Monte Carlo Simulation of the Cyclization–Chain Extension Kinetics for the Cationic Polymerization of Hexamethylcyclotrisiloxane

Marek Cypryk and Julian Chojnowski*

Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences, ul. Sienkiewicza 112, 90-363 Łódź, Poland

Received April 5, 1990; Revised Manuscript Received October 5, 1990

ABSTRACT: A Monte Carlo method has been used to simulate the kinetic dependencies related to ring–chain competition in the cationic polymerization of hexamethylcyclotrisiloxane. Several variants of mechanisms of this polymerization were considered. Good agreement between computational and experimental results was obtained for the dual mechanism comprising the direct stepwise addition of monomer to the growing chain end in competition with intra- and intermolecular condensation reactions. The additional assumption was made that the monomer molecule assists in the condensation. It was also shown that the experimental observations may conform to a pure acidolytic condensation pathway, assuming that shorter chains preferentially enter the intermolecular condensation and that the condensation is subjected to the intra–inter catalysis.

Introduction

The cationic polymerization of cyclic polysiloxanes has been extensively studied as it constitutes an important route toward siloxane polymers.[1-7] Hexamethylcyclotrisiloxane (D_3) was preferred as a model for kinetic studies, because ring strain, and, consequently, its higher reactivity, makes the polymerization more simple compared to that involving an unstrained siloxane monomer.[2,3,5-9] In particular, processes of depolymerization, chain scrambling, and cyclic oligomer repolymerization are of minor importance during the D_3 conversion. Many observations and kinetic data for the cationic polymerization of D_3 have been collected; however, the mechanism of this reaction in many points remains unclear and is the subject of controversy.[6,7] Although the kinetics of the monomer conversion is very complex,[3,5,6,9] the reaction exhibits relatively simple and unusual kinetics of the competition between the formation of cyclic oligomers and linear polymer. This type of kinetics constitutes the source of very important mechanistic information.[2,6,8,9] The purpose of this study is to simulate the basic dependencies related to the ring formation versus linear growth kinetics for assumed mechanistic pathways in D_3 polymerization. Numerical integration of the kinetic differential equations as well as their analytically solved forms has previously been used in simulation studies of the cyclization kinetics in polymerization and polycondensation systems.[10-14] We prefer to use a Monte Carlo method, because it provides simple representation of mechanistic pathways in terms of simulation and does not require restrictions on the number of reacting species.

Experimental Features of the D_3 Polymerization in the Presence of Protonic Acids Relevant to the Mechanistic Models Assumed. 1. The polymerization leads to the simultaneous formation of the linear polymer fraction and a series of cyclic and macrocyclic polysiloxanes of the $(Me_2SiO)_m$ general formula.[2,6,8]

2. A very specific size distribution of these cyclics has been observed as there is a considerable excess of those whose size is a multiple of the monomer, i.e., m = 6, 9, 12, ... = $3n$.[2,6,8] This feature excludes the back-biting mechanism of the cyclization.

3. A correlation was found between the concentration of cyclics in the polymerization system and the conformational probability of the respective ring closure (i.e., the probability that the respective open chain adopts a conformation for which end groups are in juxtaposition and in the proper orientation for the reaction toward the ring closure).[2] This feature, together with feature 2, points to the end-to-end closure mechanism of the formation of cyclics.

4. The catalytic ability of the acid is maintained throughout the reaction.[3] Thus, ring formation leads to the direct or indirect reproduction of the acid or an active propagation center.

5. Concentrations of cyclic oligomers and polymer increase linearly with monomer conversion.[2,6]

6. The concentration of cyclic oligomers at the same monomer conversion is independent of or has little dependence on the acid concentration.[15]

7. The number-average molecular mass of the polymer increases linearly with monomer conversion.[6]

8. The acid in the polymerization system is reversibly converted to end groups (silanol and silyl ester).[2,16] The stationary acid concentration in this system is small compared with the concentration of the end groups.

Mechanistic and Kinetic Models. The kinetics of the cyclic and macrocyclic formation in the cationic polymerization of D_3 could be rationalized on the grounds of one of two pathways:

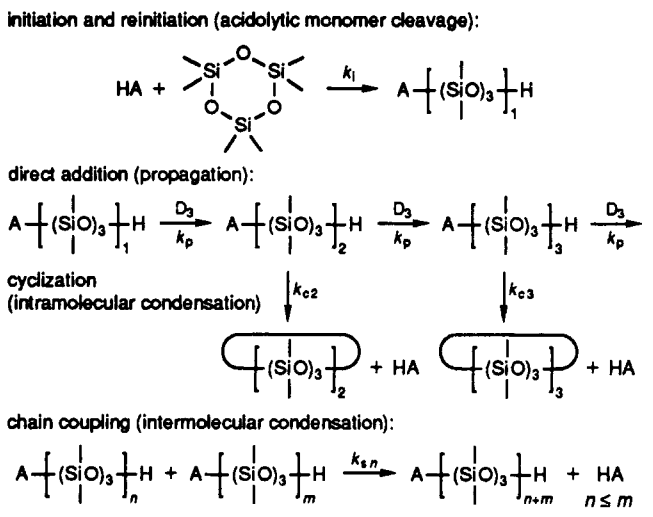
1. A dual mechanism involving the chain growth by direct addition of the monomer to the chain end (propagation) in competition with an intramolecular and intermolecular condensation between end groups leading to cyclization and chain coupling, respectively.

2. A condensation polymerization in which the acid opens the monomer ring in a similar way, but the chain growth occurs exclusively by the condensation between end groups.

In both of the mechanisms above, a condensation reaction between the end groups must lead to direct or indirect reformation of the catalyst. Several variants of these pathways will be discussed and only some of them are in agreement with the experimental results. A general

0024-9297/91/2224-2498$02.50/0

Scheme I



scheme of the process including both of the above pathways is given (Scheme I).

Each act of propagation (direct monomer addition) requires the activation of the monomer or end group with acid.[3,9] The activation–deactivation reaction is fast on the time scale of the overall chain growth; thus, the chain is growing stepwise by a direct monomer addition process in spite of the fact that no low molecular mass byproducts are released.

