accordingly decreasing. The four G' master curves of Figure 6 show at least the end of the rubberlike plateau, the height of which passes through a maximum from Be to Mg, Ca, and Ba, successively. It is noteworthy that, measured in bulk, the equilibrium storage modulus increases regularly with the ionic radius,[13] which means that the effective cross-link density is favored by the bigger cations. In consequence, Ba would form the largest size multiplets, which are however characterized by the weakest electrostatic interactions, whereas Be would exhibit just the opposite behavior. The mixing of the bulk HTP with a nonpolar solvent changes the conformational state of the polymeric backbone, and this perturbation could possibly modify the ion aggregation to an extent depending on the strength of the ion multiplets. Accordingly, a maximum multiplet size should be observed for intermediate-size cations, but this expectation needs experimental support.

The thermorheological simplicity of the HTP solutions is to be outlined, and the secondary relaxation observed is undoubtedly characteristic of the ionic component. These attractive features largely justify the choice of HTP as model compounds for ion-containing polymers. Furthermore, the rheological behavior, and especially the shear-thickening effect, could give to HTP solutions a real interest for applications.

Acknowledgment. We are very much indebted to UNIBRA (Brussels) and the "Services de la Programmation de la Politique Scientifique" for efficient support and fellowship (to G.B.). We are also grateful to G. Renders for skilled technical assistance.

References and Notes

(1) Holiday, L., Ed. "Ionic Polymers"; Applied Science Publishers: London, 1975.
(2) Eisenberg, A.; King, M. "Polymer Physics"; Stein, R. S., Ed.; Academic Press: New York, 1977; Vol. 2.
(3) Eisenberg, A. *Contemp. Top. Polym. Sci.* **1979**, *3*, 231.
(4) Broze, G.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1981**, *14*, 224.
(5) Broze, G.; Jérôme, R.; Teyssié, Ph.; Marco, C. *Polym. Bull. (Berlin)* **1981**, *4*, 241.
(6) Broze, G; Jérôme, R.; Teyssié, Ph.; Gallot, B. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 415.
(7) Broze, G.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1982**, *15*, 920.
(8) Broze, G.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1982**, *15*, 1300.
(9) Richards, D. H.; Burgers, F. J. *Polymer* **1976**, *17*, 1020.
(10) Ferry, J. D. "Viscoelastic Properties of Polymers"; Wiley: New York, 1970.
(11) Geiser, D.; Hocker, H. *Polym. Bull. (Berlin)* **1980**, *2*, 591.
(12) Hild, G.; Kohler, A.; Rempp, P. *Eur. Polym. J.* **1980**, *16*, 525.
(13) Broze, G.; Jérôme, R.; Teyssié, Ph.; Marco, C. *J. Polym. Sci., Polym. Phys. Ed.*, in press.

Reviews

Mechanism of Cyclic Acetal Polymerization. End of a Controversy?

Ryszard Szymański, Przemyslaw Kubisa, and Stanislaw Penczek*

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90-362 Łodz, Boczna 5, Poland. *Received February 9, 1982*

ABSTRACT: An analysis of the major controversies that have arisen in studies of cyclic acetal polymerization over almost 2 decades is presented. These controversies involve the structures of the polymers and the structures of the active species. Analysis of the published data has revealed that at least some polyacetals, e.g., poly(1,3-dioxolane), may be prepared either as almost exclusively cyclic or as predominantly linear macromolecules, depending on the starting monomer concentration. The initial (formed during initiation) and the final (formed during termination) end groups have clearly been observed in a number of systems. The earlier controversy whether polyacetals are linear or cyclic had at least partially been due to different starting concentrations of monomer used by various authors or different starting ratios of monomer to initiator. A new notion "critical monomer concentration" is introduced, describing a certain starting monomer concentration, below which practically all of the produced polymer must be cyclic. When, on the contrary, conditions are chosen to avoid a higher proportion of macrocycles, living polyacetals can be obtained; the dicationically living polyacetals were successfully used to prepare ABA block copolymers. Recent data on oxonium–carbenium ion equilibria have been analyzed and it is shown that the previous insistence of various authors on the uniqueness of structures of growing species cannot be sustained. Various species coexist in dynamic equilibrium and their role in the chain growth may vary according to the conditions of polymerization. For 1,3-dioxolane the carbenium–oxonium equilibrium suggests that growing species are predominantly the tertiary oxonium ions, although some alkoxycarbenium ions can also be present.

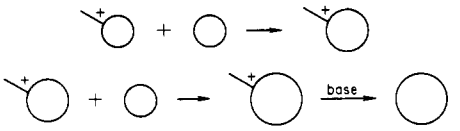
1. Origin and Nature of Controversy

There have been two major controversies in the polymerization of cyclic acetals. The first concerns the structure of the polymers, and the second the way the macromolecules grow.

Plesch,[1] following the idea expressed in Gresham's patent,[2] concluded that poly(1,3-dioxolane) (poly-**1**) and poly(1,3-dioxepane) (poly-**2**) are exclusively cyclic. This conclusion was based on studies of the end groups by chemical, IR, and ^{1}H NMR analyses. Plesch, assuming that the structure of the end groups should be related to the initiators and/or to the transfer reactions, was looking for these end groups. Not finding them, he assumed that growth proceeds by ring expansion: cationated rings add

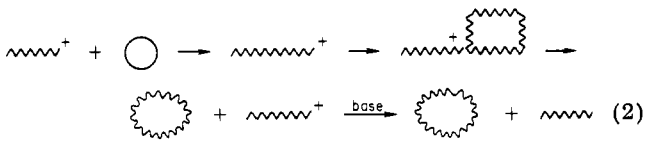
0024-9297/83/2216-1000$01.50/0

cyclic monomer, these rings produce larger cationated rings and the process continues, leading to entirely cyclic macromolecules:



(1)

Jaacks and his group maintained, on the contrary, that polyacetals are mostly linear[3] and that various proportions of cyclic oligomers and/or polymers are formed by a back-biting reaction:



(2)

Back-biting as the way by which macrocycles are formed was proposed also by Semlyen,[4] who found that the distribution of cyclic oligomers in polyacetals is in good agreement with the Jacobson–Stockmayer theory[5] (derived for random back-biting).

