

# Cationic Polymerization of a Model Cyclotrisiloxane with Mixed Siloxane Units Initiated by a Protic Acid. Mechanism of Polymer Chain Formation

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**ABSTRACT:** The structure of polysiloxane chain generated by the quenched cationic ring-opening polymerization (CROP) of 2,2-diphenyl-4,4,6,6-tetramethylsiloxane (**1**) initiated by trifluoromethanesulfonic acid was studied<sup>1</sup> by <sup>29</sup>Si NMR and by statistical methods. The sequential analysis was performed at the pentad level using the first-order Markov chain statistics. Sequences at chain extremities were studied in the polymer obtained by quenched polymerization of **1** and in polymers obtained by polymerization of this monomer with chain transfer to hexamethyldisiloxane. The results indicate that the randomization processes, such as intermolecular exchange of chain fragments and backbiting, do not occur during the polymerization of monomer **1**. Dominating is the monomer addition giving the symmetrical arrangement of siloxane units  $\rightarrow\text{OSiMe}_2\cdot\text{OSiPh}_2\cdot\text{OSiMe}_2\rightarrow$  (ca. 68%) by the ring opening at oxygen bridging methyl-substituted silicons. Only one of the two possible unsymmetrical additions occurs, i.e.,  $\rightarrow\text{OSiMe}_2\cdot\text{OSiMe}_2\cdot\text{OSiPh}_2\rightarrow$  (ca. 32%). The results are interpreted in terms of propagation accompanied by the fast deactivation mechanism. This pathway involves a formation of the terminal cyclic trisilyloxonium ion intermediate which is transformed to terminal silyl ester with incorporation of its cyclic fragment to the polymer chain. Chain growth proceeds stepwise with competitive cyclization by the intermolecular reaction of the silyloxonium intermediate with the silanol end group. Permanent initiation of new chains by the acid dominates the reaction pattern.

## Introduction

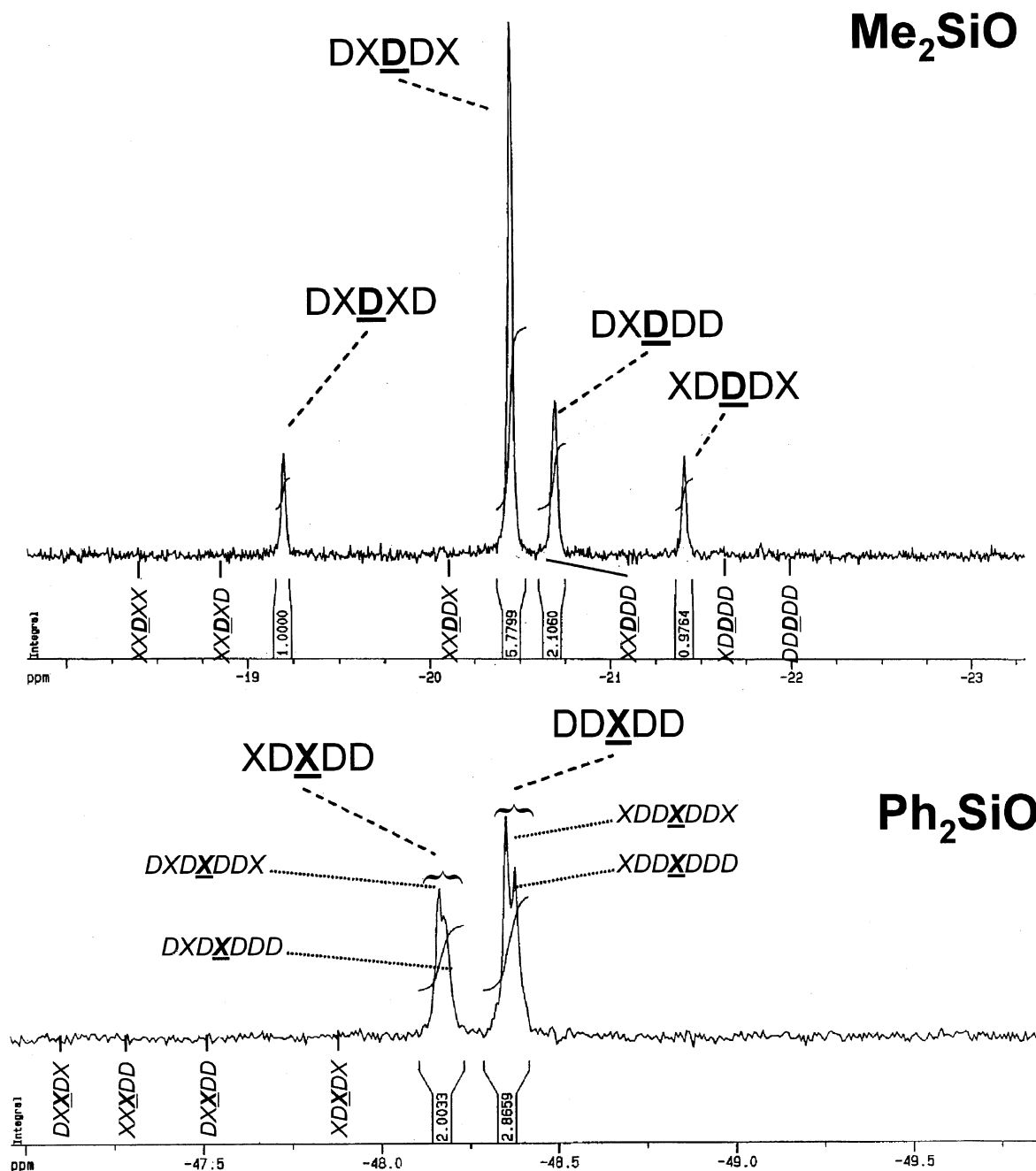
Cationic ring-opening polymerization (CROP) of cyclotrisiloxanes is a very important reaction in the synthesis of linear polysiloxanes and is extensively used in both industry and research laboratories. The mechanism of polymerization is very complex and has not yet been thoroughly elucidated. The chain mechanism involving a tertiary silyloxonium ion propagation center<sup>2</sup> does not fit into some of the features of the reaction, such as the stepwise polymer chain growth,<sup>3,4</sup> the kinetics of formation of cyclic oligomers,<sup>5,6</sup> and the relatively low rate of the polymerization initiated by the system leading to the formation of a persistent tertiary silyloxonium ion.<sup>7</sup> New approaches to the study of the cationic polymerization of cyclotrisiloxanes are needed.