The end groups, silanol and silyl ester (A), are formed as a result of monomer ring opening by the acid HA, which may be regarded as initiation. It is assumed that the initiation and reinitiation are very fast compared with the condensation and, therefore, all initiator introduced to the system is rapidly converted to end groups and the stationary concentration of the initiator is negligible compared with the concentration of end groups. (This assumption is based on the results from refs 3 and 6. It makes the calculations simpler; however, omitting it should not change general conclusions drawn in this paper as stationary concentrations of the initiator and the end groups are rapidly established in this process.[3]) Every act of cyclization or intermolecular coupling leads to the release of one acid molecule, which rapidly opens a monomer ring forming a new open chain with $n = 1$. (This assumption of the acidolytic condensation sequence is a simplification. Actually, this process is more complex.[3] The acid-producing condensation may compete with the condensation of two silanol groups producing water. Ring opening with water may occur as well. Finally, silanol and silyl ester groups are interconvertible by a hydrolysis–esterification reaction. These complications should not change the character of dependencies simulated here, since the end-group interconversion is fast compared with the condensation reactions.[16])

This initiation is irreversible due to the strain in the monomer ring. The acid is only able to open the monomer and is unable to split linear polymer or cyclic oligomer. There is no termination, depolymerization, or chain scrambling. The k_p constant assumes only one value, independent of n. The value of k_c depends on the oligomer size. In the range $1 < n < 6$ it changes irregularly, but for $n > 6$ it decreases according to the known dependence of the conformational probability of closure of a large ring on its size in the polymer homologue series, i.e., $k_c = \text{const} \times n^{-3/2}$.[17] This is also in agreement with known limiting chain size of poly(dimethylsiloxanes), starting from which Gaussian statistics can be applied to the description of the chain conformation.[18] The following variants were distinguished for Scheme I:

1. The direct monomer addition pathway with competing end-group condensation. (a) Intermolecular and intramolecular condensations show the same order in the monomer as propagation, which corresponds to the case when monomer assistance is involved in the condensation. In other words, the relative rate of condensation versus propagation is independent of the D_3 conversion. (b) The condensations occur without monomer assistance; thus, their contribution increases as the reaction proceeds. (c) The propagation and the cyclization are the only processes proceeding in the system, while chain coupling is disregarded. This case was calculated separately for both assumptions, i.e., with or without monomer assistance in the cyclization.

2. Chain growth occurs exclusively by polycondensation (no direct addition of monomer). (a) The specific rates of all condensation reactions are equal; $k_{s1} = k_{s2} = k_{s3} = \ldots = k_{sn}$. (b) The open-chain species derived from the monomer enter the intermolecular condensation with a specific rate much larger than that of the longer chains; $k_{s1} \gg k_{s2} = k_{s3} = k_{s4} = \ldots = k_{sn}$. (c) The specific rates for the first six oligomers are differentiated by a constant factor; $k_{s1} > k_{s2} > \ldots > k_{s6} = k_{s7} = \ldots = k_{sn}$.

The Method of Simulation. The Monte Carlo simulation method was used because, if reasonable assumptions are made, it provides relatively simple computing procedures for the polymerization pathways considered.

The computer calculations were performed by using a program written in Turbo Pascal on an IBM PC/XT.

A vector of integers L[14000] represented growing chains. The vector L was initialized to unity, i.e., L[i]: = 1 for all i = 1–14 000, which corresponded to the open chain HD_3A, derived from the monomer. As the reaction proceeded, each element of L contained the actual size of a growing chain (in monomer units). Since the concentration of open chains was assumed to be equal to the concentration of initiator (corresponding to the size of vector L; according to ref 2, the concentration of initiator was taken as 7×10^{-4} mol·kg^{-1}), it was easy to calculate the actual concentration of each particular oligomer $H(D_3)_nA$, which corresponded to the portion of vector elements L[i] = n.

In the same way, the concentrations of D_3 and cyclics formed in the reaction were established.

Another vector, C[12], was declared to store the numbers of small cyclics (up to 12 monomer units). Larger rings were only regarded as sums $\sum n_i c_i$, $\sum n_i c_i^2$, and $\sum n_i$ in the calculation of the polymerization degree.

Different sets of probabilities of elementary reactions were assumed, depending on the variant of mechanism.

Variant 1a: P_s (intermolecular condensation), P_p (addition of monomer), and P_{c2} (cyclization of HD_6A). All P's remain constant during the entire simulation run.

Variant 1b: Analogous to variant 1a, but P_p decreased proportionally to the monomer conversion.

Variant 1c: $P_s = 0$, P_p was either constant, as in variant 1a, or variable, as in variant 1b.

Variant 2a: The same as variant 1a, but $P_p = 0$.

Variant 2b: P_{s1} (intermolecular condensation involving at least one HD_3A molecule), P_{sn} (other than HD_3A), $P_{s1} \gg P_{sn}$.

Variant 2c: $P_{s1} > P_{s2} > \ldots > P_{s6} = P_{sn}$, where P_{si} means the probability of condensation involving at least one $H(D_3)_iA$ molecule (the lesser one); P_{s2} ..., P_{s5} were

Table I
Some Representative Simulation Results for the Addition Pathways in the Cationic Polymerization of D_3 at 30% Monomer Conversion[a]

		assumed probabilities						calculatn results		
					rel specific rates				concn of cycles, mol·kg^{-1}	
no.	var	chain coupl P_s	D_3 addn P_p	cycl $P_{c\,2}$	k_s/k_p	$k_p/k_{c\,2}$	$k_s/k_{c\,2}$	Kuhn grad $\|-q\|$	[D_6]	$\sum_{n=2}^{10}$[D_{3n}]
1[b]	exp							1.7	1.75×10^{-2}	2.5×10^{-2}
2	1c	0	0.2	0.2	0	1	0	2.3	8.3×10^{-3}	1.4×10^{-2}
3[c]	1c	0	0.2	0.2	0	1	0	2.2	6.7×10^{-3}	8.4×10^{-3}
4	1c	0	0.1	0.2	0	0.5	0	3.15	7.0×10^{-2}	1.0×10^{-1}
5	1c	0	0.2	0.1	0	2	0	1.75	7.3×10^{-4}	1.4×10^{-3}
6	1a	0.002	0.12	0.165	0.017	0.73	0.012	2.2	1.7×10^{-2}	2.5×10^{-2}
7	1a	0.001	0.12	0.165	0.008	0.73	0.006	2.13	1.2×10^{-2}	1.7×10^{-2}
8	1b	0.002	0.12	0.06	0.017	2	0.033	2.05	6.5×10^{-3}	9.4×10^{-3}
9	1b	0.005	0.2	0.2	0.025	1	0.025	2.6	2.3×10^{-2}	3.7×10^{-2}

[a] $[D_3]_0 = 1.8$ mol·kg^{-1}; $[HA]_0 = 7 \times 10^{-4}$ mol·kg^{-1}. [b] Polymerization in *n*-heptane, in the presence of CF_3SO_3H, 30 °C, $[D_3]_0 = 1.8$ mol·kg^{-1}, $[CF_3SO_3H]_0 = 7 \times 10^{-4}$ mol·kg^{-1}, from ref 2. [c] $P_p \propto [D_3]$, no monomer assistance in cyclization.

