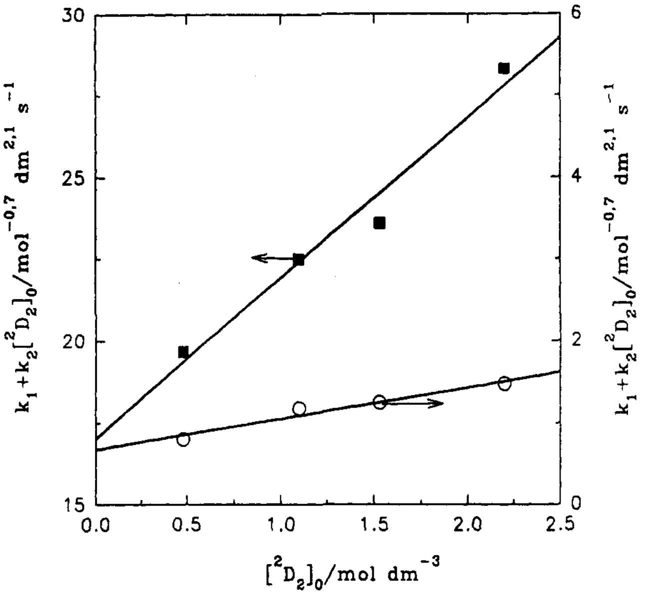


Figure 2. Dependence of the initial apparent specific rate, $k_1 + k_2[^2D_2]_0 = R_{0n}/[CF_3SO_3H]$,[1,7] $n = 3,4$, of the formation of dodecamethyl-1,4,7-trioxahexasilacyclononane, $^2D_3$, ■, and hexadecamethyl-1,4,7,10-tetraoxaoctasilacyclododecane, $^2D_4$, ○, on the monomer concentration in the polymerization of octamethyl-1,4-dioxatetrasilacyclohexane, $^2D_2$, in methylene chloride at 25 °C; $k_1(^2D_3) = 16.4$ mol$^{-0,7}$·dm^{2,1}·s^{-1}, $k_1(^2D_4) = 0.72$ mol$^{-0,7}$·dm^{2,1}·s^{-1}, $k_2(^2D_3) = 5.3$ mol$^{-1,7}$·dm^{5,1}·s^{-1}, $k_2(^2D_4) = 0.34$ mol$^{-1,7}$·dm^{5,1}·s^{-1}.

The kinetics of the monomer conversion have been studied earlier.[1] The kinetic law was determined on the basis of the initial rates.[1] The reaction was found to be first order in the substrate, second order with respect to the acid for CF_3COOH and CH_3SO_3H, and slightly lower, 1.7, for CF_3SO_3H. However, the rate and order of the reaction may be strongly influenced by association phenomena.[10,14] These factors may be eliminated if relative rates are studied. Thus, an important observation is that the ratio of the initial rate of the cyclic formation to the initial rate of the monomer conversion is independent of the initiator concentration (Table 1). Both these processes show the same order with respect to the acid. Since the monomer is converted partly to cyclics and partly to polymer, the conclusion may be drawn that the cyclization proceeds in competition with the chain propagation and both these processes may involve the same intermediate. In contrast, the cyclization shows a lower apparent external order with respect to the substrate than the monomer conversion process does as the rate of the cyclic formation relatively to the rate of the monomer consumption increases with the monomer dilution. (Since the contribution of cyclic formation to the overall polymerization is considerable at the beginning of the process, the first order of $^2D_2$ conversion observed on the basis of initial rates[1] is only a crude approximation.) Since the initial rate of the cyclic formation could be approximated by eq 2 (Figure 2), we may conclude that oligomers are formed from the propagation intermediate in two competitive ways.

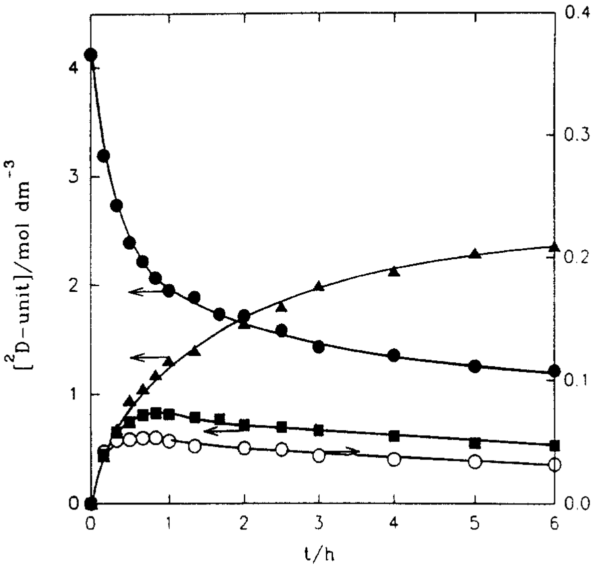


Figure 3. Time dependences of the conversion of the monomer, ●, the formation of the polymer, ▲, including all cyclics of the ^{2}D$_n$ series $n > 4$, and the formation of cyclic oligomers ^{2}D$_3$, ■, and ^{2}D$_4$, ○, for polymerization of octamethyl-1,4-dioxatetrasilacyclohexane, ^{2}D$_2$, in CH_2Cl_2 at 25 °C in the presence of trifluoromethanesulfonic acid, $[CF_3SO_3H]_0 = 1.57 \times 10^{-3}$ mol·dm^{-3}.