CROP of cyclotrisiloxanes with mixed siloxane units, such as 2,2-diphenyl-4,4,6,6-tetramethylcyclotrisiloxane,<sup>1</sup> leads to polymers having chains composed of two kinds of siloxane units. The sequences of these units are closely related to the mechanism of the polymer chain formation. Studies of the CROP of these monomers may therefore give important information leading to a better understanding of the polymerization. Cyclic trisiloxanes are suitable model monomers for this reason, since, due to the strain in their six-membered rings, the polymerization occurs more selectively. Chain extension is much faster than the processes which cause chain randomization, such as backbiting and chain transfer, and therefore it may be investigated more closely when these undesired processes can be neglected. This feature is well recognized for the anionic poly-

merization of cyclotrisiloxane, which, due to its selective course, is widely used for the controlled synthesis of polysiloxanes.<sup>8</sup> Recent studies of the anionic polymerization of a cyclotrisiloxane with mixed units proved that a high chemoselectivity and, in some cases, regioselectivity exist in this process.<sup>9–12</sup> Sequential analysis of polymers obtained in the anionic route proved to be useful in understanding of the detailed mechanism of monomer addition to the polymer chain.<sup>10</sup> We have extended this approach to obtain similar information about the CROP process. Our first attempts were successful, as they showed that the CROP of **1**, initiated by a strong protic acid, proceeds in the absence of the chain randomization processes.<sup>1</sup> Thus, the knowledge of sequence distribution in the polysiloxane obtained by the CROP of **1** should give a deeper insight into the mechanism of cationic polymerization of cyclotrisiloxanes in general. In particular, the sequential analysis using Markov chain statistics, complemented by the examination of the polymer chain structure at its extremities, was expected to give information on the mechanism of chain extension in this process.<sup>1,10</sup>

The exploration of cyclotrisiloxane CROP may be useful in relation to the possible applicability of this reaction in the controlled synthesis of polysiloxanes. It has recently been shown by Sigwalt et al.<sup>7</sup> that in some CROP's of cyclotrisiloxanes the yield of undesired cyclic products may be effectively reduced and that a high degree of molecular weight control may be achieved. In this respect, the CROP has some advantages over the anionic process. Many cationic initiators are very effective and can be easily removed from the polymer products. The CROP polymerization systems can also tolerate some functional groups that are not tolerated by the anionic systems.

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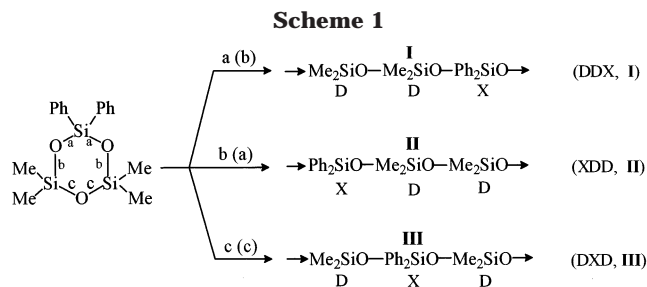


**Figure 1.**  $^{29}\text{Si}$  NMR spectrum of polysiloxane obtained by the polymerization of **1** initiated by  $\text{CF}_3\text{SO}_3\text{H}$ .  $[\mathbf{1}]_0 = 1.2 \text{ mol}\cdot\text{dm}^{-3}$ ,  $[\text{CF}_3\text{SO}_3\text{H}]_0 = 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ , and temperature  $25^\circ\text{C}$ . Conversion of **1** was 80%. Cyclics were separated by repetitive dissolving of polymer in  $\text{CH}_2\text{Cl}_2$  and precipitating in methanol.

## Results and Discussions

**Model.** The model monomer 2,2-diphenyl-4,4,6,6-tetramethylcyclotrisiloxane (**1**) was subjected to CROP initiated by trifluoromethanesulfonic acid as described in ref 1. The phenyl cleavage by  $\text{CF}_3\text{SO}_3\text{H}$ <sup>13–15</sup> is much slower than the polymerization and does not affect the sequencing of siloxane units. The polymer chain is composed of the two types of units:  $\text{Me}_2\text{SiO}$  (denoted by D) and  $\text{Ph}_2\text{SiO}$  (denoted by X), the sequence composition of which was analyzed by  $^{29}\text{Si}$  NMR at the pentad level. The assignment of the pentad signals was made earlier by Jancke et al.<sup>16</sup> A high precision in separating of the signals of pentads and quantitative integration was achieved using in tandem the gated decoupling and shifting agent techniques. The separation of signals of  $\text{Ph}_2\text{SiO}$  into heptads was even observed (Figure 1).

In the first approach, the sequential analysis was performed according to the second-order Markov chain statistics, which assumes that the polymer chain is generated by propagation on the cyclic tertiary silyloxonium ions.<sup>1</sup> The method used here is based on the first-order Markov chain. This method corresponds more accurately to the level of experimental precision and is more universal since it also fits well into other mechanisms of chain growth. Results of the sequential analysis were checked by the Monte Carlo simulation of the sequencing using probability parameters determined by Markov statistics. The method was, in general, the same that was used in our studies of the anionic polymerization of the same model monomer.<sup>10</sup> The Markov chain analysis was completed by analyzing the structure of the chain fragments at chain extremities.



In these experiments, the polymers were obtained in special ways in order to ensure that additional information about the sequences of units in the polymer chain could be obtained. Thus, quenching of the polymerization was performed in order to cap the siloxane unit sequence at the growing chain end and hence to study the instantaneous "stationary" fractions of various triads at the active propagation terminus. On the other hand, the polymerization involving chain transfer to hexamethyldisiloxane was performed in order to study triads at both chain extremities next to fragments of the chain transfer agent incorporated into the chain ends.

**Analysis of the Chain Microstructure.** The analysis of the sequences of D and X units in linear polymers based on  $^{29}\text{Si}$  NMR confirmed that the chain growth occurs without reactions of the polymer chain cleavage, which include interchain exchange of polymer segments (chain scrambling), backbiting, and interchain exchange of terminal units. The  $^{29}\text{Si}$  NMR spectrum showed signals of only those pentads which might be formed by the addition of undivided monomer units. There were no "forbidden" pentads (indicative of chain randomization), i.e.: XXXXX, XXXXD, XXXDX, XXXDD, DXXXD, DXDXD, XXDXX, XXDXD, DDDDD (Figure 1). Moreover signals of the both allowed pentads having the  $\text{Ph}_2\text{SiO}$  center unit are split into two heptads (Figure 1) as expected if randomization is excluded. Therefore, the sequencing of units is exclusively controlled by chain extension.