Table II
Some Representative Simulation Results for the Condensation Pathways in the Cationic Polymerization of D_3 at 30% Monomer Conversion[a]

		assumed probabilities						calcultn results		
		chain coupling			rel specific rates				concn of cycles, mol·kg^{-1}	
no.	var	$P_{s\,1}$	$P_{s\,6}$	$P_{c\,2}$	$k_{s\,1}/k_{s\,6}$	$k_{s\,1}/k_{c\,2}$	$k_{s\,6}/k_{c\,2}$	Kuhn grad $\|-q\|$	[D_6]	$\sum_{n=2}^{10}$ [D_{3n}]
1[b]	exp							1.7	1.75×10^{-2}	2.5×10^{-2}
2	2a	0.2	0.2	0.14	1	1.4	1.4	2.9	2.7×10^{-2}	3.1×10^{-2}
3	2a	0.2	0.2	0.002	1	100	100	2.8	4.5×10^{-4}	5.5×10^{-4}
4	2b	0.2	0.001	0.14	200	1.4	0.007	2.2	1.75×10^{-2}	2.5×10^{-2}
5	2b	0.2	0.008	0.14	25	1.1	0.057	2.3	2.2×10^{-2}	3.0×10^{-2}
6	2c	0.2	0.001	0.18	200	1.1	0.006	2.17	1.76×10^{-2}	2.5×10^{-2}
7	2c	0.2	0.008	0.22	25	0.9	0.036	2.3	2.9×10^{-2}	3.7×10^{-2}

[a] $[D_3]_0 = 1.8$ mol·kg^{-1}; $[HA]_0 = 7 \times 10^{-4}$ mol·kg^{-1}. [b] Polymerization in *n*-heptane, in the presence of CF_3SO_3H, 30 °C, $[D_3]_0 = 1.8$ mol·kg^{-1}, $[CF_3SO_3H]_0 = 7 \times 10^{-4}$ mol·kg^{-1}, from ref 2.

calculated automatically by using input values of $P_{s\,1}$ and $P_{s\,6}$ and assuming that $P_{s\,1}/P_{s\,2} = P_{s\,2}/P_{s\,3} = \ldots = P_{s\,5}/P_{s\,6}$.

Cyclization probabilities of $H(D_3)_nA$, $n > 2$, were calculated by the program according to the following rule: $P_{c\,n} = c_n P_{c\,2}$ for $n = 3$–6, where c_n's are arbitrary constants chosen by trial and error to fit the concentrations of appropriate rings to experimental values at given monomer conversion (30%); for $n > 6$ the probabilities of cyclization were assumed $P_{c\,n} = P_{c\,6}(6/n)^{3/2}$. The assumed values of c_n were, variant 1, $c_3 = 0.106$, $c_4 = 0.062$, $c_5 = c_6 = 0.092$; variants 2a and 2b, $c_3 = 0.106$, $c_4 = 0.062$, $c_5 = c_6 = 0.095$; and variant 2c, $c_3 = 0.106$, $c_4 = 0.066$, $c_5 = 0.105$.

For each element $\mathbf{L}[i]$ a random number Rand ϵ (0.1) was generated using Turbo Pascal's built-in function Random. The number was then compared with given probabilities of the elementary reactions. For instance, in variant 1a, if Rand $\leq P_s$ then intermolecular condensation of $\mathbf{L}[i]$ with $\mathbf{L}[i+1]$ occurred giving the chain of the length $\mathbf{L}[i] + \mathbf{L}[i+1]$ stored in $\mathbf{L}[i]$; an acid molecule immediately opened the next molecule of D_3, so $\mathbf{L}[i+1]$: = 1. If $P_s <$ Rand $\leq P_p$, then it was checked whether (Rand $- P_s$) $\leq (P_p)^n$, which was interpreted as synchronous addition of n monomer molecules to the chain, i.e., $\mathbf{L}[i]$: = $\mathbf{L}[i] + n$. If $(P_s + P_p) <$ Rand $\leq P_{c\,2}$, then depending on the chain length $\mathbf{L}[i]$ the following cases might occur: (a) $\mathbf{L}[i] = 1$. No cyclization occurred. (b) $2 < \mathbf{L}[i] \leq 6$. If (Rand $- (P_s + P_p)) \leq P_c(\mathbf{L}[i])$, then cyclization took place; i.e., the appropriate element of vector $\mathbf{C}$, $\mathbf{C}[\mathbf{L}[i]]$, was increased by 1 and $\mathbf{L}[i]$: = 1. (c) $\mathbf{L}[i] > 6$. If (Rand $- (P_s + P_p)) \leq P_{c\,6}(6/\mathbf{L}[i])^{3/2}$, then the cyclization occurred.

For given conversion degrees, the program printed out the concentrations of linear and cyclic oligomers and the actual polymerization degree (DP, DP_w, and DP_w/DP). The results of these simulations performed assuming different systems of probability values for each mechanistic variant were then compared with experimental data for the kinetics of the polymerization of D_3 from ref 2. Simulation runs were repeated several times, obtaining good reproducibility in the results. In all cases the distribution of cyclics $n \geq 6$ was found to be linear on a logarithmic scale (Figure 5), although the slope of the line as well as the concentrations of cycles varied depending on the $P_c/(P_p + P_s)$ ratio and on the P_s/P_p (variants 1a and 1b) or $P_{s\,1}/P_{s\,n}$ (variant 2) ratio.

Some representative data from the simulation for the addition pathways (variant 1) are collected in Table I and for condensation pathways (variant 2) in Table II. Some of them are also presented in Figures 3–5.

Results of Calculations

Concentrations of Open-Chain Oligomeric Intermediates in the Polymerization System. The calculations made for the initial period of the polymerization show how the stationary state of the process is attained and how stationary concentrations of linear intermediates able to form the rings differ for pure addition (no coupling) and pure condensation (no addition) chain growth. Some representative data are shown in Figure 1a,b.

In the addition polymerization system the stationary concentrations of oligomers are roughly the same independent of the chain length if a small range of n is considered. In contrast, in the condensation polymerization they are evidently decreasing with lengthening of the chain. This must be reflected in a faster fall of the concentration of cyclics with their sizes in the condensation polymerization system (compare parts a and b of Figure 4). If the assumption is made that the reactivity of the intermediate drops with the chain length (variant 2c), their stationary concentrations tend to be similar as in the