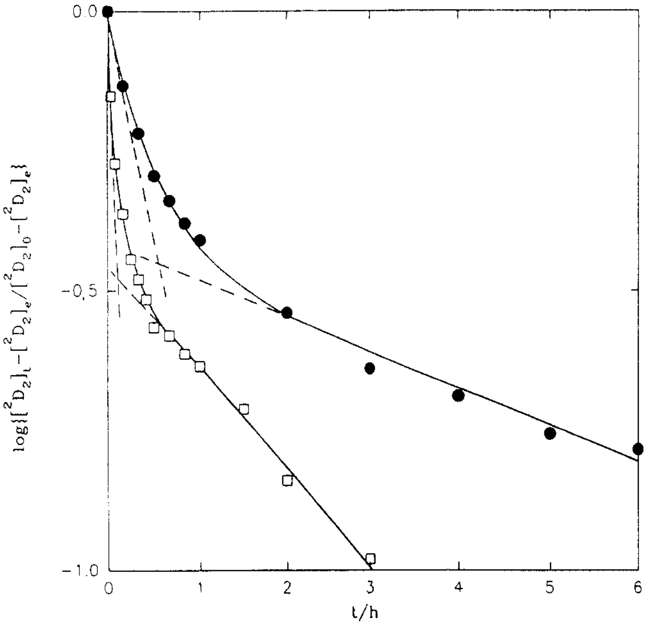


Figure 4. First-order dependence for the monomer conversion in the polymerization of octamethyl-1,4-dioxatetrasilacyclohexane, ^{2}D$_2$, in CH_2Cl_2 at 25 °C: □, $[CF_3SO_3H]_0 = 8.0 \times 10^{-4}$ mol·dm^{-3}, $[^2D_2]_0 = 1.10$ mol·dm^{-3}; ●, $[CF_3SO_3H]_0 = 1.57 \times 10^{-3}$ mol·dm^{-3}, $[^2D_2]_0 = 2.06$ mol·dm^{-3}.

$$\left(\frac{d[^2D_n]}{dt}\right)_{t=0} = (k_1 + k_2[^2D_2]_0)[CF_3SO_3H]^{1.7} \qquad (2)$$

$$n = 3 \text{ and } 4$$

Table 2. Variations of Relative to Monomer Concentrations of Dodecamethyl-1,4,7-trioxahexasilacyclononane, ^{2}D$_3$, and Hexadecamethyl-1,4,7,10-tetraoxaoctasilacyclododecane, ^{2}D$_4$, during the Polymerization of Octamethyl-1,4-dioxatetrasilacyclohexane, ^{2}D$_2$, in Methylene Chloride at 25 °C, in the Presence of Trifluoromethanesulfonic Acid, $[CF_3SO_3H]_0 = 1.57 \times 10^{-3}$ mol·dm^{-3}, $[^2D_2]_0 = 2.06$ mol·dm^{-3}

no.	time, t (min)	$[^3D_3]_t/[^2D_2]_t$	$[^2D_4]_t/[^2D_2]_t$	monomer convn[a]
1	10	0.094	0.0073	0.27
2	20	0.16	0.009	0.40
3	30	0.21		0.50
4	40	0.24	0.012	0.55
5	50	0.27	0.013	0.59
6	60	0.28	0.013	0.62
7	80	0.28	0.012	0.64
8	120	0.28	0.013	0.69
9	150	0.29	0.014	0.73
10	180	0.31	0.013	0.77
11	240	0.30	0.013	0.80
equilibrium	state[b]	0.30	0.013	1.00

[a] $[^2D_2]_0 - [^2D_2]_t/([^2D_2]_0 - [^2D_2]_e)$. [b] From ref 1.

Internal Kinetics. The monomer conversion time dependence is complex since the reaction slows down strongly as it proceeds. Two periods of the polymerization could be distinguished. The fast reaction period is first, followed by the slow reaction period (Figures 3 and 4).

Internal kinetics for the formation of cyclic oligomers are also complex. The concentration–time dependence curves show distinct maxima (Figure 3), thus giving evidence of kinetic enhancement of the cyclics over their concentration at equilibrium. As a rule, this feature is not observed in the polymerization of cyclotetrasiloxane D$_4$.[14] The maximum for ^{2}D$_3$ formation and that for ^{2}D$_4$ are attained at approximately the same time. After maximization the concentrations decrease to a soon-established quasi-stationary state in which the ratio of the concentrations of ^{2}D$_2$/^{2}D$_3$ and ^{2}D$_4$ is constant and as found in the equilibrium state (Table 2). However, absolute cyclic concentration values continue to decrease slowly until the equilibrium of the whole process is reached after a relatively long time. It may be concluded that the equilibria between cyclics are established much earlier than the equilibrium between cyclics and the polymer. Evidently, there is a mechanism capable of direct interconversion of lower cyclic oligohomologues including the monomer ^{2}D$_2$.

There is also a correlation between the formation–time dependence of lower cyclics and the monomer conversion–time dependence since the maximum of the cyclic concentration curves appears at a time when the transition between the slow and fast reaction periods is observed (Figure 4). After the concentration of oligomers reaches a maximum, the conversion of the monomer ^{2}D$_2$ becomes slow. The formation of the polymer fraction also distinctly slows down. These features indicate that the mechanism of the polymer formation and the mechanism of the monomer interconversion are coupled to each other. Presumably, the chain propagation and the cyclic interconversion proceed through the same intermediate.