The triad resulting from monomer addition to the growing chain consists of D and X units arranged in one of the three possible ways, **I**, **II**, and **III** (Scheme 1). The sequence of the three units at the chain end depends on the site of the opening of the monomer ring and on direction of the addition of its opened form to the growing chain. There are three nonequivalent sites of opening of the monomer ring marked as **a**, **b**, and **c** in Scheme 1 and two ways of addition of the opened monomer to the propagation center, as it may be added either by nucleophilic oxygen or by electrophilic silicon. In the anionic polymerization of cyclosiloxanes, the monomer is added by silicon. In the CROP, the addition depends on the mechanism of polymerization. If the active center on the polymer is cationic or at least electrophilic, the addition of the monomer should occur through its nucleophilic part, i.e., by oxygen. In this case, the opening of the monomer ring at each of the three sites (**a**, **b**, **c**) gives respective arrangement marked by **I**, **II**, or **III** in Scheme 1. However, the reverse addition is expected for the activated monomer mechanism. In this case, opening at **a**, **b**, **c** would give sequences **II**, **I**, and **III**, respectively (Scheme 1).

**Analysis using Markov Statistics.** The aim of our study was to determine the contributions to the chain structure from the three sequences of Scheme 1. The

sequential analysis based on the Markov statistics was performed in an analogous way to that described in the study of anionic polymerization of **1**.<sup>10</sup> This analysis involves a set of equations (available as Supporting Information) which are numerically solved giving probabilities and conditional probabilities of the monomer additions **I**, **II**, and **III** (Scheme 1, Table 1), corresponding to the relative rates of the three modes of the monomer addition. However, the statistical method itself is not sufficient to achieve our goal, as the set of equations obtained by this method gives at least two equivalent solutions symmetrical to each other, i.e.,  $P_I$ ,  $P_{II}$ , and  $P_{III}$  and  $P_{II}$ ,  $P_I$ , and  $P_{III}$ . The method cannot differentiate between the order of units **I** and **II** for the obvious reason that the analytical method does not distinguish between the directions of chain growth. The pair of unsymmetrical pentads, such as XD $\overline{\text{D}}$ XD and DX $\overline{\text{D}}$ DX, appear as only one  $^{29}\text{Si}$  NMR signal, and consequently, these pentads are indistinguishable. In some cases, especially when one or two of the three probabilities are equal to zero, the Markov chain analysis gives more than two equivalent solutions. Paradoxically, in the case of the absolutely regular structure of the chain (when the monomer ring is opened exclusively at one site and the opened monomer unit added in one direction), the method gives no information about the site in which the monomer is opened and added to the growing polymer chain.

The results of the sequential analysis by the Markov chain method for the polymerization of the model monomer in the presence of  $\text{CF}_3\text{SO}_3\text{H}$  and in the presence of the  $\text{CF}_3\text{SO}_3\text{H} + \text{Me}_3\text{SiOSO}_2\text{CF}_3$  mixture are presented in Table 1. As many as four equivalent solutions are obtained for each of these polymerizations, and only one of them is the real solution, according to which the polymer chain is formed. The information from this very burdensome and tedious analysis is therefore very limited. The results in Table 1 point to only two modes of the monomer addition, as one of the three possibilities in each experiment is zero. Two solutions point to additions **I** and **III**, while two others point to **II** and **III** (Scheme 1).

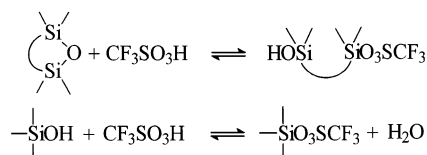
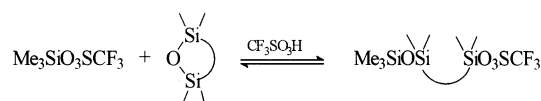
**The Sequence Analysis at the Chain Extremities.** The statistical calculations are complemented by the investigation of terminal sequences in the polymer chain. A similar approach was successfully used in studies of the anionic polymerization of the model monomer.<sup>10</sup> In those studies, the initial sequence was analyzed. The initiation by  $\text{Me}_3\text{SiOLi}$  introduced the  $\text{Me}_3\text{SiO}-$  group at the beginning of the chain. The  $^{29}\text{Si}$  NMR chemical shift of this group depends on the order of units in the neighboring triad which allows one to determine the contribution from the three possible ways whereby the monomer can be added to the initiator. Because of the structure similarity, the addition to the active propagation center was expected to occur in a similar way, allowing the choice of the Markov analysis solution appropriate to the course of the polymerization.<sup>10</sup> The analogous method cannot be used for the cationic polymerization because the initiation is more complex. Protic acid opens the monomer ring generating the interconvertible ester and silanol end groups, according to a simplified Scheme 2.<sup>17</sup> The end group interchange is fairly fast on the polymerization time scale and the chain grows in two directions,<sup>17</sup> no matter if it occurs on activated ester or silanol centers (see further discussion).

**Table 1. Probabilities of Monomer Addition I, II, and III Found from Markov Statistical Analysis, Where Bold Face Values Represent True Solutions**

no. exp	[CF <sub>3</sub> SO <sub>3</sub> H] <sub>0</sub>	[CF <sub>3</sub> SO <sub>3</sub> SiMe <sub>3</sub> ] <sub>0</sub>	quenched at monomer convn, %	P <sub>I</sub>		P <sub>II</sub>		P <sub>III</sub>		P <sub>I</sub>	P <sub>II</sub>	P <sub>III</sub>
				P <sub>I/I</sub>	P <sub>I/(II+III)</sub>	P <sub>II/I</sub>	P <sub>II/(II+III)</sub>	P <sub>III/I</sub>	P <sub>III/(II+III)</sub>			
1	3.2 × 10 <sup>-3</sup>	0	95	0.37	0.33	0.01	0	0.62	0.66	<b>0.35</b>	<b>0.004</b>	<b>0.65</b>
										0.005	0.32	0.67
										0.63	0.003	0.32
										0.005	0.68	0.32
2	1 × 10 <sup>-3</sup>	0	98	0.3	0.36	0	0	0.7	0.64	<b>0.34</b>	<b>0.0</b>	<b>0.66</b>
										0.001	0.39	0.61
										0.63	0	0.37
										0	0.61	0.39
3	1 × 10 <sup>-3</sup>	1 × 10 <sup>-2</sup>	89	0.15	0.31	0	0	0.85	0.69	<b>0.27</b>	<b>0.001</b>	<b>0.73</b>
										0.001	0.35	0.65
										0.66	0.001	0.34
										0.0	0.65	0.35
4	4.5 × 10 <sup>-2</sup>	0	92	0.32	0.3	0	0	0.68	0.7	<b>0.31</b>	<b>0</b>	<b>0.69</b>
										0	0.31	0.69
										0.70	0	0.30
										0	0.69	0.31
5	3 × 10 <sup>-2</sup>	0	98	0.35	0.29	0	0.01	0.65	0.7	<b>0.30</b>	<b>0</b>	<b>0.70</b>
										0	0.29	0.71
										0.70	0	0.30
										0	0.71	0.29