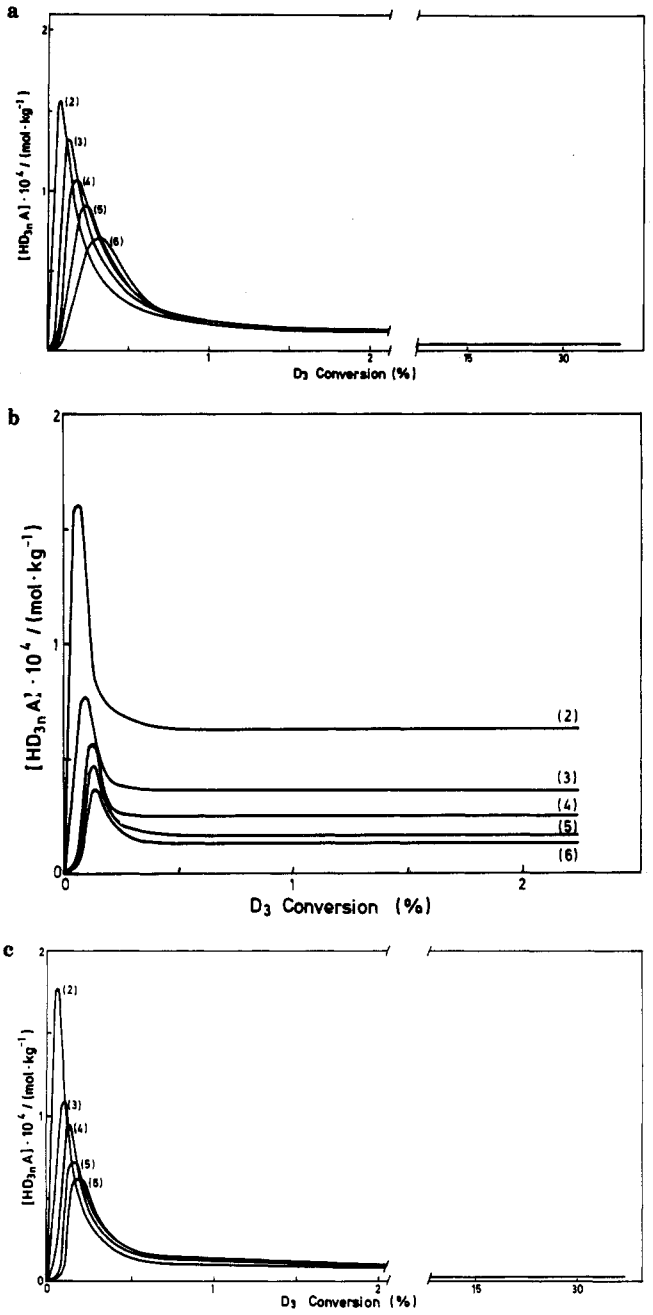


Figure 1. (a) Simulated concentrations of linear oligomers $HD_{3n}A$, n = 2–6, in the initial period of polymerization of D_3 assuming a pure addition mechanism (variant 1c); for simulation parameters see Table I, no. 2. Each curve corresponds to the oligomer marked in parenthesis. $[D_3]_0$ = 1.8 mol·kg^{-1}; $[HA]_0$ = 7 × 10^{-4} mol·kg^{-1}. (b) Same as part a, assuming a pure condensation pathway (variant 2a, Table II, no. 2). (c) Same as part a, assuming a condensation mechanism of oligomers depending on their length (variant 2c, Table II, no. 6).

addition polymerization system (Figure 1c).

The concentrations of linear species in both polymerization systems initially pass through a maximum, adopting values that are evidently larger than in the stationary state. This linear oligomer enhancement may be particularly high for the addition mechanism and may be reflected in some irregularity of the function of cyclic concentration versus monomer conversion in the initial period. However, the shape of the curve representing linear oligomer concentration versus monomer conversion in the nonstationary course period depends to a considerable extent on relative rates of the component reactions.

Variation of the Degree of Polymerization of the Linear Chain Fraction. In the direct addition pathway (variant 1), the number-average degree of the polymerization DP_n increases linearly with the monomer conversion for variant 1a (Figure 2a). Curving of the dependence is observed for variants 1b and 1c; however, up to 60% of conversion the deviation from linearity may not be large enough to be recognized in an experimentally measured dependence (Figure 2b). In contrast, for all cases of the pure condensation pathway (variant 2) the DP_n function is linear up to high monomer conversion (Figure 2c). Thus, the linear dependence determined experimentally by Sigwalt[6] is in good agreement with both the addition and the pure condensation chain growth pathways and in principle cannot serve for the differentiation of these mechanisms.

Concentration of the Cyclic Products in the System. Concentrations of individual cyclic D_{3m} oligomers in the D_3 cationic polymerization system have been studied[2,6] and were found to increase linearly with D_3 conversion. Computational results for variant c of the addition mechanism, i.e., disregarding the chain coupling, disagree with these experimental observations. The contribution from the cyclization predicted for this variant either decreases as the reaction proceeds (if monomer assistance is assumed) or it is changing along an S-shaped curve for the no monomer assistance case (Figure 3a). On the other hand the concentrations of cyclic species increase linearly with the monomer conversion for the addition mechanism regarding the chain-coupling process and assuming the monomer assistance in the condensation processes (variant 1a) (Figure 3b). However, the dependence curves upward for the variant 1b with no monomer assistance in condensations. Straight lines for variant 1a are not coming from the origin, which is a consequence of the enhancement of the open-chain oligomers in the initial period of the reaction (Figure 1a).

For the first two variants of the pure condensation mechanism the dependence of the ring–oligomer concentrations on the monomer conversion is represented by a straight line (Figure 3c). Only the differentiation of the rate of several first oligomers (variant 2c) leads to some deviation from linearity (Figure 3c). Generally, the comparison of these computational results with the experimental data points to the importance of the condensation reactions in the D_3 cationic polymerization system. The observed dependencies of the rate of the cyclic generation on the monomer conversion[2,6] cannot be understood on the ground of the pure addition polymerization mechanism; however, they may be explained by pathways involving a condensation polymerization scheme itself or in combination with the addition pathway.

Dependence of the Rate of Cyclic Formation on Its Size. This dependence may be discussed in a meaningful way only for the range of ring size $n > 6$ for which the conformation of respective open chains can be described in terms of Gaussian statistics. In this range rates of the ring formation simulated for pathways considered here as well as those found experimentally decrease regularly with an increase in ring size. The cyclic concentration in the system at a given conversion may be approximated by the following general equation:

$$[C_n] = an^{-q}, \quad n \geq 6 \tag{1}$$

where a and q are constant for the series and their values are determined by the kinetics of cyclization competing with linear growth.

The variation of the q value with the reactivity ratio toward chain extension and ring formation is presented