In the second stage of the process ^{2}D$_2$ is formally transformed only to the polymer fraction and possibly to macrocycles. It is worth noting that the monomer conversion time curve, in the first-order semilogarithmic plot, tends to become linear in this reaction period, Figure 4. Thus, the polymerization is first order with respect to the monomer during this period. The slope is much lower than the initial slope which indicates that the specific rate of the transformation of ^{2}D$_2$ into the polymer is lower in the second stage. Kinetic features of the polymerization in both stages are different, and conditions for the polymer formation are changed. This implies that more than one active propagation center participates in the polymer chain formation. The relative concentrations of various propagation centers are changing up to the moment when the quasi-stationary concentrations of cyclics is established. Once the quasi-stationary state is obtained the reaction proceeds as first order, which indicates that the stationary state is extended to the active propagation species. Thus, various active propagation structures are somewhat related

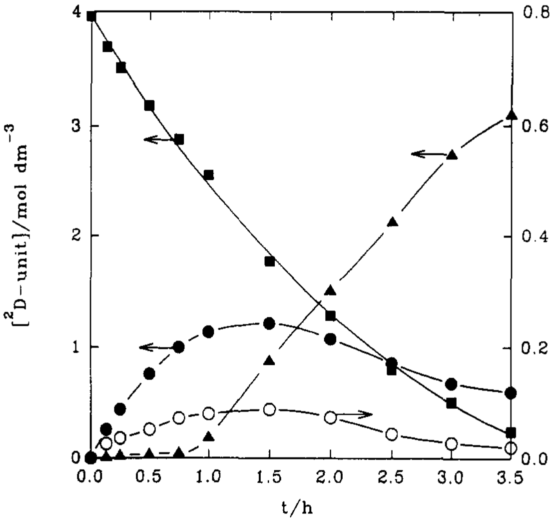


Figure 5. Time dependences of the monomer conversion ■, the polymer formation ▲, and the cyclic formation of ${}^2D_2$, ●, and ${}^2D_4$, ○, for the polymerization of dodecamethyl-1,4,7-trioxahexasilacyclononane, ${}^2D_3$, in CH_2Cl_2, at 25 °C in the presence of trifluoromethanesulfonic acid, $[CF_3SO_3H]_0 = 8.0 \times 10^{-4}$ mol·dm^{-3}.

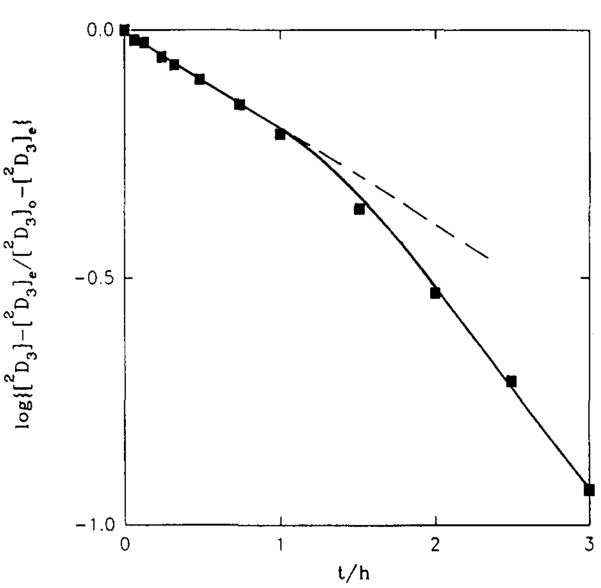


Figure 6. First-order dependence for the monomer conversion in the polymerization of dodecamethyl-1,4,7-trioxahexasilacyclononane, ${}^2D_3$, in CH_2Cl_2 at 25 °C. $[CF_3SO_3H]_0 = 8.0 \times 10^{-4}$ mol·dm^{-3}, $[{}^2D_3]_0 = 1.32$ mol·dm^{-3}.

to structures of cyclic oligomers which appear in the system.

These general conclusions are fully confirmed in studies of the polymerization of the higher analogue, ${}^2D_3$ (Figures 5 and 6), and in the depolymerization experiments (Figure 7). The ${}^2D_3$ is initially converted mostly to ${}^2D_2$ and, in a smaller part, to ${}^2D_4$. Very little polymer is formed in the first stage of the process. Concentrations of both cyclics ${}^2D_2$ and ${}^2D_4$ achieve a maximum at approximately the same time of the reaction. When the ${}^2D_3$ conversion–time dependence is presented in the first order (semilogarithmic) plot (Figure 6), in contrast to the behavior of the ${}^2D_2$ polymerization system, the reaction accelerates as it proceeds. It should be also noticed that the rate of the polymer generation initially is increasing as the polymer formation–time curve adopts an S-shape. These observations may indicate that the active propagation center formed from ${}^2D_2$ adds ${}^2D_3$ faster than the active center generated from ${}^2D_3$.