**Table 2. Fractions of Pentads in Copolymers Obtained by Quenched Polymerization of 1 Determined Experimentally (<sup>29</sup>Si NMR) and Simulated by the Monte Carlo Method, Assuming the Conditional Probability Values Given in Table 1**

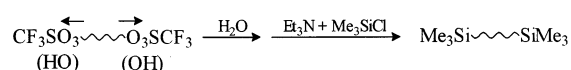
no. exp	DXDDD	XDDDX	DXDDX	DXDXD	DDXDD	XDXXD	XDDDD	XXDDD	XDXXD	DXXDD	XDXXD
1 exp	0.147	0.076	0.369	0.075	0.185	0.142	0.001	0.002	0.001	0.002	0
1 sim	0.147	0.074	0.371	0.072	0.186	0.145					
2 exp	0.159	0.072	0.367	0.069	0.180	0.154	0	0	0	0	0
2 sim	0.151	0.075	0.358	0.075	0.183	0.151					
3 exp	0.153	0.065	0.389	0.059	0.188	0.146	0	0	0	0	0
3 sim	0.143	0.071	0.381	0.071	0.191	0.143					
4 exp	0.147	0.065	0.391	0.064	0.197	0.136	0.001	0	0	0	0
4 sim	0.140	0.070	0.386	0.069	0.193	0.139					

**Scheme 2****Scheme 3**

Addition of trimethylsilyl triflate as the chain initiation species according to Scheme 3 makes the system even more complex as initiation in this system also requires the assistance of free acid.<sup>17–20</sup> Thus, in the presence of silyl ester, both mechanisms of initiation may operate simultaneously.

**End Sequence Capping Experiment.** The insight into the structure of chain ends generated by quenching of the polymerization seemed to be more conclusive. In the absence of Me<sub>3</sub>SiO<sub>3</sub>SCF<sub>3</sub> initiation occurs as shown in Scheme 2. The chain is growing in both directions since the end groups are interconvertible. The polymerization was quenched by adding a large excess of water which transforms the ester end groups into silanol functions. Quenching was followed by a quantitative silylation of silanol end groups with the Me<sub>3</sub>SiCl + Et<sub>3</sub>N mixture, which introduced Me<sub>3</sub>SiO group at both chain ends (Scheme 4).

The triad neighboring to Me<sub>3</sub>SiO is the triad which was at the reactive chain end at the moment of quench-

**Scheme 4**

ing. It was formed from the last monomer molecule incorporated into the chain. The analysis of this triad was made in the same way as that in the initiation experiment in anionic polymerization,<sup>10</sup> i.e., by determination of relative intensities of the <sup>29</sup>Si NMR signals of Me<sub>3</sub>SiDDX, Me<sub>3</sub>SiDXD and Me<sub>3</sub>SiXDD (Figure 2). The interpretation of these results is not straightforward, as the proportions of triads depend not only upon the relative rates of the monomer ring opening at the three respective sites but also on the relative rates of the reaction of the respective chain ends with monomer. Thus, the less reactive the chain end is, the higher is the probability of its occurrence. The result of the quenching experiment presented in Table 3 gives important information related to the chain extension mechanism. The <sup>29</sup>Si NMR spectrum of the quenched and silylated sample showed only two signals of the Me<sub>3</sub>Si end groups which corroborates the results from the statistical method, indicating that the monomer ring is opened only in two places of three and added in one direction. The quenching experiment highlights the monomer addition modes **I** and **III** (Scheme 1), since the signal of Me<sub>3</sub>SiDDX is absent. Addition **II** does not occur and two of the four solutions of statistical equations may therefore be eliminated.

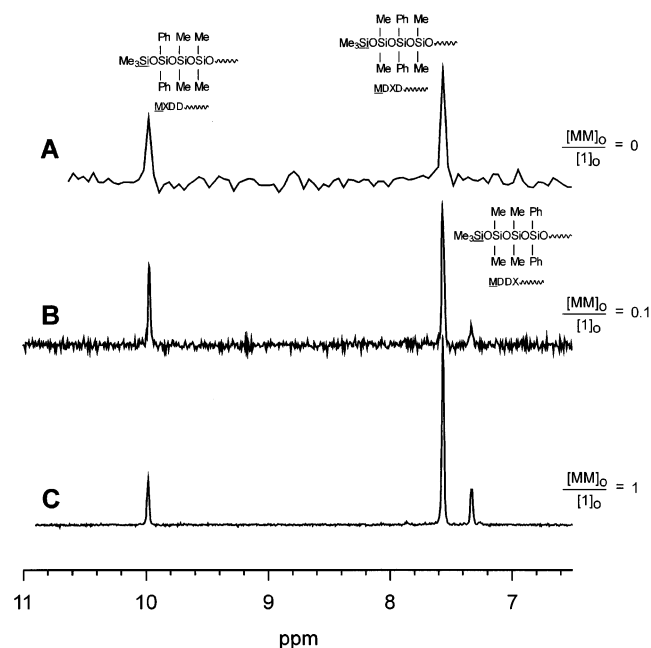
**Chain Transfer Experiment.** The result obtained from the capping experiment is very close to one of the results obtained from the Markov statistics, i.e., the one



**Table 3. Comparison of Result of Quenching Experiment in Polymerization of 1 with Those of Chain Transfer to Me<sub>3</sub>SiOSiMe<sub>3</sub> at Different Initial Concentration Ratios of [MM]<sub>0</sub>/[1]<sub>0</sub>**

no.	exptl conditions [1] <sub>0</sub> = 1.2 mol·dm <sup>-3</sup> , temp 25 °C, <sup>a</sup> solvent <i>n</i> -hexane			no. av deg of polym, $\bar{n}$	contribution of chain end triads			
	[MM] <sub>0</sub> /[1] <sub>0</sub>	[CF <sub>3</sub> SO <sub>3</sub> H] <sub>0</sub>	% convn [MM]		<i>M</i>  XDD	<i>M</i>  DXD	<i>M</i>  DDX	MDDX / MXDD
1 <sup>b</sup>	0	3 × 10 <sup>-3</sup>		41.4	0.39	0.61	0	0
2	0.1	5 × 10 <sup>-3</sup>	35	14.3	0.32	0.60	0.08	0.25
3	0.2	2.5 × 10 <sup>-3</sup>	80	5.7	0.28	0.60	0.12	0.43
4	0.25	5 × 10 <sup>-3</sup>	46	2.8	0.18	0.69	0.13	0.72
5	0.5	5 × 10 <sup>-3</sup>	49	1.04	0.18	0.68	0.14	0.78
6	1	5 × 10 <sup>-3</sup>	34	1.48	0.17	0.69	0.14	0.82
7	1	5 × 10 <sup>-3</sup>	60	1.53	0.17	0.67	0.16	0.94
8 <sup>c</sup>	4	5 × 10 <sup>-3</sup>	13	1.49	0.16	0.69	0.14	0.88

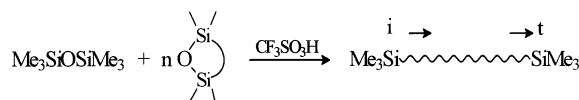
<sup>a</sup> In experiments 1, 3, and 7; temperature is 30 °C. <sup>b</sup> Chain quenching experiment. <sup>c</sup> Experiment without solvent.