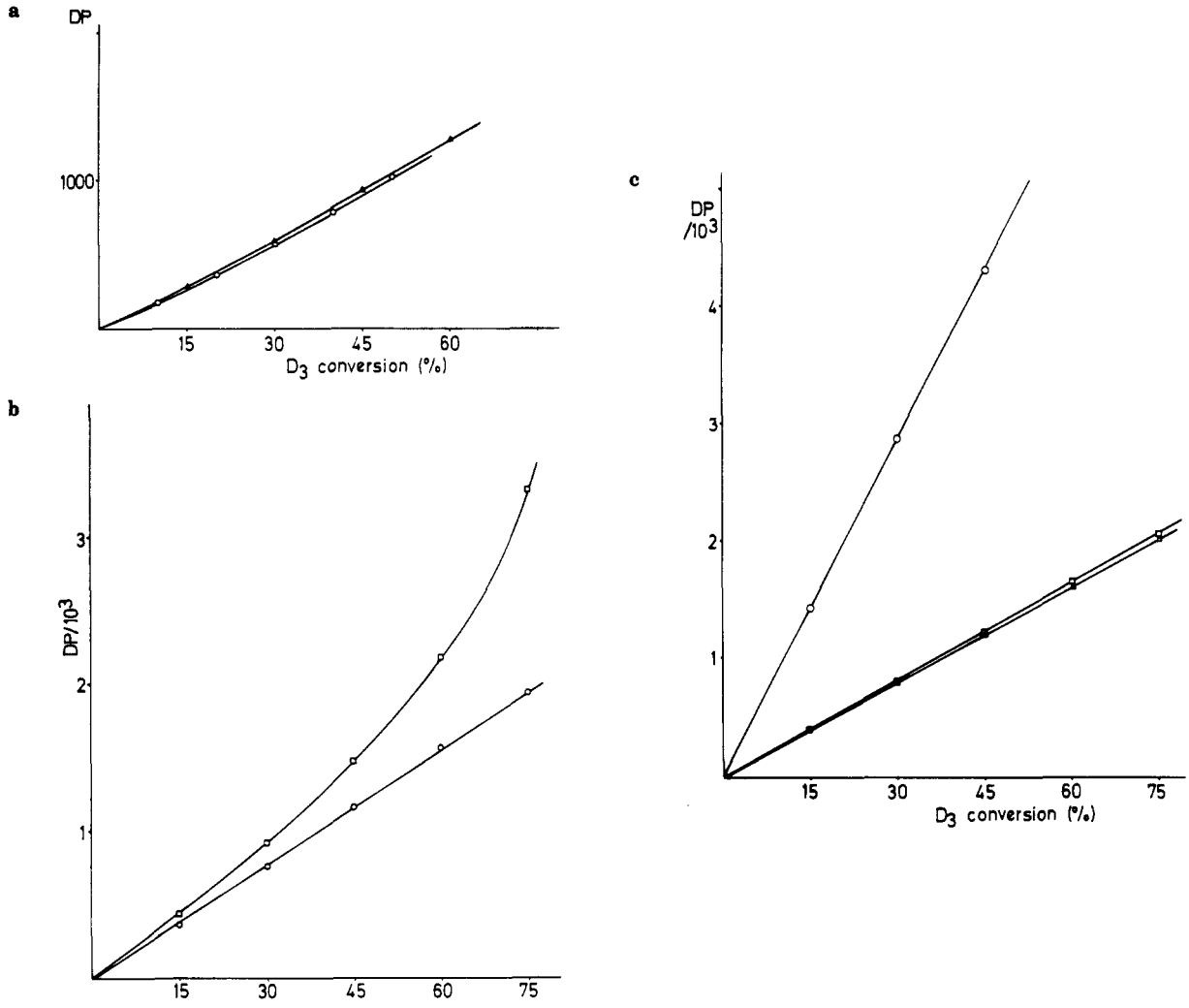


Figure 2. Dependence of the number-average degree of polymerization of the linear fraction on the monomer conversion. (a) Pure addition polymerization (variant 1c): (○) simulation 2 (Table I), assuming monomer assistance in cyclization; (▲) simulation 3 (Table I), no monomer assistance in cyclization. (b) Addition–condensation mechanism (variants 1a and 1b): (○) simulation 6 (Table I) (variant 1a); (□) simulation 8 (Table I) (variant 1b). (c) Pure condensation polymerization (variant 2): (○) simulation 2 (Table II) (variant 2a); (△) simulation 4 (Table II) (variant 2b); (□) simulation 6 (Table II) (variant 2c).

in Figure 4. The gradient $|-q|$ strongly decreases when the contribution from the cyclization is diminished in the range of a low relative probability of the linear growth to the cyclization, i.e., when P_p/P_c (or P_s/P_c) < 1. The variation of $|-q|$ with the contribution of cyclization is much smaller when the ratio is larger than 1. For the addition pathway the gradient approaches the limiting value $|-1.5|$ when the relative rate of cyclization becomes low.

The limiting value for the pure condensation polymerization mechanism with no differentiation of the chain extension rate is $|-2.5|$. The same value was predicted by Yuan et al.[14] from calculations based on a rigorous analytical treatment of the polycondensation system. The limiting slope is, however, definitely lower for the condensation mechanism with the preferential coupling of the short chains (variants 2b and 2c). In a case involving a large reactivity differentiation in the chain extension process $|-q|$ may also acquire a value close to 1.5 (Figure 4c).

The simulation of the dependence (1) on a double-log plot is compared with the experimental values from ref 2 in Figure 5. Good agreement between the computational and experimental data was found for variants 1a, 2b, and 2c, taking into account that the agreement of experimental data with the statistical Kuhn theory obtained in ref 2 may be considered a crude approximation only.

After the simulated concentrations of cyclics had been fitted to experimental values, a deviation between calculated and observed slopes was found, which could be minimalized to 0.4–0.5 (Table I, no. 6; Table II, no. 4, 6). It should be admitted that it is difficult to fit parameters to obtain agreement in both the gradient and the concentration. When discussing possible reasons for these deviations it should be taken into account that the sizes of cyclics and corresponding chains considered here were rather small to expect strict agreement of the experiment with theory based on Gaussian statistics. Since the maximum is observed at 15-mer on the equilibrium distribution curve in the transition region, i.e., 18-mer–30-mer, some flattening of the curve may occur, giving rise to the deviation.

Discussion of the Mechanism of D_3 Polymerization

The Direct Monomer Addition Pathway. According to results of the simulations the observed kinetics of the cyclic oligomer formation in the D_3 cationic polymerization system could be explained on the basis of the addition mechanism of the chain growth competing with intramolecular and intermolecular reactions between end groups if additional provision is made that the monomer molecule participates in the reaction between end groups. In a simplified picture the propagation could be addition of