The depolymerization of isolated linear polymer fraction in the presence of CF_3SO_3H has also been followed, Figure 7. It leads to the competitive formation of all three cyclics

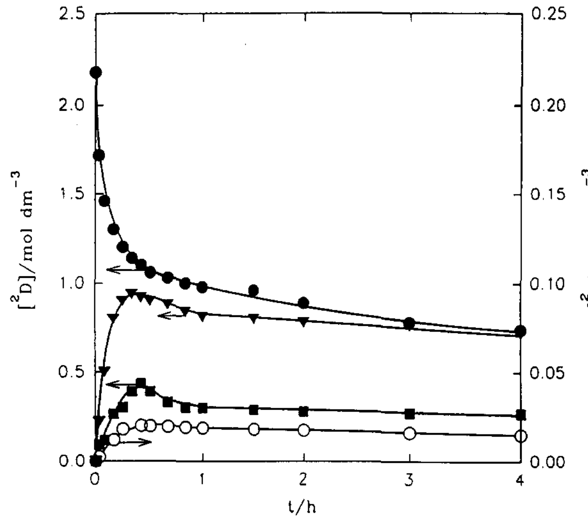


Figure 7. Concentration time dependences for cyclics ${}^2D_2$, ▼, ${}^2D_3$, ■, and ${}^2D_4$, ○, for the depolymerization of linear polyoxybis(dimethylsilylene) in methylene chloride at 25 °C in the presence of trifluoromethanesulfonic acid. Initial polymer concentration in ${}^2D$ units was $[\text{polymer}]_0 = 1.10$ mol·dm^{-3}, $[CF_3SO_3H]_0 = 8.0 \times 10^{-4}$ mol·dm^{-3}. ●: the monomer concentration–time dependence for the polymerization of ${}^2D_2$ under the same conditions; i.e., in CH_2Cl_2, at 25 °C, initial monomer concentration in ${}^2D$ units was 1.1 mol·dm^{-3}.

${}^2D_2$, ${}^2D_3$, and ${}^2D_4$. Concentrations of all these cyclics achieve a maximum after more or less the same polymer conversion. Then the concentrations very slowly diminish to reach their equilibrium values. Thus, unexpectedly, some kinetic enhancement of ${}^2D_2$, ${}^2D_3$, and ${}^2D_4$ is observed in the depolymerization process, which may be interpreted by assuming that a fraction of macrocycles is formed by another mechanism than that which functions in the formation of the ${}^2D_2$–${}^2D_4$ fraction. It is worth mentioning that Sigwalt and co-workers interpreted some of their results on the polymerization of D_3, such as the formation of large amounts of D_6, by competitive operation of two different mechanisms of the cyclization.[15,17]

Mechanism of the Oligomer Formation and Propagation. The monomers based on ${}^2D_2$ are composed of more than one repeating oxybis(dimethylsilylene) unit; thus, the comparison of concentrations of the individual cyclics of various sizes gives some additional information on the mechanism of their formation. An important observation is that during all of the polymerization process ${}^2D_3$ appears in the system at a higher concentration than ${}^2D_4$ which is the multiple of the monomer. Thus, no kinetic enhancement of the representatives of the [oxybis(dimethylsilylene)]$_{2n}$ series over oligomers with an odd number of repeating units was observed at least when protic acid such as CF_3SO_3H, CH_3SO_3H, and CF_3CO_2H were used as initiators. (It is in contrary to our first reports which were erroneous.[1,6] The kinetic enhancement of ${}^2D_4$ over ${}^2D_3$ was, however, noticed in the polymerization of ${}^2D_2$ initiated with some Lewis bases.)

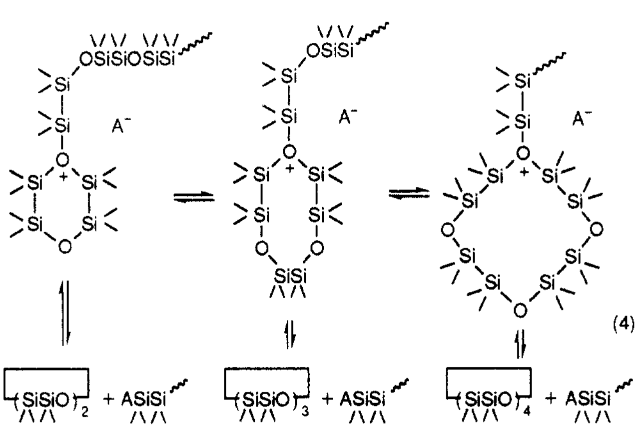
This results permits rejection of two mechanisms of the cyclic oligomer formation. Cyclics are not generated by ring expansion involving insertion of the monomer, eq 3a,

$$ {}^2D_2 + {}^2D_2 \nrightarrow {}^2D_4 \tag{3a} $$

$$ {}^2D_2 + -{}^2D_2- \xrightarrow{{}^2D_2} -{}^2D_4- \nrightarrow {}^2D_4 \tag{3b} $$

nor are they formed by linear growth followed by cyclization as a result of the intramolecular reaction between end groups (end to end ring closure, end-biting), eq 3b. Both of the above mechanisms should lead to a transient excess of $^2D_4$ over $^2D_3$. This behavior is in contrast to that of the polymerization of hexamethylcyclotrisiloxane D_3 where a considerable excess of D_{3n} oligomers is observed which is interpreted in terms of the end to end ring-closure scheme.[10] Instead, the polymerization of unstrained octamethylcyclotetrasiloxane D_4 does not exhibit the excessive formation of the monomer multiple cyclics[14] being similar in this feature to the polymerization of $^2D_2$.