**Figure 2.** Comparison of <sup>29</sup>Si NMR spectra in the range of Me<sub>3</sub>Si resonance of the polysiloxane obtained by polymerization of **1** initiated by CF<sub>3</sub>SO<sub>3</sub>H: (A) polymerization quenched by addition of water followed by silylation of silanol end groups by Me<sub>3</sub>SiCl/Et<sub>3</sub>N; (B and C) polymerization in the presence of Me<sub>3</sub>SiOSiMe<sub>3</sub> (MM) quenched by water at ca. 50% of the monomer conversion. Spectrum A was taken on a Bruker MSL 300, and spectra B and C were taken on a Bruker DRX 500 spectrometer.

with dominating symmetrical addition **III**. However, choosing this solution is somewhat risky as the ratio of the signal intensities of the terminal triads DDX and DXD may be seriously affected by the difference in reactivities of the respective chain ends ~DDX\* and ~DXD\*. To verify the results of the Markov analysis, the chain transfer reaction was explored.

The cationic polymerization of hexamethylcyclotrisiloxane initiated with CF<sub>3</sub>SO<sub>3</sub>H in the presence of hexamethyldisiloxane, MM (M = Me<sub>3</sub>SiO), was found to occur with an intensive chain transfer leading to the MD<sub>3n</sub>M species.<sup>21</sup> The chain transfer constant was evaluated to be 0.29 in benzene at room temp. The polymerization of **1** performed in the presence of large amounts of MM should lead to chains which are terminated at both sides by Me<sub>3</sub>SiO groups, according to the general scheme, Scheme 5. At one extremity lies the fragment of the transfer agent which has initiated the polymer chain, while the fragment terminating the chain is built to the other extremity. The polymerization must be quenched when a considerable amount of the

**Scheme 5****Scheme 6**

transfer agent remains unreacted to avoid a significant contribution of the chain transfer to the terminal Me<sub>3</sub>SiO units.<sup>1</sup> This transfer, although slower than that to MM<sup>21</sup> could affect the structure of the chain ends.

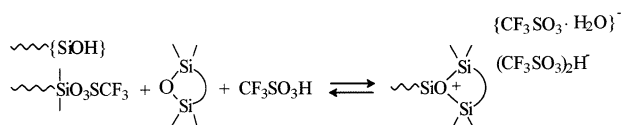
At a large [MM]/[1] ratio, the opened monomer is mostly blocked from both sides by MM fragments, according to Scheme 6; i.e., MDXDM and MXDDM should dominate.

Thus, an equal intensity of unsymmetrical signals MXDD and MDDX is expected, which seems to be the case (Table 3, Figure 2). Moreover, the ratio of the number of symmetrical to unsymmetrical sequences, i.e., **III**/(**I** + **II**), which is observed in the chain transfer experiments is close to that obtained from the capping experiment. It is also close to that resulting from one of the two possible solutions of the Markov equations. This solution is accepted as the real solution (values boldfaced in Table 1). Thus, both experiments, end capping and chain transfer, complement each other and allow to select the right solution from the set of solutions resulted from first-order Markov statistics, according to which the polymerization occurs.

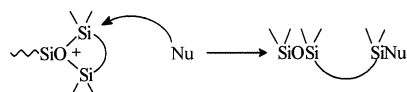
Further conclusion is that the signal of MXDD corresponds to the terminal unit, while that of MDDX is the signal of the unit initiating the other chain as a result of chain transfer. The number of acts of the polymer chain initiation is equal to the number of acts of the polymer chain termination. Thus, intensities of both signals should be the same if the polymer chain initiation and termination reactions occur exclusively with the mediation of M units. However, this is not the case. When the ratio of initial concentrations of MM to monomer is decreasing, the ratio of chain opening by MM to the chain termination by MM decreases, too. Thus, the initiation of the polymer chain by opening the monomer by the MM fragment competes with the opening of the monomer by the acid. This experiment clearly illustrates the role of permanent initiation by an acid in cationic polymerization of cyclosiloxanes. Since the stationary concentration of CF<sub>3</sub>SO<sub>3</sub>H subsists throughout the polymerization, initiation by the acid is continued until all monomer is consumed, which is the reason for a rather broad molecular weight distribution of the polymer. The presence of the ester does not seem

Scheme 7

1. chain end formation according to Scheme 2
2. chain end activation

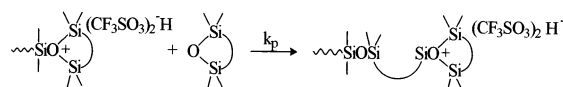


3. chain extension

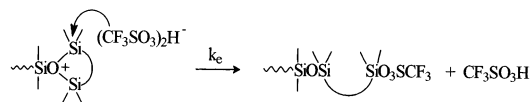


Scheme 8

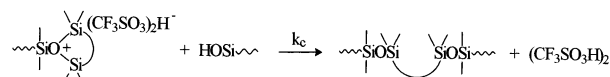
1. Propagation by monomer addition if Nu is a monomer



2. Chain extension with deactivation if Nu is a counter-ion



3. Chain extension by condensation if Nu is a silanol end group



to affect the polydispersity index, which is within the range 1.5–2.2.<sup>1</sup>

Since the ratio of the number of symmetrical triads to the total number of both unsymmetrical triads (Table 3) does not seem to be affected by the initial [MM]/[1] concentration ratio, it can be concluded that the monomer ring is opened at similar sites in both initiation and propagation.

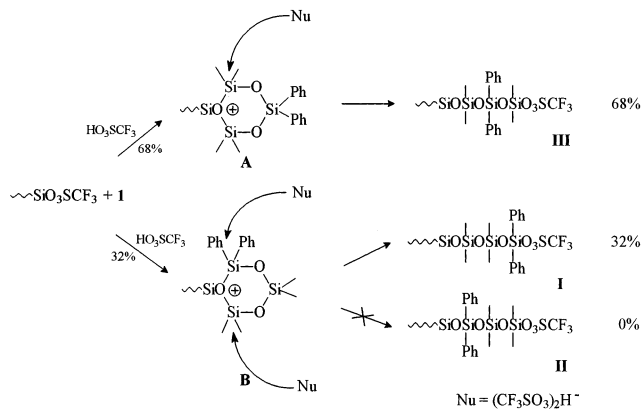
Inspection of the data in Table 1, as well as the comparison of results of the Markov analysis with those of the capping and chain transfer experiments, shows that the site of ring opening depends little on the structure of chain ends. The probability of ring opening values are very close to the respective conditional probability values, i.e.,  $p_{I/I} \approx p_{I/(II+III)} \approx P_I$  and  $p_{III/I} \approx p_{III/(II+III)} \approx P_{III}$  (Table 1).