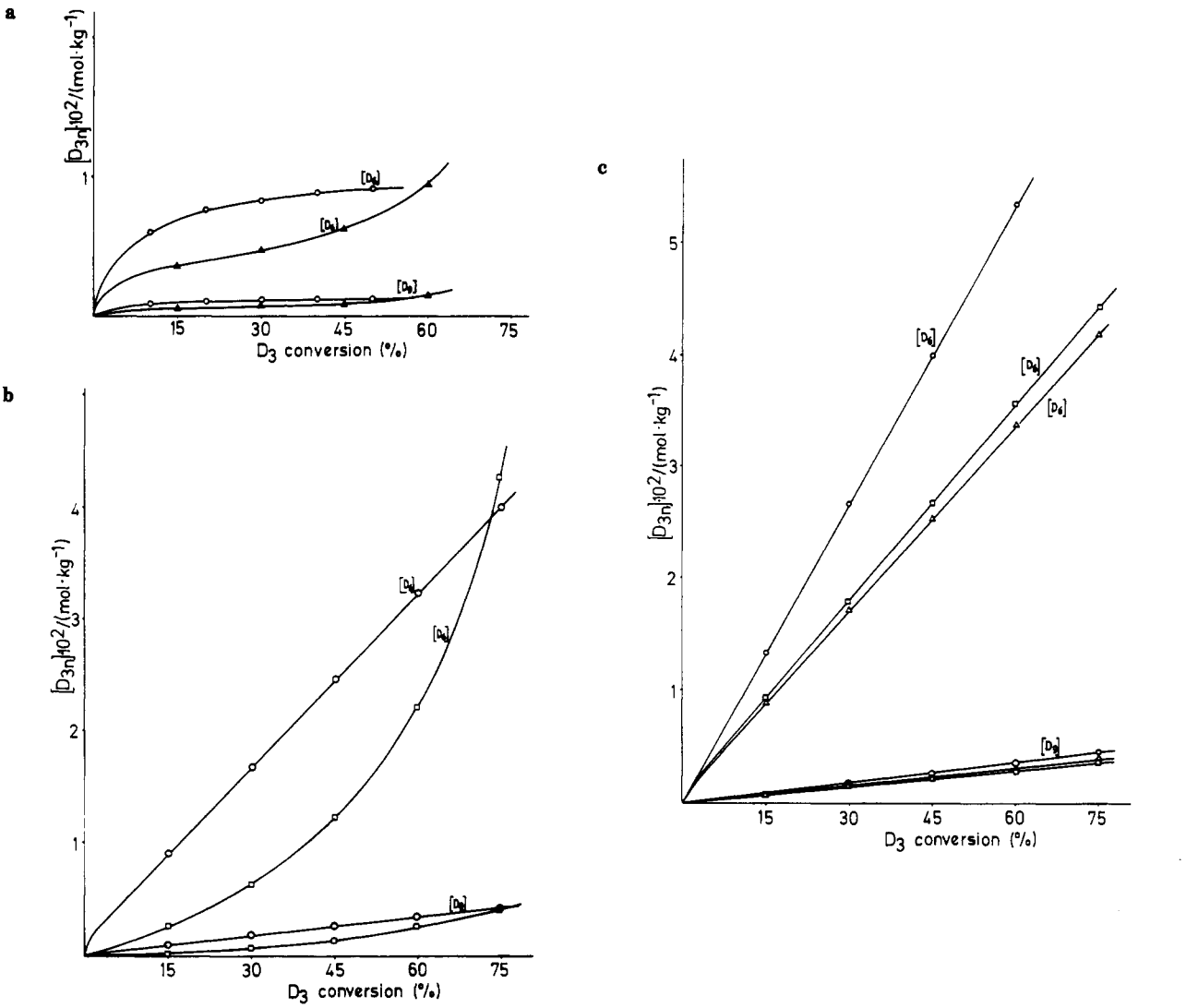
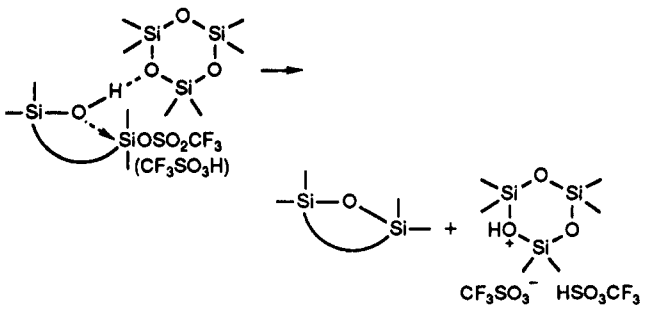


Figure 3. Dependence of D_6 and D_9 concentrations on the monomer conversion. (a) Pure addition polymerization (variant 1c): (O) simulation 2 (Table I), assuming monomer assistance in cyclization; (▲) simulation 3 (Table I), no monomer assistance in cyclization. (b) Addition–condensation mechanism (variants 1a and 1b): (O) simulation 6 (Table I) (variant 1a); (□) simulation 8 (Table I) (variant 1b). (c) Pure condensation polymerization (variant 2): (O) simulation 2 (Table II) (variant 2a); (△) simulation 4 (Table II) (variant 2b); (□) simulation 6 (Table II) (variant 2c).

the acid-activated monomer to the end group (silanol or silyl ester) or monomer addition to the activated end group as discussed elsewhere.[3,9] (Actually, the mechanism is more complex and it should also regard the participation of water molecules and the formation of hydrogen-bonded complexes.[3,19] It is possible that the intermediate complex in addition to the acid and water comprises both the monomer and the end group. In such a case both these reacting species are activated simultaneously.) Since the activation–deactivation reaction is fast, the chain grows stepwise. The ring closure reaction is of the condensation type and an analogous intermolecular process should take place. Although, due to a low concentration of the reactive species, the ring formation process strongly dominates over the intermolecular condensation, the latter is also important and it is impossible to explain the experimental data observed so far on the grounds of the addition growth pathway without regarding the chain-coupling condensation.

It should be admitted that the participation of the monomer molecule in the ring formation or in the chain coupling is reasonable in the light of recent kinetic results on the polycondensation of oligosiloxanediols in acidic media.[20] The condensation requires the simultaneous transfer of a proton to a weak base.[20] Hexamethylcyclotrisiloxane is a stronger base than a chain or other cyclic polysiloxane.[19] Thus, a proton is likely to be transferred to the monomer in the cyclization according to the following scheme:



The intermediacy of a *tert*-siloxonium ion in the condensation step would also explain the monomer assistance. (Such a monomer-stabilized silylenium ion could only exist as a short-lived species that is not likely to survive more than one act of the monomer addition. Thus, it should be considered as an intermediate in the monomer addition in the propagation but not as the chain carrier species. The chain formation requires many repeating activation–

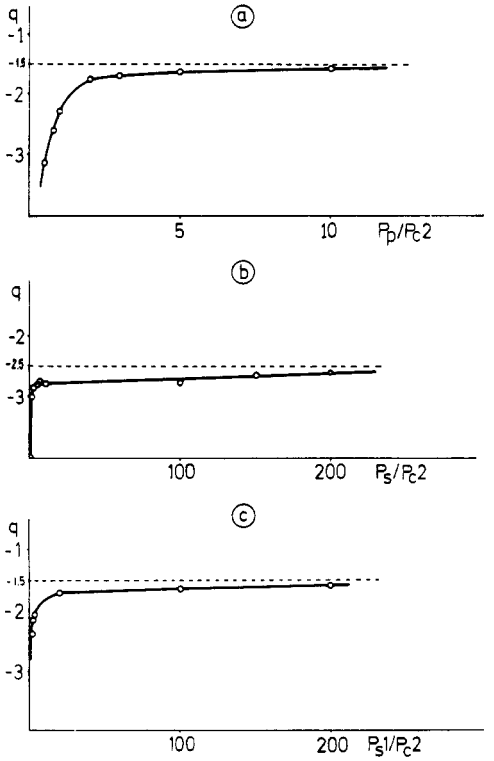
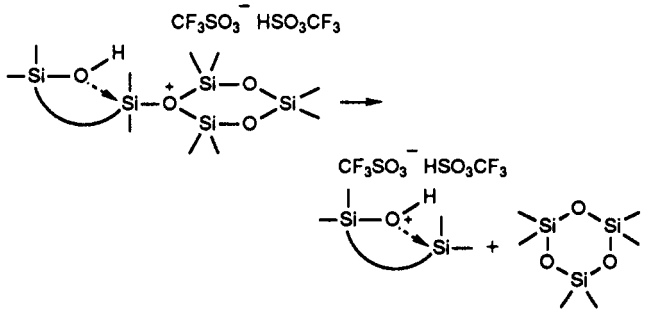


Figure 4. Dependence of the gradient of cyclic oligomer concentration on the linear growth/cyclization probability ratio: (a) pure addition mechanism (variant 1c), assuming monomer assistance in cyclization, $P_p = 0.2$; (b) pure condensation mechanism (variant 2a), $P_s = 0.2$; (c) pure condensation mechanism (variant 2c), assuming variable probabilities of condensation depending on chain length, $P_{s1} = 0.2$, $P_{s6} = 0.001$.

monomer addition–deactivation sequences.)