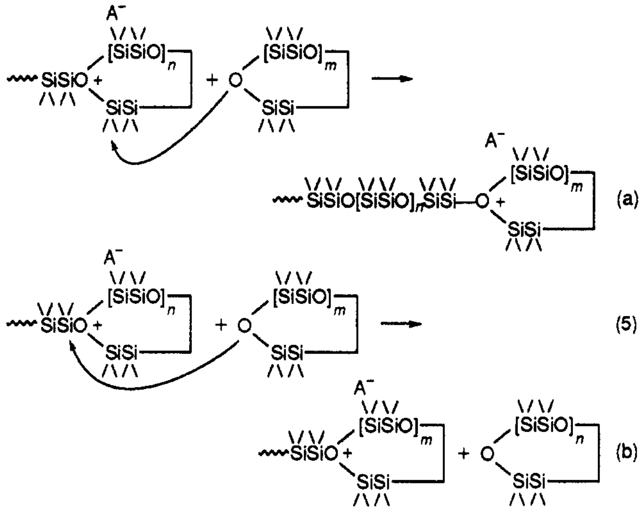
Kinetic results prove that a mechanism of transformation of various lower cyclic oligomers into each other is in operation in the polymerization of $^2D_2$. It may be further concluded that this mechanism of ring interconversion is somewhat coupled to the mechanism of chain propagation, and it is highly possible that both these reactions proceed via the same intermediate. The one mechanism which perfectly fits all of these observations involves the transient formation of cyclic tertiary oxonium ion intermediate. This pathway is analogous to that which is in operation in the ring-opening cationic polymerization of some cyclic ethers and acetals.[4,9,18,19] The cyclics are interconverted by isomerization of the cationic active chain ends through ring expansion–ring contraction according to eq 4. Similar isomerization was observed in the polymerization of cyclic ethers and acetals[20,21] and was postulated to occur in the polymerization of cyclic siloxanes.[14,15,22]

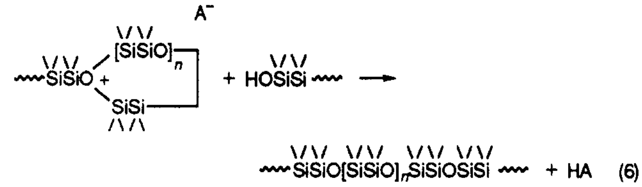


The attack of the counterion on exocyclic silicon bound to the oxonium center leads to the conversion of the cationic center into an inactive center, possibly the ester or silanol end group (the counterion A⁻ may have a complex structure including water and/or acid molecules), with regeneration of the cyclic (eq 4). However, the same transformation to the inactive center may take place without the reformation of the cyclic if the attack is directed to an endocyclic silicon at the oxonium center. In such a case the cyclic moiety of the cationic center is opened and it extends the chain.

The analogous nucleophilic attack of the monomer or its oligohomologue results in the reformation of the cationic active center, eq 5a,b. The structure of the new center formed, i.e., the size of the oxonium ion ring, corresponds to the structure of the attacking nucleophile. The propagation occurs when the attack of the monomer or its homologue is directed to the ring, eq 5a. If, however, the attack occurs at the exocyclic silicon atom, there is only exchange of the cyclic moiety in the active propagation center, eq 5b. The contribution of this reaction to the cyclic interconversion process in the beginning of the polymerization of $^2D_2$ is represented by the $k_2[^2D_2]_0[CF_3SO_3H]^{1.7}$ component in eq 2.

There is also the possibility of the reaction of the propagation center with the silanol end group leading to chain coupling by the condensation process, eq 6.

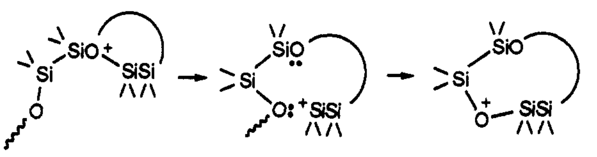




In the initial period of the polymerization of $^2D_2$ the propagation proceeds through the addition of the monomer molecule to the active propagation center built of the monomer species producing the same type of the cationic active center. However, the center may also be transformed into the $^2D_3$ cationic center and further to the $^2D_4$ cationic center. Also, $^2D_3$ and $^2D_4$ species formed according to eqs 4 and 5b may react as monomers with the active center. Thus, the propagation becomes a complex process involving various combinations of the cyclic cationic centers and cyclic monomer structures. It is an interesting case of a copolymerization system in which comonomers and active propagating centers may be interconverted. The reactivity for various monomer-active center combinations is different, which is partly responsible for the deviation from first-order kinetics in the first stage of the process. In the second stage, when these cyclic species are in pseudoequilibrium, the relative contribution from each of these combinations is not changed with progress of the reaction, and linear dependence in the first order plot is observed.

As the reaction proceeds, other cyclic oligohomologues are formed and the whole spectrum of active propagating center structures appears. In the polymerization of $^2D_2$ these new centers must be less reactive toward the monomer and the polymer formation slows down strongly, deviating from the first-order run. Instead, in the polymerization of $^2D_3$ the new center formed from $^2D_2$ reacts faster with the monomer $^2D_3$; thus, the specific rate of the $^2D_3$ conversion is increased.

The maximum on the concentration time curves for the lower cyclics in the depolymerization process may be interpreted in terms of a dichotomy in the mechanism of the formation of ring species. The lower cyclics are readily formed by the mechanism involving the isomerization of the active propagation center, eq 3. It is possible that this isomerization occurs by a dissociative pathway with transient formation of a very short lived silylenium ion or by a borderline type of the mechanism involving an incipient silylenium ion according to eq 7. In this type of dissociative pathway the incipient or a very short lived silylenium ion is migrating to a neighboring oxygen. Such a mechanism is not likely to operate in the formation of macrocycles which are formed much more slowly as a result of back-biting or end to end ring closure. Certainly, the


(7)

classical S_N2 mechanism for the active center isomerization cannot be a priori rejected. The proximity effect favors the formation of smaller cycles by the S_N2 route in comparison with macrocycles as well.