Other authors supported one side or the other;[6-8] these contributions produced some new data, but they did not resolve the controversy, which may be recapitulated as follows:

Plesch observed the formation of exclusively cyclic polyacetals and, arguing that no cyclization mechanism can account for 100% cyclization efficiency, proposed that macrorings are formed not by cyclization of linear macromolecules but directly through expansion of the cationated rings.

Some of the other workers in this field, finding also linear polyacetals, argued that a mechanism involving growth of linear macromolecules accompanied by their cyclization may sufficiently well describe the observed distribution of cyclic and linear polymers.

Thus the problematic point is as follows: Are polyacetals exclusively cyclic indeed as required by the ring expansion theory or are they a mixture of linear and cyclic polymers, resulting from cyclization accompanying growth of linear macromolecules?

In order to find the reason for the apparent discrepancies between the results of different groups, Plesch studied the influence of water and showed that the proportion of secondary to tertiary oxonium ions (corresponding to cyclic and linear growing macromolecules) depends on concentration of water. Thus he concluded that under "dry conditions", a ring expansion mechanism operates, whereas in the presence of water, linear macromolecules are formed.[9]

More recently, we have shown that in the practically dry systems ($[H_2O] \ll [HOSO_2CF_3]_0$ and the same for the series of experiments) living poly-1 can be either mostly (almost exclusively) cyclic or mostly linear, depending on the starting concentration of monomer and initiator.[10]

Thus we conclude that both groups whose opinions are described above are partially right (or partially not right); i.e., they are right in describing the structure of polymers prepared in their own system and not right in their criticism of the other group.

In this paper we deal first with the end-group problem, then we comment on the ring–chain equilibria in cyclic acetals, and finally we present our view on the mechanism of polymerization. In this way we intend to show how and why the controversy emerged and explain why under certain conditions cyclic or linear macromolecules may prevail.

2. End Groups in Polyacetals

Poly(oxymethylene) prepared by polymerization of formaldehyde and then end blocked with acetic anhydride is known to have exactly two end groups per macromolecule (IR vs. osmometry)[11]

$$n\mathrm{CH_2O} \xrightarrow{\text{anionic}} \mathrm{HO(CH_2O)_{n-1}CH_2OH} \xrightarrow{(\mathrm{AcO})_2\mathrm{O}} \mathrm{AcO(CH_2O)_{n-1}CH_2OAc} \quad (3)$$

Copolymers of 1,3,5-trioxane (**3**) with **1** and homopolymers of **3** were also shown to contain hydroxyl end groups[12] and methoxy end groups (Zeisel method);[13] some proportion of cyclic macromolecules was also found.[14] However, some of these end groups could have been formed by secondary processes such as chain transfer. Thus it became necessary to study the end groups in model systems, freed from impurities.

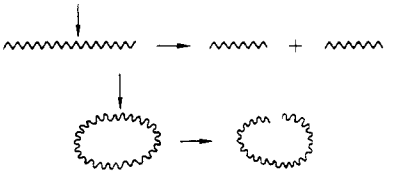
Poly-**1** was the first and subsequently the most frequently studied model system. In the first study, aimed at determining the structure of the growing species and the end groups, **1** was polymerized with $HClO_4$ as initiator.[1] The initial concentrations of monomer and initiator were in the ranges $[1]_0 \sim 1\text{–}2$ mol·L^{-1} and $[HClO_4]_0 \sim 10^{-2}\text{–}10^{-3}$ mol·L^{-1}. The resulting polymers had low polymerization degrees, usually between 10 and 30 (vapor pressur osmometry). This was much below the $([1]_0 - [1]_e)/[HClO_4]_0$ ratio, which was in the range 200–1000.

Different end groups, including OH, OCH_3, $\overline{OCHO}$, and NH_2 (from the terminating agent), were sought but none was found either by IR and ^{1}H NMR spectroscopy or by chemical analysis.[1] After this first report claiming the cyclic structure of the polymers, the problem of end groups in polyacetals received much attention. For the determination of end groups, Jaacks developed a method based on the GLC analysis of the products of the acid hydrolysis of the polymers, because ethoxy-terminated polyacetal gives ethanol.[3] Using this method, Jaacks found ethoxy end groups in quantities equivalent to $0.82[HClO_4]_0$ in polymers prepared at $[1]_0 = 3.6$ mol·L^{-1} and $[HClO_4]_0 = 2.8 \times 10^{-3}$ mol·L^{-1} and terminated with C_2H_5ONa.

The same method, used by Plesch for an apparently similar system, $[1]_0 \sim 1\text{–}2$ mol·L^{-1} and $[HClO_4]_0 \sim 10^{-2}\text{–}10^{-3}$ mol·L^{-1} (note, however, the difference in $[1]_0$), gave different results: only minute amounts of ethoxy end groups ($<0.05[HClO_4]_0$) were found.[15]

Later, the same group tried to determine the active species in the polymerization of **1** by Saegusa's method ($C_6H_5O^-$ addition to the macrocations).[16] No macromolecules containing $CH_2CH_2OCH_2OC_6H_5$ end groups were found. This, again, supported the idea that macromolecules of poly-**1** prepared with $HClO_4$ are exclusively cyclic, and in order to be cyclic they have to grow as rings, at no stage of growth becoming linear.

These results were in conflict also with another work of Jaacks and Kelen, in which the simultaneous presence of linear and cyclic macromolecules was shown.[17] These authors, in the almost forgotten work, used another approach and studied the dependence of the decrease of $\overline{DP}_n$ (measured by viscosity) as a function of the time of acidolysis.



(4)

Table I
Comparison of $\overline{DP}_n$(calcd)[a] with the Measured $\overline{DP}_n$ Values[b]

$[1]_0$, mol·L^{-1}	$10^3[\text{initiator}]_0$, mol·L^{-1}	$\overline{DP}_n$ calcd	$\overline{DP}_n$ end groups	$\overline{DP}_n$ osmometry
5.40[c]	4.05	1150	1300 } UV	1390
5.40[c]	2.75	1690	1730 } UV	1770
5.40[c]	1.10	4190	5240 } UV	4350
4.05[c]	4.70	700	650,[e] 575[e] } ^{1}H NMR	
4.05[c]	1.95	1690	1380[f] } ^{1}H NMR	
4.05[d]	5.2	750	1000,[g] 920[g] } ^{1}H NMR	

[a] $\overline{DP}_n$(calcd) = ($[1]_0 - [1]_e$)/$[\text{initiator}]_0$. [b] Not less than 85% of the expected amount of polymer was recovered after purification. [c] $C_6H_5CO^+SbF_6^-$ initiator. [d] $(C_2H_5)_3O^+SbF_6^-$ initiator. [e] From initial C_6H_5COO and terminal OC_2H_5 groups. [f] From initial C_6H_5COO groups. [g] From initial C_2H_5O and terminal $P^+(n\text{-Bu})_3$ groups.