The Pure Condensation Polymerization Scheme. The classic condensation polymerization scheme, in which the chain growth occurs exclusively as the result of repeating sequences of acidolytic (hydrolytic) ring-opening reaction and acid-(water) forming condensation assuming the equal reactivity of all open chain species and the classic chain extension–ring formation competition, cannot be taken into consideration. With regard to a great tendency for the cyclization of linear functional siloxane oligomers in acidic systems and the low stationary concentrations of open-chain intermediates in the polymerization system, such a mechanism would lead to the exclusive formation of cyclic oligomers.[3] Moreover, the relative rate of ring formation with respect to chain growth would be strongly dependent on the initial initiator concentration, which is not observed.[15] For these reasons the pure condensation polymerization was once rejected.[3]

Recent kinetic results concerning the acid-catalyzed condensation of oligosiloxanols in methylene chloride solution disclosed, however, some unusual features of this

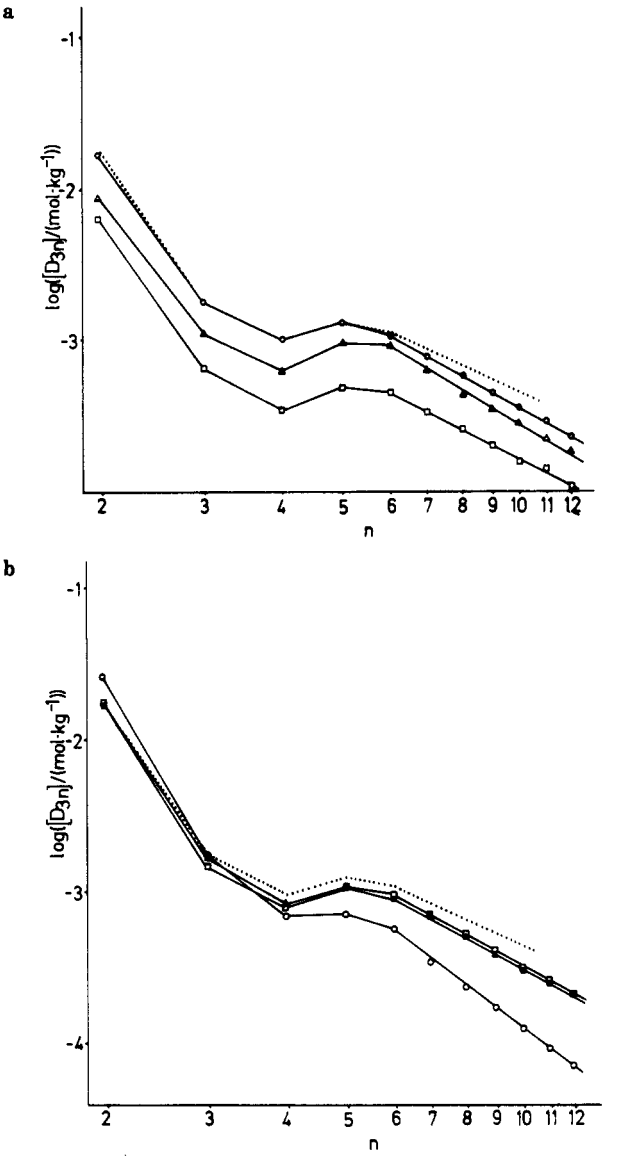


Figure 5. Distribution of D_{3n} cyclic oligomers in the simulation of the polymerization of D_3 at 30% monomer conversion. A dotted line represents the experimental data (40 wt. % of D_3, [HA] = 7×10^{-4} mol·kg^{-1} in *n*-heptane).[2] (a) (○) Simulation 2 (Table I) (variant 1c); (△) simulation 6 (Table I) (variant 1a); (□) simulation 8 (Table I) (variant 1b). (b) (○) Simulation 2 (Table II) (variant 2a); (△) simulation 4 (Table II) (variant 2b); (□) simulation 6 (Table II) (variant 2c).

reaction,[20] which have also changed the view on the possibility of the pure acidolytic (hydrolytic) condensation mechanism operating in the cationic polymerization of cyclic siloxanes. It was shown that the intermolecular condensation is strongly catalyzed by the functional group on the other end of the open-chain intermediate. This means that the reactivity of the open-chain intermediate strongly depends on its length and that there is a preference for the reaction of shorter chains, in particular the one derived from the monomer. It was further demonstrated that the reaction is subjected to a phenomenon that was referred to as intra–inter catalysis. An intermolecular condensation that is catalyzed intramolecularly by a group on the other chain end may compete with an analogous intramolecular condensation catalyzed similarly, but intermolecularly, by the end group originating from another molecule. (The end group assists by receiving a proton from the silanol group entering in the condensation, thus the assistance by the monomer molecule is not involved in this mechanism.) In this case, both reactions, cycliza-

tion and chain extension, show the same order and the dilution does not change the contribution from the cyclization. The intra–inter catalysis could also explain why the yield of cyclics, in the condensation polymerization discussed here, is independent of the concentration of the open-chain species in the system, equivalent to the initial concentration of the initiator.

Thus, the nontrivial condensation polymerization pathway involving the preferential reaction of shorter chains and the intra–inter catalysis remains in agreement with the experimental results. However, it should be noted that in the condensation polymerization, the end groups appear in a very low concentration, which disfavors the intra–inter catalysis. On the other hand, the yield of cyclics does not seem to change with temperature,[2] which means that the cyclization and the chain extension processes show the same activation energy. This observation is an argument in favor of the pure condensation chain growth.