**The Mechanism of the Chain Growth.** The new set of results obtained with monomer **1** allow us to distinguish between some mechanistic concepts. Thus, the all outcomes of the sequential analysis may be understood on the ground of a mechanism involving the tertiary trisiloxonium ion intermediate formed by the activation of the silyl ester or silanol group<sup>22</sup> by acid (Scheme 7). The existence of these ions derived from cyclic oligosiloxanes is well documented experimentally and by theoretical calculations.<sup>2,23</sup> Their role as intermediates in the CROP of cyclosiloxane was considered.<sup>2,24,25</sup>

The oxonium ion ring is opened by a nucleophile which leads to chain extension. Three types of nucleophiles can fulfill this role. Therefore, three mechanisms of the chain growth are considered (Scheme 8).

The chain propagation according to reaction 1 (Scheme 8) is in disagreement with the results of this study, as a considerable role of the initiation by acid observed in the chain transfer to MM experiment points to a very

Scheme 9



short life of the oxonium ion compared to the time scale of the polymer chain formation. This mechanism does not fit to some other features of the CROP of cyclosiloxanes mentioned in the Introduction.

Instead the chain extension with the deactivation mechanism (reaction 2, Scheme 8) corroborates well with present results and with the number of earlier observations. Thus, the polymerization initiated by  $\text{Ph}_3\text{C}^+(\text{C}_6\text{F}_5)_4^- + \text{HSiR}_3$  producing the pertinent tertiary siloxonium ion<sup>2</sup> occurs relatively slowly<sup>7</sup> because the counterion  $\text{B}(\text{C}_6\text{F}_5)_4^-$  is a very weak nucleophile and is a poor deactivator of the trisiloxonium ion with the chain extension. The activation–chain extension with deactivation reaction cycle should be accompanied by ester end group exchange. Indeed, a fast exchange on the <sup>19</sup>F NMR time scale of the  $\text{CF}_3\text{SO}_3\text{Si}^-$  groups was observed in the CROP of a cyclosiloxane.<sup>25</sup> The mechanism is in agreement with stepwise increase of molecular weight<sup>4,20</sup> and high apparent order of the reaction in acid.<sup>3,17,20</sup>

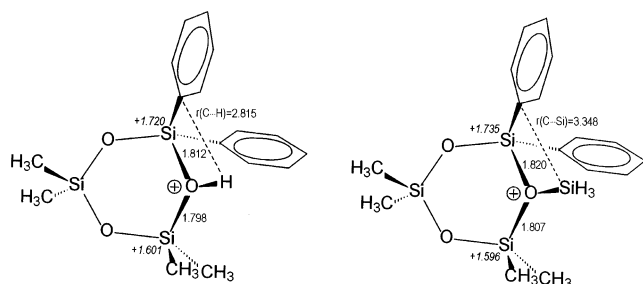
Recent calculations proved that the silicon atom in the endocyclic position in the trisiloxonium ion should be attacked by a nucleophile more easily than the one in the exocyclic position.<sup>23</sup> Thus, deactivation via chain extension is more likely to occur than the deactivation according to reverse reaction 2 in Scheme 7.

The reaction between the trisiloxonium ion and silanol group according to Scheme 8, reaction 3 contributes little to the linear chain formation because of a very low concentration of silanol groups. On the other hand, this reaction occurs intensively intramolecularly producing significant amounts of cyclic products.

There are two possible configurations of the cyclic oxonium ion formed from the model monomer, **A** and **B** (Scheme 9). The symmetrical structure **A** gives upon opening the DXD sequence exclusively. Thus, this is the structure which is opened at **c**. Since the oxygen bridging two dimethyl-substituted silicons is more basic than that of the neighboring diphenyl-substituted silicon, structure **A** is more easily formed. Consequently, the opening at **c**, which leads to triad **III**, is preferred.

However, the contribution of the pathway involving structure **B** is significant. The formation of the tertiary oxonium ion center on less basic oxygen bridging  $\text{Ph}_2\text{Si}$  and  $\text{Me}_2\text{Si}$  in **1** may seem strange. However, this structure may be somehow stabilized by the interaction of the exocyclic silicon in the ion with the *ipso*-carbon of the phenyl ring, as shown in the HF/3-21G\* optimized geometries of the secondary and tertiary siloxonium ions (Scheme 10).<sup>1</sup> At this level of theory, the unsymmetrical structures of secondary and tertiary oxonium ions are

Scheme 10



lower in energy than the corresponding symmetrical structures by 11.7 and 7.5 kJ/mol, respectively.

The structure **B** has two nonequivalent sites of possible nucleophilic attack, i.e., silicon bound to two methyl groups and silicon with two phenyl substituents, leading to sequences  $\sim$ DDX and  $\sim$ XDD, respectively (Scheme 9). However, the attack is directed exclusively to the diphenyl-substituted silicon which is more electrophilic due to the electron withdrawing effect of the phenyl groups. Indeed, *ab initio* calculations (HF/3-21G\*) show that the partial positive charge on phenyl-substituted silicon in a model trisilyloxonium ion formed by attachment of  $\text{SiH}_3^+$  to the monomer molecule is by 0.14 e larger than the charge located on methyl-substituted silicon (Scheme 10). Moreover, the  $\text{Ph}_2\text{Si}-\text{O}$  bond is by 0.013 Å longer than the  $\text{Me}_2\text{Si}-\text{O}$  bond in the oxonium center. These results suggest that  $\text{Ph}_2\text{Si}-\text{O}$  bond should be cleaved by nucleophile more smoothly than the  $\text{Me}_2\text{Si}-\text{O}$  bond. The early transition state of the reaction is predicted, in which the steric hindrance of phenyl groups may be less important.

Alternative to the tertiary oxonium ion mechanism of the chain formation (Scheme 7) are the activated monomer mechanism assuming the addition of protonated monomer to the silanol end group and the simple condensation mechanism involving the acid catalyzed silanol–silylester or silanol–silanol condensation without intermediacy of the tertiary oxonium ion.

The activated monomer mechanism is little probable as it implies that the DDX triad is formed by the attack of weakly nucleophilic  $-\text{SiPh}_2\text{OH}$  on the less electrophilic center, i.e., dimethyl-substituted silicon. This pathway does not explain in a consistent way the formation of cyclic products either.