The Mechanism of the Generation of the Tertiary Silyloxonium Centers. In analogy to the cationic polymerization of cyclic siloxanes[12,23] the following reactions should be considered in the $^2D_2$ polymerization system.


$$CF_3SO_3H + \text{-SiSiOSiSi-} \rightleftharpoons CF_3SO_3SiSi\text{-} + HOSiSi\text{-} \quad (8)$$

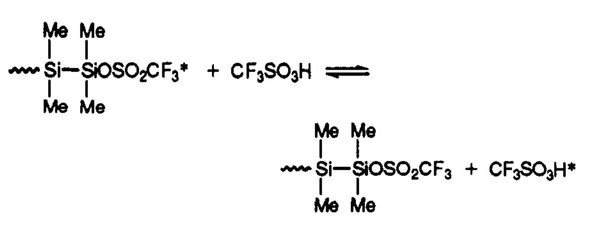

$$\text{-SiSiOH} + \text{-SiSiOH} \rightleftharpoons \text{-SiSiOSiSi-} + H_2O \quad (9)$$


$$\text{-SiSiOSO}_2CF_3 + H_2O \rightleftharpoons \text{-SiSiOH} + CF_3SO_3H \quad (10)$$

The acid opens the monomer ring by the cleavage of the siloxane bond which leads to the formation of silyl ester and silanol reactive end groups according to general eq 8, which also makes an allowance for the possibility of analogous reaction of the cleavage of an oligomer ring or the polymer chain and reversibility of all these processes. The silanol end group may undergo homofunctional condensation producing water according to eq 9. Finally, there is fast end group interconversion reaction according to eq 10.[23] Water and possibly silanol forms strong complexes with acid,[13,14,24] which may modify eqs 8–10.

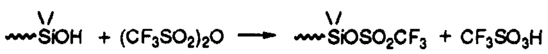
The confirmation of the above scheme represented by eqs 8–10 comes from the NMR studies. When CF_3SO_3H is added to the monomer in CD_2Cl_2 at room temperature a single signal is observed in ^{19}F NMR at −78.18 ppm (Figure 8). This signal is broadened when the temperature is lowered and eventually is split into two signals. One signal, stronger, at −77.97 ppm (−60 °C) is identified as belonging to an ester end group, as it corresponds to the signal of the model compound $CF_3SO_3SiMe_2SiMe_3$, $\delta(^{19}F) = -77.9$ ppm in CD_2Cl_2. The second signal, weaker, at −79.31 ppm is identified as triflic acid. Since the initial concentration of the acid is small and the reactions 8–10 occur relatively fast, the acid, end groups, and water may appear in stationary concentrations.

The fastest process of the reaction sequence (8–10) is presumably the end group interconversion eq 8, as judged from studies of analogues reactions in the polysiloxane system.[24,25] This reaction may be responsible for the coalescence of the ester and acid signal. However, another process should be taken into account. This is the direct exchange reaction between the ester and acid according to eq 11. The following observation gives support for the


$$\sim Si(Me)_2\text{-}Si(Me)_2OSO_2CF_3^* + CF_3SO_3H \rightleftharpoons \sim Si(Me)_2\text{-}Si(Me)_2OSO_2CF_3 + CF_3SO_3H^* \quad (11)$$

importance of reaction 11. Triflic anhydride was introduced to the $^2D_2 + CF_3SO_3H$ polymerization system represented by the ^{19}F NMR spectrum in Figure 8C. The spectrum after the anhydride addition taken at −60 °C is shown in Figure 8D. Separate signals for the ester end group and for the acid underwent coalescence into a singlet signal which indicated that the rate of the acid–ester exchange was considerably enhanced. The increase of the rate of the end group exchange according to eq 10 had not been expected since the water and silanol group concentration was reduced according to reactions of eqs 12 and 13. Instead, the acid–ester exchange rate according to eq

$$H_2O + (CF_3SO_2)_2O \longrightarrow 2CF_3SO_3H \quad (12)$$


$$\sim SiOH + (CF_3SO_2)_2O \longrightarrow \sim SiOSO_2CF_3 + CF_3SO_3H \quad (13)$$

11 should have been enhanced as the concentration of these species was increased on the anhydride addition. (The formation of complexes of the acid with water and silanol is again ignored.)

Conclusions from the ^{19}F NMR spectra are confirmed by ^1H and ^{29}Si NMR spectra of these systems. After the introduction of the anhydride at −60 °C the ^{29}Si NMR signal appears at 39.9 ppm assigned to the silicon atom covalently bound to the ester group, although this signal is not seen in the spectrum before the anhydride addition.