Is a Ring Expansion Mechanism Possible? Our considerations were confined only to those two mechanistic pathways that, in our opinion, are most likely to operate in this system. We did not consider the ring expansion mechanism proposed recently by Sigwalt,[6] because it is not compatible with the earlier observation of the correlation between ring concentration in this polymerization system and conformational probability of the ring closure.[2] In the ring expansion mechanism, growing chains preserve their cyclic structures over time and there is no ground for the existence of any correlation of this type. Since arguments quoted in ref 2 were said to be insufficient for rejecting the ring expansion pathway,[6] we would like to discuss briefly these earlier results, the conclusiveness of which, in our opinion, seems to be underestimated. In particular, we would like to point out that the value of the slope q in ref 2 shown also in the plots of Figure 5a,b is not sole evidence for the correlation of the rate of cyclic formation with the conformational probability of the ring closure. After all, the slope value also depends on other factors shown in the present paper. There exist, however, other features in the dependence of log $[(D_3)_n]$ versus log n that give strong evidence for the existence of the discussed correlation:

(1) In all cases observed in ref 2, this dependence, which is irregular in the range of small rings, becomes regular for rings equal to or larger than the limiting size for the poly(dimethylsiloxane) chain ($n = 6$), i.e. the size from which the conformations of PDMS chains conform to Gaussian statistics. This limiting size was determined in independent studies from the size distribution function of the rings in the equilibrated PDMS system.[18]

(2) Starting from this limiting size value, all the dependencies of log $[(D_3)_n]$ on log n observed in ref 2 are linear, which is in agreement with the shape of the Kuhn function of the conformational probability of ring closure on its size.[17]

(3) The shape of the dependence under consideration also shows a close similarity to the equilibrium size distribution of the cyclics in the range of smaller rings $n < 6$, in which Gaussian statistics are not applied. In particular, a submaximum at $n = 5$ and a subminimum at $n = 4$ appear or at least an inflection point at this place is observed. It should be noted that the characteristic shape of the equilibrium distribution (i.e., the subminimum and submaximum) reflects the change in the conformational probability of the ring closure, as the probability of the ring opening of unstrained cyclics in the polymer homologue series increases proportionally to the ring size.[21]

In addition, it should be pointed out that the observation of the above characteristic features of the discussed correlation is possible only if some other kinetic conditions for the reaction are met. Thus, the fact that no correlation is observed would not prove that there is no end-to-end closure. Conversely, the observation of these correlation features as shown in ref 2 gives unequivocal evidence that the cyclic oligomer formation is accompanied or preceded by an act of ring closure.

Some features of the distribution function, such as the relatively high yield of D_9 observed for the D_3 polymerization in methylene chloride pointed out in ref 6, may be interpreted in terms of the intramolecular interaction between end groups, which increases the population of the cyclic conformation of the chain, favoring ring closure. Moreover, it is highly possible that the ring-shaped complex between end groups is the intermediate in the cyclization. However, it is not univocal with the ring expansion mechanism. The cyclic complex comprising two ends and the uncomplexed open-chain form are in dynamic equilibrium, which is established rapidly on the propagation reaction time scale.

References and Notes

(1) Lichtenwalner, H. K.; Sprung, H. S. *Encyclopedia of Polymer Science and Technology*; J. Wiley and Sons, Inc.: New York, London, Sydney, Toronto, 1970; Vol. 12, pp 464–503. Chojnowski, J.; Rubinsztajn, S.; Wilczek, L. *Actual. Chim.* **1980**, *3*, 56.
(2) Chojnowski, J.; Ścibiorek, M.; Kowalski, J. *Makromol. Chem.* **1977**, *178*, 1351.
(3) Chojnowski, J.; Wilczek, L. *Makromol. Chem.* **1979**, *180*, 117.
(4) Wright, P. V. In *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier: London, 1984; Vol. 2, Chapter 14, p 1055. Patnode, W.; Wilcock, D. F. *J. Am. Chem. Soc.* **1946**, *68*, 358. Hurd, D. T. *J. Am. Chem. Soc.* **1955**, *77*, 2998. Ishizuka, S.; Aihara, T. *J. Chem. Soc. Jpn.* **1956**, *59*, 1198. Andrianov, K. A.; Jakushkina, S. E. *Vysokomol. Soedin.* **1959**, *1*, 613. Reichsfeld, V. O.; Ivanova, A. G. *Vysokomol. Soedin.* **1962**, *4*, 30. Kendrick, T. C. *J. Chem. Soc.* **1965**, 2027. Andrianov, K. A.; Szkolnik, M. I.; Kopylov, V. M.; Bravina, N. N. *Vysokomol. Soedin. Ser. B* **1974**, *16*, 893. Chojnowski, J.; Mazurek, M.; Ścibiorek, M.; Wilczek, L. *Makromol. Chem.* **1974**, *175*, 3299. Lebrun, J. L.; Sauvet, G.; Sigwalt, P. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 757. Sauvet, G.; Sigwalt, P. IUPAC 6th International Symposium on Cationic Polymerization and Related Processes, Abstracts, Ghent, 1983; p 71.
(5) Sauvet, G.; Lebrun, J. L.; Sigwalt, P. In *Cationic Polymerization and Related Processes*; Goethals, E. J., Ed.; Academic Press: New York, 1984; p 237.
(6) Sigwalt, P. *Polym. J.* **1987**, *19*, 567.
(7) Chojnowski, J. In *Silicon Chemistry*; Corey, J. Y., Corey, E. R., Gaspar, P. P., Eds.; Ellis Horwood Ltd.: Chichester, 1988; p 297.
(8) Chojnowski, J.; Mazurek, M.; Ścibiorek, M.; Wilczek, L. *Makromol. Chem.* **1974**, *175*, 3299.
(9) Wilczek, L.; Chojnowski, J.; Rubinsztajn, S. *Makromol. Chem.* **1986**, *187*, 39.
(10) Ercolani, G.; Mandolini, L.; Mencarelli, P. *Macromolecules* **1988**, *21*, 1241.
(11) Gordon, M.; Temple, W. B. *Makromol. Chem.* **1972**, *152*, 277.
(12) Matyjaszewski, K.; Zieliński, M.; Kubisa, P.; S łomkowski, S.; Chojnowski, J.; Penczek, S. *Makromol. Chem.* **1980**, *181*, 1469.
(13) Sarmoria, C.; Valles, E.; Miller, R. D. *Makromol. Chem., Makromol. Symp.* **1986**, *2*, 69.
(14) Yuan, X.-F.; Masters, A. J.; Nicholas, C. V.; Booth, C. *Makromol. Chem.* **1988**, *189*, 823.
(15) Ścibiorek, M. Ph.D. Thesis, Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences in Łódź, Łódź, 1981.
(16) Wilczek, L.; Chojnowski, J. *Makromol. Chem.* **1983**, *184*, 77.
(17) Kuhn, W. *Kolloid-Z.* **1934**, *68*, 2.
(18) Wright, P. V.; Beevers, M. S. In *Cyclic Polymers*: Semlyen, J. A., Ed.; Elsevier: London, New York, 1986; pp 85–131.
(19) Wilczek, L.; Chojnowski, J. *Macromolecules* **1981**, *14*, 9.
(20) Chojnowski, J.; Rubinsztajn, S.; Wilczek, L. *Macromolecules* **1987**, *20*, 2345.
(21) Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 1600.

Registry No. Hexamethylcyclotrisiloxane, 541-05-9.