The sequential analysis made in this study provides also arguments against the simple condensation mechanism. Since the silanol and silyl ester groups are interconvertible both structures of unsymmetrical triads,  $\sim$ DDX and  $\sim$ XDD, should appear, while only the former is observed. The absence of XX diads and DDDD tetrads (XDDDD pentads) excludes the head to head and tail to tail condensation, i.e.,  $\text{DDX}\cdots\text{XDD}$  and  $\text{XDD}\cdots\text{DDX}$  combinations. In particular, the latter combination is expected to occur easily in the condensation mechanism. Moreover, the sequence distribution is independent of the ester-to-silanol ratio, as the same sequence distributions were observed for  $\text{CF}_3\text{SO}_3\text{H}$  and  $\text{CF}_3\text{SO}_3\text{H} + \text{CF}_3\text{SO}_3\text{SiMe}_3$  initiating systems.

## Conclusions

The analysis of sequences of siloxane units in the polymer obtained by ring-opening polymerization of 2,2-diphenyl-4,4,6,6-tetramethylcyclotrisiloxane (**1**) in *n*-hexane initiated by  $\text{CF}_3\text{SO}_3\text{H}$  showed that the microstructure of the polymer chain is formed exclusively in

the chain extension process. The prevailing is the monomer ring opening at oxygen bridging two dimethyl-substituted silicon which gives rise to the symmetrical arrangement of the siloxane units in the monomer unit added to the polymer chain ( $\sim$ DXD). Solely one of the two possible unsymmetrical arrangements ( $\sim$ DDX) occurs, which means that there is only one unsymmetrical opening of the monomer ring and only one way for the addition of its opened form to the polymer chain.

Regarding previous kinetic and mechanistic studies of the CROP of cyclosiloxanes, the sequence analysis is in agreement with a stepwise chain growth which occurs on the silylester terminal group. The ester group reacts with the acid and monomer with the transient formation of the terminal cyclic trisilyloxonium ion. This ion is decomposed to the ester and acid with the incorporation of its cyclic moiety into the polymer chain (“chain extension with deactivation”). Thus, the oxonium ion is not a carrier of the kinetic chain in propagation, but instead, it plays a role of the transitory intermediate in each step of the monomer addition. The mechanism assuming the *tert*-oxonium ion intermediate explains also the formation of cyclic products which are generated by the reaction of this intermediate with the silanol end group at the other chain end (“end-to-end ring closure”, “end-biting”). In this reaction and in the analogous intermolecular process one linear chain disappears and the acid is reformed. It opens the monomer ring initiating a new chain (“permanent initiation”) which leads to a stationary concentration of the acid and of the growing chains.

The sequence analysis indicates that the contribution of intermolecular condensation to the chain growth is negligible and the operation of the activated monomer mechanism little probable.

## Experimental Section

**Chemicals.** *n*-Hexane (Aldrich 99+%) used as a solvent and *n*-dodecane (Aldrich 99+%) used as a standard for gas chromatography were purified by fractional distillation from sodium under dry argon to ampules with Rotaflo stopcock.<sup>26</sup>

Triethylamine (wasserfrei purum, Loba Feinchemie) was used without any additional purification.

Trimethylchlorosilane (ABCR) was purified by distillation under argon to ampule with Rotaflo stopcock.

Hexamethyldisiloxane (ABCR) was dried and purified by refluxing and distillation from  $\text{CaH}_2$  under argon to the ampule with Rotaflo stopcock. Purity checked by gas chromatography was 99.8%.

**Initiators.** Trifluoromethanesulfonic acid (Aldrich 99+%) and trimethylsilyl trifluoromethanesulfonate (Aldrich 99%) were distilled on high vacuum line and were stored in an ampule with Rotaflo stopcock under dry argon.

**Monomer.** 2,2-Diphenyl-4,4,6,6-tetramethylcyclotrisiloxane, **1**, was prepared by reaction of 1,3-dichloro-1,1,3,3-tetramethyldisiloxane (ABCR) with diphenylsilanediol (ABCR), according to the procedure described earlier.<sup>27</sup> The monomer was purified by recrystallization from *n*-hexane and distillation on a high vacuum line. It was stored in an ampule with Rotaflo stopcock under dry argon.

**Polymerization.** Polymerization of monomer **1** was carried out in a thermostated (30 °C) 50 mL glass Schlenk type reactor under dry argon. The solution (50% v/v) of monomer **1** (2.280 g,  $6.6 \times 10^{-3}$  mol) in *n*-hexane (3.24 mL) was placed in the reactor thoroughly purged with argon. *n*-Dodecane (150 g,  $8.8 \times 10^{-4}$  mol) was introduced as a standard for the gas chromatography analysis. The initiator, trifluoromethanesulfonic acid ( $4.0 \times 10^{-3}$  g,  $2.8 \times 10^{-5}$  mol) was introduced with a Hamilton precision syringe to the solution under a flow of argon. After 5 min the reaction was quenched by introducing



of the reaction mixture into 50 mL of cold water. The conversion of monomer determined by gas chromatography was 70%. The organic layer was separated, washed three times with 100 mL of cold water and dried over  $\text{CaCl}_2$ . SEC analysis showed that the polymer consisted 60% polymer fraction ( $\bar{M}_n$   $1.40 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$ ,  $\bar{M}_w/\bar{M}_n$  2) and about 40% of cyclic fraction. Cyclics were separated from the linear polymer by repetitive precipitation of the polymer from methylene chloride solution in methanol. Cyclics were not observed in the SEC chromatogram and  $^{29}\text{Si}$  NMR spectrum of the isolated polymer. Solvent was removed by keeping the polymer on high vacuum line.

Since the reaction was fast, the time of quenching was determined in a separate polymerization experiment.

**End Sequence Capping Experiment.** Polymerization of monomer **1** was carried out in a 50% v/v solution in *n*-hexane in a thermostated (25 °C) 50 mL glass Schlenk type reactor under dry argon. The monomer **1** (1.60 g,  $4.6 \times 10^{-3}$  mol), *n*-dodecane (0.15 g,  $8.8 \times 10^{-4}$  mol), and *n*-hexane (2.20 mL) were placed in the reactor. Initiator, trifluoromethanesulfonic acid ( $2.6 \times 10^{-4}$  mol, 0.040 g) was introduced with a Hamilton precision syringe. The mixture was immediately shaken. The reaction was quenched after 5 s by introduction 50 mL of cold water (5 °C) to the reaction mixture which was immediately vigorously shaken. The conversion of monomer was 50% (GC analysis). The polymer solution was immediately washed three times with 100 mL of cold water, the organic layer was separated and dried over  $\text{CaCl}_2$ , and then a mixture of trimethylchlorosilane (4.280 g, 0.04 mol) and triethylamine (3.840 g, 0.038 mol) was added to react with silanol end groups. SEC analysis showed polymer fraction ( $\bar{M}_n$   $1.2 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$ ,  $\bar{M}_w/\bar{M}_n$  2.6) and oligomer fraction. Then 10 mL of hexane was added to polymer solution. Silylated polymer was washed three times with 100 mL of cold water, dried over  $\text{CaCl}_2$  and a remaining solvent was removed by evaporation on a high vacuum line. Then, the polymer was dissolved in methylene chloride and precipitated in methanol. The precipitation procedure was repeated twice and the polymer was dried on high vacuum line. Cyclics were not observed in SEC and  $^{29}\text{Si}$  NMR analysis.