The mechanism of the initiation should be in agreement with the kinetic law of the polymerization. According to our earlier study,[1] the initial rate of the polymerization is close to second order with respect to the acid and close to first order with respect to the monomer. We assumed that the monomer is mostly consumed in the propagation which should be of first order in monomer and of first order in the active propagation center. Thus, the stationary concentration of the active propagation center is

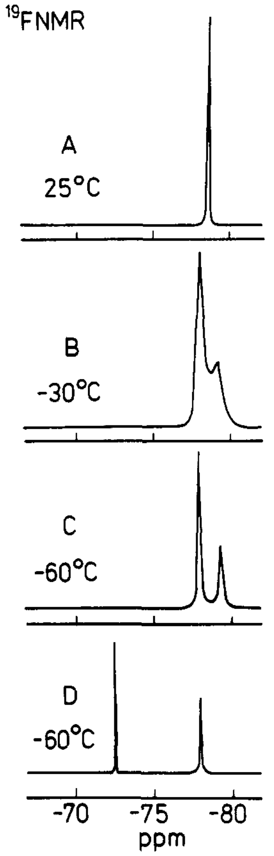
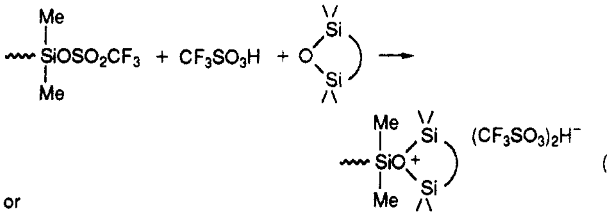


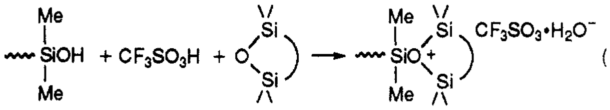
Figure 8. ^{19}F NMR spectra of the polymerization system of octamethyl-1,4-dioxatetrasilacyclohexane, $^2D_2$, in CD_2Cl_2 initiated with CF_3SO_3H at various temperatures. $[CF_3SO_3H]_0 = 0.1$ mol·dm^{-3}, $[^2D_2]_0 = 2.2$ mol·dm^{-3}. The spectrum 8D is taken under the same conditions as the 8C after introduction of trifluoromethanesulfonic anhydride, signal at −72, 73 ppm, $[(CF_3SO_2)_2O]_0 = 0.3$ mol·dm^{-3}.

proportional to the square of the initial acid concentration which means that two molecules of acid participate in the formation of the center.

The cyclic tertiary siloxonium ion is thus generated by acid activation of the end group according to eqs 14 and 15.


(14)

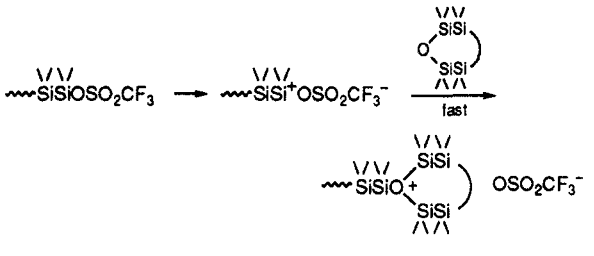
or


(15)

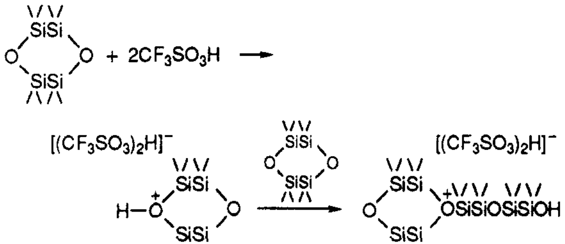
Since the ester group may be directly exchanged by the acid according to eq 11, the generation of the active centers through the activation of the ester groups, eq 14, seems to be plausible. Most of the acid initially introduced to the system is transformed into the ester; thus, the stationary concentration of the ester group is independent of the monomer concentration which fits well to the first-order kinetics of the overall polymerization with respect to the monomer.

Certainly, eqs 14 and 15 as well as eqs 4 and 5 are oversimplified. They do not explain the influence of water on the rate and activation parameters of the reaction observed earlier.[1] According to the earlier studies of the cationic polymerization of cyclic siloxanes, water participates in the formation of the active center and the counterion may contain more than one molecule of water.[14,26,27]

The question may arise whether the oxonium ion propagation center can be formed directly by ionization of the ester group without the activation by the acid molecule according to eq 16. Since most of the acid introduced to the system is converted to the ester the stationary concentration of the ester group should be approximately proportional to the initial concentration of the acid, which would lead to the first order of the polymerization with respect to the initiator. Thus, the self-ionization mechanism seems to be in disagreement with the second-order kinetics with respect to the acid. However, the apparent order in acid of the monomer conversion is slightly lower than 2,[1] and this deviation could be interpreted in terms of the competition of reaction 14 with reaction 16. If this was the case the ester itself could be the initiator of the reaction. In order to check this possibility the experiment was performed exploring the model ester $Me_3SiMe_2SiOSO_2CF_3$ as an initiator. The ester containing a small amount of triflic acid was introduced to the 2 mol·dm^{-3} solution of $^2D_2$ in methylene chloride to obtain 0.01 mol·dm^{-3} solution of the ester. Relatively fast polymerization was observed induced by the acid contamination of the ester. However, no reaction occurred for at least 100 h after the introduction to this system of 3 × 10^{-3} mol·dm^{-3} of 4-methyl-2,6-di-*tert*-butylpyridine, which is able to form a complex with the protic acid but due to a bulky structure is not able to neutralize other cationic centers. This result clearly proves that the ester itself cannot be the initiator of the polymerization of $^2D_2$. It has been shown earlier that the triflic ester end group in a polysiloxane chain is unable to initiate the polymerization of cyclic siloxanes.[14,23]


(16)

Another initiation route which should be taken into consideration is the formation of the oxonium ion by activation of the monomer with a complex comprising two acid molecules according to eq 17. (This pathway requires the second order of the polymerization with respect to $^2D_2$. However, the complex mechanism of the polymerization and approximate form of the kinetic law determined in ref 1 does not permit the rejection of the contribution from this mechanism.)