As illustrated in (4), when a linear macromolecule breaks, its $\overline{DP}_n$ is (statistically) halved, but when a cyclic macromolecule breaks, its $\overline{DP}_n$ is preserved.

Analysis of the dependence of $\overline{DP}_n$ on time indicated that indeed both linear and cyclic macromolecules are present.[17]

Still later, Ponomarenko et al.,[6] using the ^{14}C tracer method, reported quantitative incorporation of the C_2H_5 group from $(C_2H_5)_3O^+SbCl_6^-$ initiator into polymer.

Further systematic studies of the end groups have been undertaken in this laboratory.[18,19]

A. Poly-1 Initiated with Carbenium Ions. Initiation of the polymerization of 1 with $C_6H_5CO^+SbF_6^-$ made it possible to use UV light to observe the benzoate end groups $C_6H_5C(O)OCH_2CH_2OCH_2$ (λ_{max} = 230 nm, ϵ_{max} 1.16 × 10^4 mol^{-1}·L·cm^{-1}). Good agreement was found between the measured and calculated $\overline{DP}_n$, assuming that the polymerization is living (no transfer affecting $\overline{DP}_n$ and no termination) and that one initiator molecule produces one macromolecule.

The same initial groups (coming from initiator) were observed in poly-1 by ^{1}H NMR when 1-d_6 was used as monomer.[19] In this study the FT ^{1}H NMR technique could successfully be applied, because hydrogen atoms were mostly present in the end groups:

$$C_6H_5C(O)OCD_2CD_2OCD_2\text{–}... \quad (5)$$

The small and exactly known percentage of hydrogen atoms present in the chain due to incomplete deuteration was used as the internal standard. In Figure 1 the FT ^{1}H NMR spectrum (1200 scans) of poly-1-d_6, initiated with $C_6H_5CO^+SbF_6^-$ initiator and terminated with $C_2H_5O^-Na^+$, is given. $\overline{DP}_n$ calculated by assuming that one molecule of initiator produces one macromolecule and $\overline{DP}_n$ found from initial and from terminal end group content agree quite well with each other.[19]

Agreement between the $\overline{DP}_n$ calculated and found from the end groups can, however, be misleading when there is a possibility of cyclization. This agreement only tells us that all of the initiator used is bound to linear macromolecules that were living at the moment of termination.

The observed equality would consequently hold also if linear macromolecules constitute only a small fraction of the polymeric material, the remainder being cyclic.

Thus in order to estimate the proportion of linear and cyclic fractions, one should compare the $\overline{DP}_n$ from end groups with $\overline{DP}_n$ determined independently, e.g., by osmometry. For an exclusively linear polymer these two values are equal; with increasing proportion of cyclic polymer, the difference between them increases.

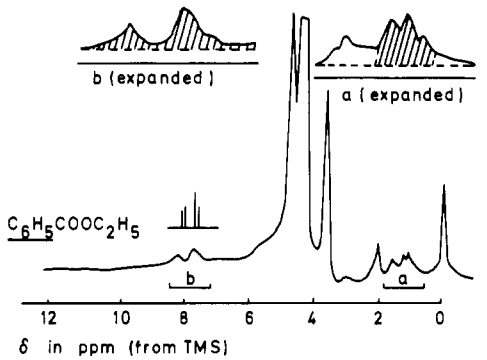


Figure 1. 60-MHz FPT ^{1}H NMR spectrum of poly(1,3-dioxolane-d_6) (poly-1-d_6) initiated with $C_6H_5CO^+SbF_6^-$ and terminated with C_2H_5ONa in CD_3NO_2 solvent. Number of accumulated scans = 1200. The stick spectrum indicates the absorptions of aromatic protons of ethyl benzoate. Polymerization conditions: [1-d_6]$_0$ = 4.05 mol·L^{-1}, $[C_6H_5CO^+SbF_6^-]_0$ = 4.7 × 10^{-3} mol·L^{-1}, CD_3NO_2 solvent, −15 °C. Reprinted with permission from ref 19. Copyright 1978 Huethig und Wepf Verlag.

Let us assume two cases, A and B. In the former, only linear macromolecules are formed, whereas in the latter, linear and cyclic macromolecules coexist:

$$\text{case A:} \quad I + nM \rightarrow I\text{–}M_n\text{–}$$

$$\text{case B:} \quad I + nM \rightarrow I\text{–}M_{n-m}\text{–} + \text{cyclic-}M_m \quad (6)$$

where I denotes initiator, M monomer, I end group, and –M– polymer unit.

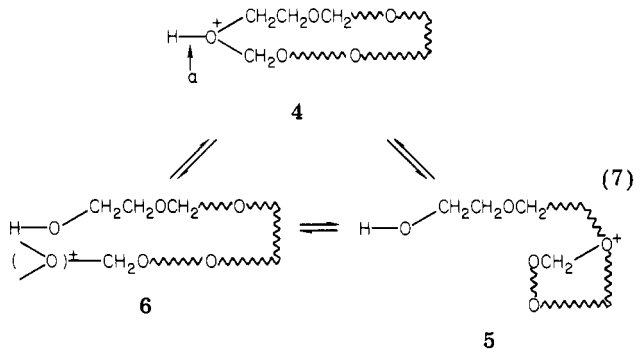
For both cases $\overline{DP}_n$(calcd) = n. The $\overline{DP}_n$ found from end groups is also the same for case A and case B when all of the initiator I is bound to polymer, as shown in the scheme above.

On the contrary, the $\overline{DP}_n$ determined from osmometry differs for both cases; it is always lower in case B, because the same number of monomer molecules is engaged in a larger number of macromolecules.

Thus for predominantly linear polymer, when transfer agents (e.g., H_2O) are eliminated, there should be a triple agreement: between $\overline{DP}_n$ calculated, $\overline{DP}_n$ found from the end groups, and $\overline{DP}_n$ determined by, e.g., osmometry. Agreement of this kind was observed for poly-1, and some representative data are given in Table I.