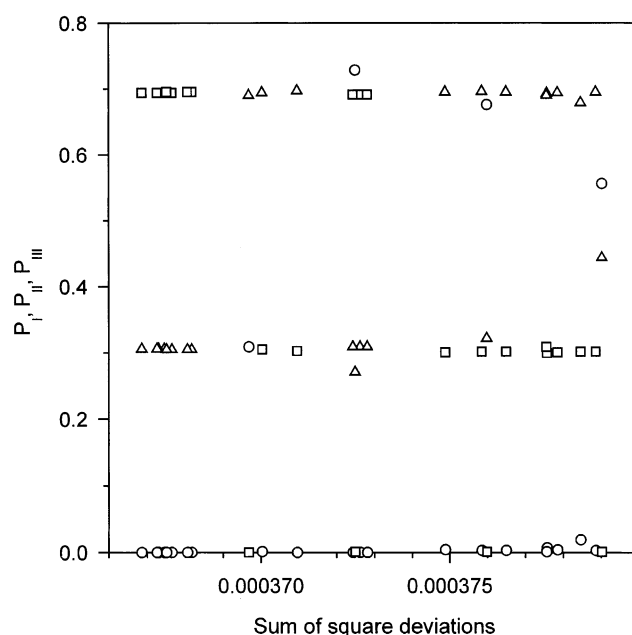
**Chain Transfer Experiment.** Polymerization of monomer **1**, in the presence of hexamethyldisiloxane MM was carried out in a thermostated (25 °C) 50 mL glass Schlenk type reactor under dry argon. The monomers **1** (2.20 g,  $6.4 \times 10^{-3}$  mol), MM (0.104 g,  $6.4 \times 10^{-4}$  mol) and *n*-dodecane (0.15 g,  $8.8 \times 10^{-4}$  mol) were placed in reactor purged with argon. The initiator ( $4.0 \times 10^{-3}$  g,  $2.7 \times 10^{-5}$  mol) was introduced with a Hamilton precision syringe. After 3 min, the reaction was quenched by adding of the reaction mixture into 50 mL of cold water. The conversion of monomer determined by gas chromatography was 50%. The organic layer was separated, washed three times with 100 mL of cold water and dried over  $\text{CaCl}_2$ . Organic solvent was removed from polymer by evaporation on high vacuum line. Number-average degree of polymerization for obtained polymer determined from  $^{29}\text{Si}$  NMR spectrum was  $\text{DP}_n = 14.3$ .

**Analysis.**  $^{29}\text{Si}$  NMR spectra were taken with Bruker MSL 300 and Bruker DRX 500 spectrometers. Molar contents of pentads were determined by  $^{29}\text{Si}$  NMR using techniques securing quantitative integration, i.e., gated decoupling and addition of  $\text{Cr}(\text{acac})_3$  described in ref 10.

SEC analysis was performed with a LDC Analytical equipped with an RI detector, using toluene as a solvent and PS standards (Polyscience) for calibration. The battery of two columns were used: PSS SDV 100C and PSS SDV 10<sup>4</sup>C, for both columns: dimension  $8 \times 300$  mm, size of particles 5  $\mu\text{m}$ , flow rate 0.7 mL/min, and temperature 20 °C.

GC analysis was carried out using Hewlett-Packard 6890 GC system working with thermal conductivity detector using capillary column: HP 190592–023, length 30 m, diameter 0.53 mm, carrier gas He 5 mL/min, and detector temperature 250 °C. Temperature program: 60 °C isothermal for 3 min, from 60 to 240 °C heating 10 °C/min, 240 °C isothermal for 15 min.

**Computational Methods.** All mathematical procedures applied here (statistical analysis, Monte Carlo simulations and



**Figure 3.** Dependence of the fractions of monomer additions  $P_I$ ,  $P_{II}$ , and  $P_{III}$  on the sum of square deviations, obtained by numerical analysis for the polymerization of **1** initiated by  $\text{CF}_3\text{SO}_3\text{H}$  (Table 1, experiment 4): (○)  $P_I$ ; (□)  $P_{II}$ ; (△)  $P_{III}$ .

quantum mechanical calculations) were described earlier.<sup>10</sup> Because the monomer openings marked as **a** and **b** for cationic and anionic polymerizations were interchanged and because two above-mentioned mechanisms may operate in the cationic systems, the designation of conditional probabilities changed and the corresponding changes to the statistical equations were made. Thus, the indices I, II, and III were used instead of a, b, and c, according to Scheme 1. For example,  $p_{I/I}$  denotes the conditional probability of monomer addition creating the DDX sequence to the polymer chain terminated with the  $\text{Ph}_2\text{Si}$  unit. Analogously,  $p_{I/(II+III)}$  denotes the conditional probability of monomer addition creating the same sequence to the polymer chain terminated with the  $\text{Me}_2\text{Si}$  unit. The set of statistical equations for cationic polymerization of **1** is available as a Supporting Information. These equations were solved numerically. To ensure that all the possible solutions were correctly found, the behavior of the function was examined over the full space of conditional probabilities by running several optimizations varying the starting probability values from 0 to 1. The all sets of optimized probabilities of monomer openings were then plotted against the corresponding values of the minimization function. The example of such a plot is shown in Figure 3. Calculated conditional probabilities are collected in Table 1. These values were used to simulate the polymer chain growth by a Monte Carlo method. The selected results of simulation are shown in Table 2. Ab initio calculations were carried out using Gaussian 98 series of programs.<sup>29</sup> Equilibrium geometries and energies of cyclic silyloxonium ion resulting from addition of a proton or of the  $\text{SiH}_3^+$  group to the monomer **1** were calculated at the HF/3-21G\* level.<sup>30</sup> Local charges were calculated by the Mulliken method.<sup>30</sup>

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**Supporting Information Available:** A scheme giving a set of statistical equations describing pentad distribution, a table giving the set of statistical equations for cationic polymerization of **1**, a table giving Cartesian coordinates of HF/3-21G\* optimized structures of monomer **1** and all secondary and tertiary oxonium ions derived from **1** by attachment of  $\text{H}^+$  and  $\text{SiH}_3^+$ , respectively, and a figure giving examples of SEC of the quenched CROP of **1** system. This material is available free of charge via the Internet at <http://pubs.acs.org>.



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