(17)

Although the chain growth by the monomer addition to the oxonium ion active propagation center seems to be of primary importance in the polymerization of the cyclic silaether, the role of condensation reactions in the chain extention process, eq 6, should not be neglected either.

The oxonium ion active propagation centers must appear in a low concentration being in equilibrium with the silyl ester end group. Attempts at the detection of these ions by direct experiment in the low-temperature ^{29}Si, ^{19}F, and ^1H NMR spectroscopy of the $^2D_2$ polymerization systems were unsuccessful. For example, only a single resonance of silicon bound to the ester is observed in CD_2Cl_2 solution at −60 °C, using a 300-MHz spectrometer. The signal appears at 39.85 ppm about 8 ppm upfield from the resonance of the corresponding silicon atom of the model ester $CF_3SO_3SiMe_2SiMe_3$ (48.6 ppm), thus in the region of the covalently bonded ester group. This is in contrast to the cationic polymerization of cyclic ether, where corresponding tertiary oxonium ions were directly observed in high-resolution spectra of ^1H NMR,[28] ^{19}F NMR,[29] and ^{13}C NMR.[30] No tertiary trisilyloxonium ions have so far been observed. However, mono- and disilyloxonium ions have recently been detected by the NMR spectroscopy.[31]

The kinetic evidence for the oxonium ion structure of the active propagation center in the polymerization of cyclic silaether implies that a similar mechanism may operate in cationic polymerization of certain cyclic siloxanes. In particular, results obtained here give support to the oxonium ion pathways postulated for the polymerization of D_4.[15,22,32]

Experimental Part

Solvents and Initiator. The purification of methylene chloride and trifluoromethanesulfonic acid was described in ref 1. Dideuteriodichloromethane (Merck) for NMR spectroscopy was dried over CaH_2 and distilled on a high vacuum line to an ampule closed with Rotaflo stopcock.

Monomers. Octamethyl-1,4-dioxatetrasilacyclohexane, $^2D_2$, was synthesized and purified according to the description in ref

1. Dodecamethyl-1,4,7-trioxahexasilacyclononane, $^2D_3$, was isolated from products of the cationic polymerization of $^2D_2$ carried out in CH_2Cl_2 at 25 °C. Initial monomer concentration was 0.45 mol·dm^{-3}. The polymerization was quenched at 30% of monomer conversion with an excess of Et_3N. The solvent was evaporated, and precipitated $^2D_2$ was separated. The remaining part was distilled. The fraction distilling at 60–65 °C/10^{-2} mmHg was collected. The purity of $^2D_3$ checked by gas–liquid chromatography was better than 99%.

Polymer. Polyoxybis(dimethylsilylene) for studies of the kinetics of depolymerization was prepared as described in ref 7.

Reagents and Model Compounds. 2.6-Di-*tert*-butyl-4-methylpyridine, synthesized in the Center of Molecular and Macromolecular Studies, was purified by vacuum distillation. Its purity was confirmed by gas–liquid chromatography and ^1H NMR analysis. Bis(pentamethyldisilanyl) ether (**1**) was synthesized according to the description in ref 33. Pentamethyldisilanyl trifluoromethanesulfonate (**2**) was synthesized by mixing of 5.6 g (0.02 mol) of **1** with 5.7 g (0.02 mol) of trifluoromethanesulfonic anhydride. A catalytic amount (10^{-3} mol·dm^{-3}) of trifluoromethane sulfonic acid was added. The mixture was kept at ambient temperature for 20 h. Then, it was distilled. Nine g of **2** was obtained (yield 80%) bp 30 °C/0.1 mmHg. NMR (in CD_2Cl_2): $\delta(^{19}F) = -77.91$ (52) ppm; $\delta(^{29}Si) = 46.6$ ppm, -18.3 ppm; $\delta(^1H) = 0.54$ ppm, 0.21 ppm.

Kinetics. All operations in the preparation of solution for kinetic studies and in the measurement of the reaction rate of $^2D_2$ were performed using a high vacuum technique to avoid traces of water and oxygen. It was necessary because fortuitous water affects the rate[1] and the active cationic centers in the polymer undergo easily oxygenation generating silaacetal groups in the chain.[1] Kinetics were followed by sampling and analysis by gas–liquid chromatography. The experimental procedure in kinetic studies in the high vacuum technique is described in detail in ref 1. The kinetic experiment on the polymerization of $^2D_3$ was performed under prepurified argon.

Analysis. The NMR spectra were recorded with a Bruker 300 MSL instrument operating at 300 MHz for ^1H, 59.6 MHz for ^{29}Si, and 282.4 MHz for ^{19}F. The solvent was CD_2Cl_2. The gel permeation chromatography (GPC) analysis were made with a LKB2150-HPLC PUMP filter with an Optilab 903 interferometric detector. The Waters column system including 1000A, 500A, and 2·100A columns was used. The solvent was THF, and the flow rate was 0.7 mol/min. The gas–liquid chromatography (GLC) analyses were performed with a Jeol JGC 1000 instrument fitted with a thermal conductivity detector, using a 2-m column, $d = 3$ mm, filled with 10% OV101 on Varaport 60/80 mesh, temperature 40–250 °C programmed 15 °C/min, temperatures: detector 260 °C, injector 220 °C; internal standard tridecane.

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