It has to be noted that all of the polymers prepared (Table I) were obtained at relatively high initial monomer concentration.

B. Poly-1 Initiated with Protonic Acids. In the polymerization of cyclic acetals initiated with protonic acids the following set of equilibria has to be taken into account (polymerization of 1 is taken as an example):



4

6 5 (7)

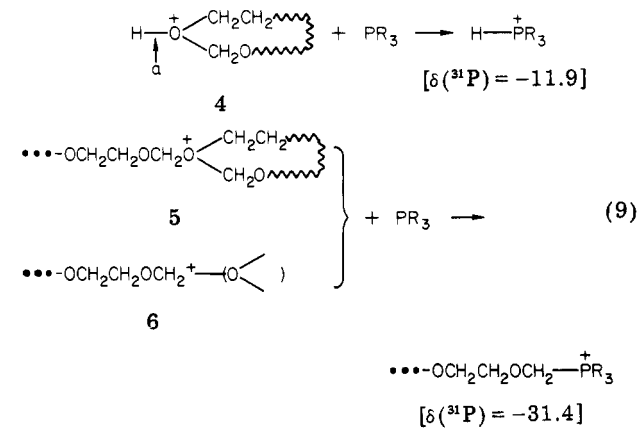
The notation $ROCH_2^+$–(O<) is introduced to indicate that linear species $ROCH_2$ may exist in the form of carboxonium ion $ROCH_2^+$ or oxonium ion (both species being in equilibrium) and that various oxygen atoms (i.e., from monomer, linear polymer, or cyclic polymer) may participate in formation of the corresponding oxonium ion. The ligand –(O<) shown in parentheses does not count in the stoichiometry.

Scheme 7 shows that linear living macrocation **6** either can bite its own initial end group (nucleophilic attack by the OH group), giving **4**, or can bite any unit within a macromolecule, giving macrooxonium ion **5** (nucleophilic attack by the acetal oxygen atom). Of course, since in **4** the weakest bond is bond a, a proton can be transferred to other oxygen atoms in the same macromolecule or in another one, cyclic or linear.

In order to determine the concentration of species **4** and **5** + **6** we used the ion-trapping method, which consists of reacting a living cationic system with tertiary phosphine:[20]

$$\cdots\text{-}OCH_2CH_2OCH_2^+\text{-}(O<) + PR_3 \rightarrow \cdots\text{-}OCH_2CH_2OCH_2\overset{+}{P}R_3 \quad (8)$$

Reaction of R_3P with the secondary macrooxonium ions (like **4**) would give the tertiary phosphonium ions by breaking the weakest bond, bond a, in **4**, whereas its reaction with macrocarboxonium ions and/or tertiary macrooxonium ions (**5** and **6**) should lead to the quaternary phosphonium cations:



4 [$\delta(^{31}P) = -11.9$]

5 6 (9)

[$\delta(^{31}P) = -31.4$]

It has been shown that when R is n-C_4H_9 in the phosphine used for ion trapping, the reactions in (9) are irreversible.[20]

Results of ion trapping for two different starting ratios $[M]_0/[I]_0$ are shown in Figure 2.[10]

Comparison of spectrum 2a and spectrum 2b ($([M]_0 - [M_e])/[I]_0$ = 6850 and 18, respectively) shows that concentrations of both species change with the $[M]_0/[I]_0$ ratio. Increasing concentration of initiator $[HOSO_2CF_3]_0$ and decreasing concentration of monomer $[1]_0$, which favor the formation of polymer of lower degree of polymerization,

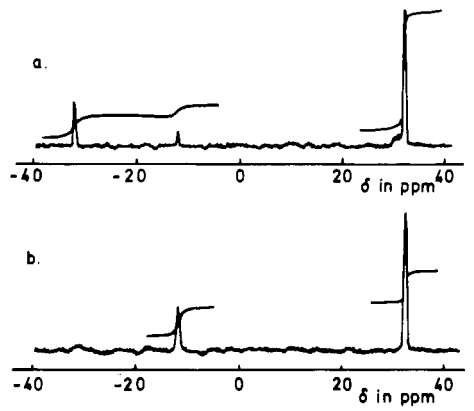


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of poly(1,3-dioxolane) initiated with $HOSO_2CF_3$ and terminated with $P(n\text{-}C_4H_9)_3$. (a) Polymerization conditions: $[1,3\text{-dioxolane}]_0$ = 7.4 mol·L^{-1}, $([1]_0 - [1]_e)/[I]_0$ = 6850, $[HOSO_2CF_3]_0 = 1.0 \times 10^{-3}$ mol·L^{-1}, solvent CH_2Cl_2, temperature –15 °C, time 24 h, $[P(n\text{-}C_4H_9)_3] = 8.0 \times 10^{-3}$ mol·L^{-1}. Spectrum recorded at –70 °C, 6000 scans. (b) $[1,3\text{-dioxolane}]_0$ = 1.1 mol·L^{-1}, $[HOSO_2CF_3]_0 = 2.2 \times 10^{-2}$ mol·L^{-1}, $([1]_0 - [1]_e)/[I]_0$ = 18, solvent CH_2Cl_2, temperature –15 °C, time 24 h, $[P(n\text{-}C_4H_9)_3] = 4.65 \times 10^{-2}$ mol·L^{-1}. Spectrum recorded at –70 °C, 270 scans. Chemical shifts in ppm from 85% H_3PO_4. Reprinted with permission from ref 10. Copyright 1979 Huethig und Wepf Verlag.

result in a shifting of the equilibrium between secondary and tertiary oxonium ions in the direction of secondary oxonium ions (**4**) (macrocycles).

These results show that depending on the polymerization conditions, which govern the $\overline{DP}_n$, living poly-1 can have mostly a form of secondary cyclic oxonium ions (**4**) or tertiary linear or cyclic oxonium ion (cf. (7)). After killing of these macroions, cyclic macromolecules are formed from **4**, cyclic and linear macromolecules are formed from **5**, and linear macromolecules are formed from **6**. Thus various authors using different polymerization conditions could get different proportions of cyclic and linear poly-1. Indeed, Plesch worked, as indicated in section 2, mostly with low $[M]_0$ and low $([M]_0 - [M]_e)/[I]_0$ ratios and concluded that polymers were cyclic,[1] whereas Jaacks worked with higher $[M]_0$, prepared polymers of higher $\overline{DP}_n$, and observed the presence of linear macromolecules.[17]

Thus as determined by Jaacks, polymer having $\overline{DP}_n$ = 25 contains only 12% linear fraction; this proportion increases, however, to 45% linear fraction for polymer with $\overline{DP}_n$ = 220.[17]

This difference as a reason of controversy has not been taken into account during the long-lasting discussion.[9,21-24]

Although end-to-end cyclization was considered (and rejected) earlier,[1,16] it was not appreciated that this reaction may lead to the different proportion of macrocyclics, depending on the reaction conditions. A high proportion of macrorings may result at low $\overline{DP}_n$, but with increasing $[M]_0/[I]_0$ ratio, the proportion of macrorings decreases and for sufficiently high $\overline{DP}_n$ the polymer, although the same mechanism may operate, may be predominantly linear. This can also be observed for a given polymerization with a stepwise increase of $\overline{DP}_n$.

These kinetic phenomena are discussed in section 4, whereas in the next section we discuss the ring–chain equilibrium.

3. Proportion of Macrocyclics in Polyacetals at Equilibrium Conditions

Apart from the influence of the $\overline{DP}_n$ on the proportion

of macrocyclics in the polymer (due to the end-to-end cyclization), this proportion depends also on the starting monomer concentration as a consequence of the ring–chain equilibrium, which we discuss first in this section.

Indeed, whenever the active species in the growing polymer can react with any unit within a chain, closing a macrocycle, i.e., when the equilibrium

$$-M_{n+m}- \rightleftharpoons \text{cyclic-}M_n + -M_m- \quad (10)$$

holds, there will be always a certain proportion of cyclic-M_n present in the product (total polymer). For the equilibrated system the concentration of macrocyclics of a given polymerization degree is given by the Jacobson–Stockmayer theory.[25-27]

$$[\text{cyclic-}M_n] = An^{-5/2} \quad (11)$$

As follows from eq 11, the concentration of a macrocycle of a polymerization degree n, [cyclic-M_n], does not depend on the polymerization conditions ($[M]_0$, temperature) and is exclusively a function of n (the parameter A is a constant for a given polymer, providing that $\overline{DP}_n$ of the linear fraction is sufficiently high and all rings are strainless). Therefore the sum of the concentrations of all rings, $\sum_{n=1}^{\infty}$[cyclic-M_n], is independent of conditions, including the starting monomer concentration. Thus we may conclude that one of the consequences of the ring–chain equilibrium is the dependence of the proportion of rings in the product on $[M]_0$. There is a certain starting monomer concentration at and below which all of the polymer should be cyclic. This has to be remembered when data of various authors working at different $[M]_0$ are compared.

Thus there is a certain monomer concentration, say $[M]_{crit}$, which is equal to this sum:

$$[M]_{crit} = \sum_{n=1}^{\infty} [\text{cyclic-}M_n] \quad (12)$$

It follows that if the starting monomer concentration $[M]_0$ is equal to $[M]_{crit}$ (which in real systems may, however, depend to a certain degree on solvent and $\overline{DP}_n$ of the linear fraction), then practically all of the product must be cyclic. Because in real systems monomer and lower cyclic oligomers are strained, $[M]_{crit}$ (as defined by (12)) depends to a certain degree on the temperature. Therefore the proportion of the rings will change from unity when $[M]_0 < [M]_{crit}$ to its minimum value at the highest attainable $[M]_0$ (i.e., in the bulk).

Semlyen determined A for poly-1[4] and using his data we have calculated the proportion of rings in the polymerization of 1 by summation (12).

According to Figure 3, when 5.0 mol·L^{-1} of polymer is produced only 17% of it is cyclic. When, however, $[M]_0 - [M]_e \sim 1$ mol·L^{-1}, almost all of it is cyclic and $\overline{DP}_n$ measured should be lower than $\overline{DP}_n$ calculated (assuming living conditions). This was indeed observed.[1,15]

Semlyen's treatment of his data was criticized by Plesch, arguing that one cannot use the Jacobson–Stockmayer theory if the presence of linear molecules is not confirmed. However, their presence follows directly from Semlyen's data and could tacitly be assumed because the concentrations of rings of polymerization degree from 2 to 9 in the product were found to be independent of $[M]_0$. This means that proportions of rings are dependent on $[M]_0$ and this strongly indicates that both cyclic and linear polymers were present, justifying the application of the Jacobson–Stockmayer theory, and thus Semlyen's treatment.

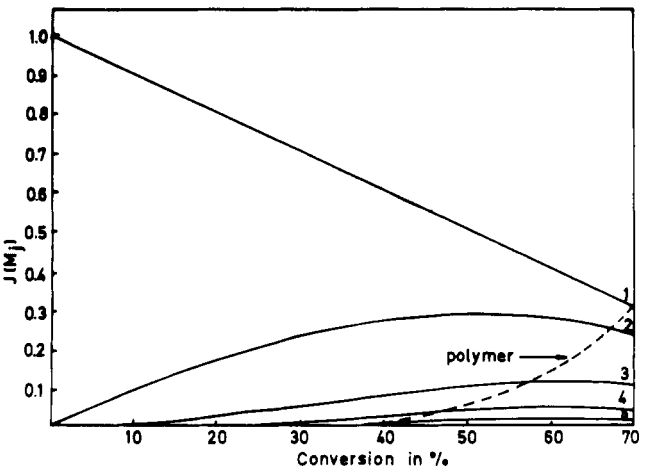


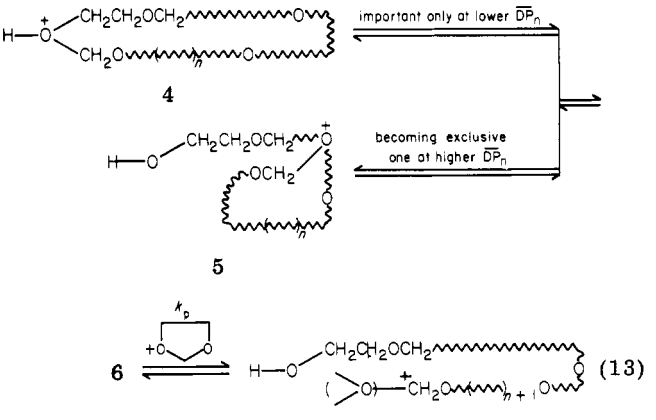
Figure 3. Computer simulation of the dependence of the concentration of macrocycles j[cyclic-M_j] (in moles of monomeric units per liter) on monomer conversion ($j = \overline{DP}_n$). Numbers assigned to each curve give the degree of polymerization of a given macrocycle. The broken line corresponds to the polymer concentration. Reprinted with permission from ref 29. Copyright 1980 Huethig und Wepf Verlag.

4. Kinetically Enhanced Proportion of Macrocyclics

In the previous section we discussed the influence of $[M]_0$ on the proportion of rings in the product at equilibrium. Before equilibrium is attainable the concentration of rings of various sizes can, however, change due to kinetic control.

Schulz[7] and Yamashita[8] observed indeed that during polymerization of acetals having larger rings (e.g., 1,3,6,9-tetraoxacycloundecane) initiated with protonic acids, cyclic dimers, trimers, and tetramers are practically the only species formed in the early stages of polymerization. Schulz and others have subsequently shown that the final polymer does contain the end groups and that at certain conditions the polymer $\overline{DP}_n$ determined from the end groups is close to the $\overline{DP}_n$ calculated for a living system.[28]

These results indicate clearly that there should be a mechanism in which for lower $\overline{DP}_n$ mostly cyclics are formed, which then are converted to mostly linear polymer, when higher $\overline{DP}_n$ is reached. The basic scheme, in which linear growth competes with cyclization by back-biting to any unit in the chain and by end-to-end closure, is as follows:[29]



(13)

In (13) the linear growing macromolecule having an initial OH group and a growing center $-OCH_2^+-(O<)$ prop-

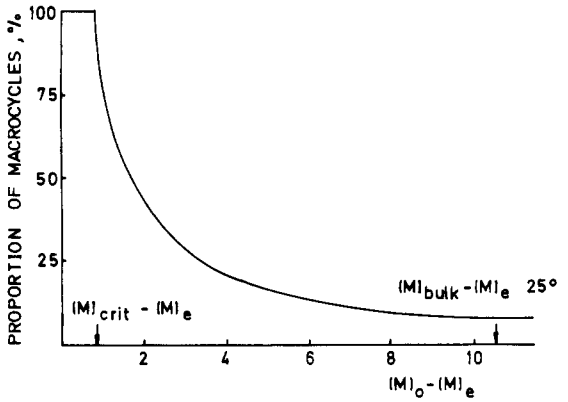


Figure 4. Dependence of the proportion of macrocycles on the starting monomer concentration calculated on the basis of data reported in ref 4.

agates with a rate constant k_p. Two cyclization processes compete with this linear growth, namely, end-biting, with a rate constant k_e, and back-biting (k_b) to any unit of the chain.

It has been shown (Figure 4) by computer simulation that this scheme may lead to the kinetics with all of the features of the kinetics observed by Schulz[7] and Yamashita.[8] For these calculations we assumed that the probability of the end-to-end closure is, according to the theory of polymer conformation,[25-27] a function of a polymerization degree $\overline{DP}_n^{-3/2}$.

According to Figure 4, at lower conversions the monomer is practically completely transformed into cyclic oligomers. Only when conversion exceeds a certain value (35% for the chosen conditions; this value may, however, vary, depending on the values of the rate constants and their ratios) does linear polymer start to appear. The fractions of cyclic oligomers go through maxima. These maxima are reached for higher oligomers at the higher monomer conversion.

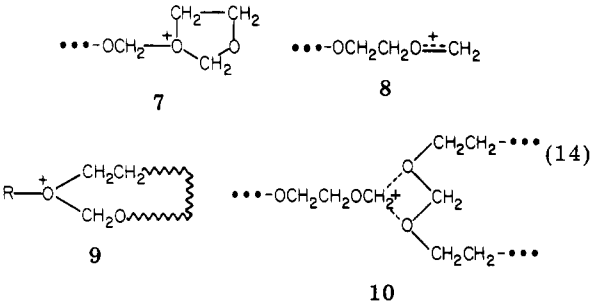
In the extreme case, when $k_e \gg k_b,k_p$, i.e., when end-to-end closure is strongly favored, almost all of the monomer will form initially macrocycles although the chain growth involves a small fraction of active centers located on linear macromolecules. Only at very late stages do these oligomers start to polymerize to larger linear macromolecules.

Thus this section explains facts considered for some time to be paradoxical: in the early stages the macromolecules are predominantly cyclic whereas at higher conversions linear polymer appears. As we have explained, at lower conversions chains are short and predisposed to close into rings by end-to-end closure. At higher conversions chains become long enough to make it too difficult for the ends to meet and close the ring.

5. Chemical Nature of Active Species

An analysis of structures of the growing species proposed by various authors for the cationic polymerization of cyclic acetals leads to the striking conclusion that most authors did not consider the possibility of different species coexisting in dynamic equilibrium but selected only one structure, insisting on its exclusive presence.

Thus tertiary oxonium ion involving monomer[3] (structure 7 in (14)), carboxonium ions[30,31] (8), secondary or tertiary oxonium ions (proton or carbenium ions attached to the macrocycles (9)), growing by expansion,[1] and tertiary oxonium ions (10) involving macromolecules, growing in the conventional manner,[22,32] were considered to be the only growing species:



Structure 10 accounted for the fast exchange between carboxonium and the tertiary oxonium ion.

Some authors, however, considered conversion of one kind of growing species into others with progressing conversion of monomer into polymer. Kučera, for instance, considered the coexistence of carboxonium and oxonium ions[33] whereas one of us proposed an increase in the proportion of species 10 with increasing conversion.[22]

The most thorough discussion of the structure of the growing species, based on the facts available at that time, was published by Russian authors.[30] They eventually came to the conclusion that the growing centers are alkoxycarbenium (carboxonium) ions, relying heavily in their judgment on the analogy with the mechanism of hydrolysis of cyclic acetals.[34,35] Later, during the 1st Ring-Opening IUPAC Symposium (1975), Plesch summarized arguments favoring the ring-expansion theory.[9]

There is one common point in the cited papers: both the Russian authors and Plesch attempted to draw conclusions by comparing some factors from systems studied under different conditions: hydrolysis in water in the Russian paper and comparison of the activation parameters in Plesch's paper. In the latter, $\Delta H^{\ddagger}_p$ and $\Delta S^{\ddagger}_p$ calculated for the polymerization of 1, assuming that [initiator]$_0$ = [growing species], were compared with $\Delta H^{\ddagger}_p$ and $\Delta S^{\ddagger}_p$ of poly-THF and the observed difference was used as an argument for a difference of the actual mechanism of growth. One has to be extremely careful in making this kind of comparison because $\Delta H^{\ddagger}_p$ and $\Delta S^{\ddagger}_p$ clearly depend on the solvating power of the constituents of the system toward the ground and transition states of the active species. This is clearly seen when we compare, for instance, $\Delta H^{\ddagger}_p$ and $\Delta S^{\ddagger}_p$ in the polymerization of THF in bulk and in ca. 50 vol % CCl_4 solution:[36]

	bulk	50 vol % CCl_4
$\Delta H^{\ddagger}_p$, kcal·mol^{-1}	14.0	9.0
$\Delta S^{\ddagger}_p$, cal·mol^{-1}·deg^{-1}	−18	−36

$\Delta H^{\ddagger}_p$ and $\Delta S^{\ddagger}_p$ change so much (the changes compensate each other) that any comparison of two different systems (different monomers and/or solvents) is meaningless. One has to remember that the monomers themselves are the strongest solvating agents and that THF and 1 differ remarkably in basicity (nucleophilicity). Thus the solvating ability of the active species by mixtures of 1 and THF with the same solvent will differ dramatically.

Thus we shall not discuss all of the secondary information, these many assumptions and "ifs", the interested reader can find in the above cited papers. Instead we confine ourselves only to the recent new facts.

6. Reaction of $CH_3OCH_2^+$: A Model of One of the Growing Species with Monomers: 1 and 3

The early arguments,[37] completely ruling out the presence of alkoxycarbenium ions in the polymerization of 1, have to be dismissed on the basis of the new facts. These arguments were based on experiments performed under

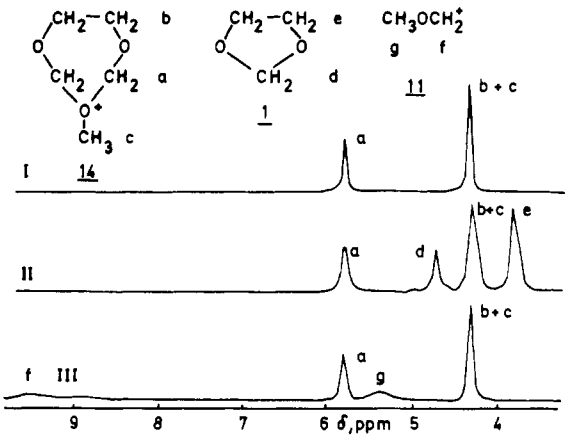
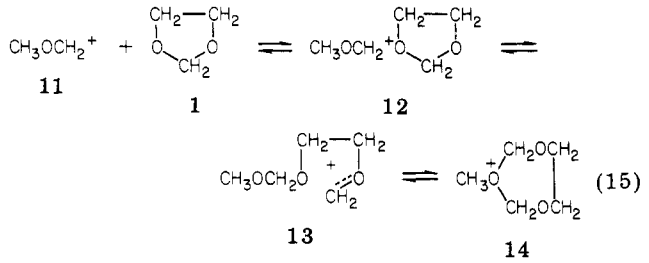


Figure 5. ^1H NMR spectra of the 1,3-dioxolane–$CH_3OCH_2^+SbF_6^-$ system: (I) $[1,3\text{-dioxolane}]_0 = 1.85 \times 10^{-2}$ mol·L^{-1}, $[CH_3OCH_2^+]_0 = 1.85 \times 10^{-2}$ mol·L^{-1}; (II) $[1,3\text{-dioxolane}]_0 = 6.2 \times 10^{-2}$ mol·L^{-1}, $[CH_3OCH_2^+]_0 = 2.3 \times 10^{-2}$ mol·L^{-1}; (III) $[1,3\text{-dioxolane}]_0 = 2.2 \times 10^{-2}$ mol·L^{-1}, $[CH_3OCH_2^+]_0 = 4.0 \times 10^{-2}$ mol·L^{-1}. All spectra in liquid SO_2 at −70 °C. Reprinted with permission from ref 39. Copyright 1982 Huethig und Wepf Verlag.

conditions chosen in an incorrect way to draw conclusions about the polymerization. In the early experiments $CH_3OCH_2OClO_3$ was reacted in CH_2Cl_2 solvent with 1 at 0 °C. But $[1]_0$ was almost equal to $[1]_e$ and no polymerization could take place. Consequently, only H^- transfer from 1 to $CH_3OCH_2^+$ cation was observed. Thus it was concluded incorrectly[37] and then repeated by others that ···$-OCH_2CH_2OCH_2^+$ cation cannot be a growing species since it abstracts H^- ion much faster than it adds a monomer molecule. Jaacks corrected himself in the next paper, showing that when $[1]_0 > [1]_e$, polymerization could proceed and only a small fraction of initiator was involved in H^- transfer.[21]

This interaction was recently reexamined by ^1H and ^{13}C NMR, with $CH_3OCH_2^+SbF_6^-$ (or SbF_5^-Cl) as a model.[38] It has been shown that at low concentration of 1 and at sufficiently low temperature to avoid H^- transfer (H^- transfer from 1 to $CH_3OCH_2^+$ becomes immeasurably slow below −30 °C),[39] the actual reaction proceeds as follows:



The spectra are clean and no signals other than those due to the species shown in (15) could be found (Figure 5). Okada and others studied the same system previously and found complicated NMR patterns due, in our opinion, to side reactions.[31] Their conclusions were based on the erroneous assignment of signals (e.g., the 11.1-ppm signal was assigned to the $-OCH_2^+$ ion, which actually absorbs at 9.5 ppm).[40] In our hands, at low temperatures (below −70 °C) 1 taken in excess over $CH_3OCH_2^+$ gives a system in which 14 and 1 can be observed separately. Analysis of the chemical shifts led to the determination of the equilibrium constants for (15).[39] For instance

$$[14]/[13] = 4 \times 10^4 \quad (-70\ °C) \qquad (16)$$

and

$$[12]/[13] = 1.3 \times 10^2 \quad (-70\ °C)$$

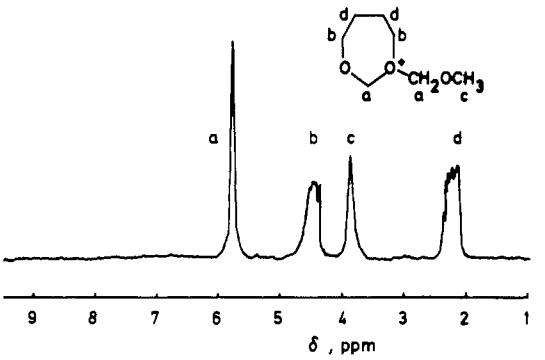
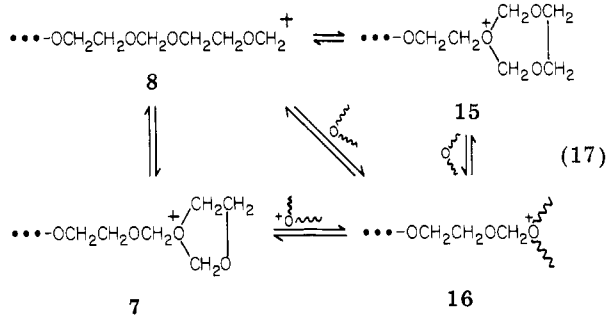


Figure 6. ^1H NMR spectrum of the 1,3-dioxepane–$CH_3OCH_2^+SbF_6^-$ system: $[1,3\text{-dioxepane}] = 2.65 \times 10^{-2}$ mol·L^{-1}, $[CH_3OCH_2^+] = 2.65 \times 10^{-2}$ mol·L^{-1}, liquid SO_2, −70 °C. Reprinted with permission from ref 39. Copyright 1982 Huethig und Wepf Verlag.

It is interesting to note that when 1 is added to the system consisting mainly of **14**, no formation of larger rings is observed. This implies that **14** may react slower with 1 than its higher cyclic homologues as well as the noncyclic tertiary oxonium ions.

Thus, as follows from the studies of the model systems, **14**, not taken into consideration in the earlier works, is a predominant form of oxonium ion in the polymerization of 1. Also in our earlier reviews, before we discovered the presence of **14**, this species was not taken into account. However, it has to be stressed that in the reaction of $CH_3OCH_2^+$ with 1,3-dioxepane (seven-membered ring), only a very low concentration of the nine-membered cationated ring (analogous to **14**) was observed. Thus although equilibrium 15 seems to be a general feature of the polymerization of cyclic acetals, the proportion of the enlarged rings as active species may differ substantially from one system to another.

In (15), involving $CH_3OCH_2^+$, cation **14** is formed by back-biting. In the real polymerization system the 1,3,5-trioxepanium cation alkylated by polymer can be formed in the same way but could not be observed by currently available methods because of fast exchange with other components of the system, as shown schematically in (17) for the polymerization of 1,3-dioxolane:



The scheme shown in (17) is a simplified version of the more detailed set of equilibria discussed by us elsewhere.[41] For instance, the "polymeric" active species **16** can be formed from **8** either by a unimolecular back-biting (i.e., intramolecular interaction) or by intermolecular reaction with a foreign macromolecule.

Species **7**, **8**, **15**, and **16** can react with monomer in the propagation step. Thus the old question "Are the active species in the polymerization of cyclic acetals oxonium or carboxonium ions?" has to be reformulated as follows: What is the relative concentration of different species, and to what extent do the given species participate in the building up of the macromolecules?

The proportions of various species and their contributions to the chain growth do not necessarily have to coincide. Moreover, these proportions may differ substantially not only from one monomer to another but also for a given monomer and set of polymerization conditions (solvent, temperature, and other variables).

The fast dynamic equilibria between species as shown in (17) do not allow at present the determination of the absolute concentrations of various species directly in the polymerization conditions.

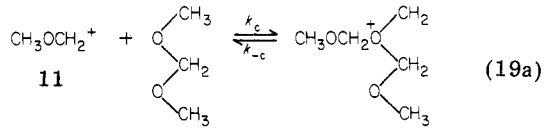
The carbenium–oxonium equilibria, studied recently in our laboratory,[38] shed at least some light on the position of equilibria involving other species and the rates of their interconversions.

In a previous study of the reaction of $CH_3OCH_2^+$ with 1,3-dioxolane, we established that in the set of equilibria

$$\mathbf{12} \rightleftharpoons \mathbf{13} \rightleftharpoons \mathbf{14} \qquad (18)$$

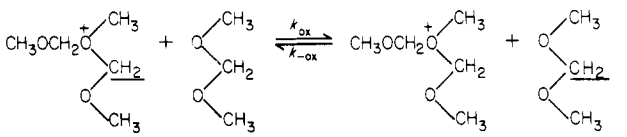
14 predominates and that at −70 °C in SO_2 solution the following ratio holds: [**12**]/[**13**]/[**14**] = 0.3/0.003/99.7.

Thus for the system



11 **17** **18** (19a)

and



18 **17** **18** **17** (19b)

reactions 19a and 19b correspond to propagation on the carboxonium ions and oxonium ions, respectively. The rate constants were found to be $k_c = 2 \times 10^6$ $M^{-1}\cdot s^{-1}$ and $k_{ox} = 2 \times 10^4$ $M^{-1}\cdot s^{-1}$, respectively (both at −70 °C in liquid SO_2). Thus, quite unexpectedly, the carboxonium ions (structure **8** in (17)) are only 10^2 times more reactive toward a linear acetal than the tertiary oxonium ions, similar to active species **16**. Therefore, from both points of view, namely, the proportion of a given active species and its contribution to the chain growth, the tertiary oxonium ions predominate. Among oxonium ions, species **15** are most abudant for 1,3-dioxolane.

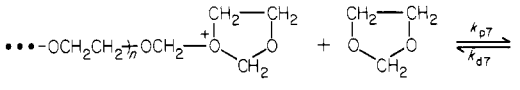
At this point a question has to be asked: why in the polymerization of 1,3-dioxolane the rate constant of propagation[42,43] measured by various groups was not higher than 3×10^2 $M^{-1}\cdot s^{-1}$ at 25 °C whereas the oxonium ion (reaction 19) similar to oxonium ions in this propagation reacts with dimethoxymethane at −70 °C with a rate constant exceeding 10^4 $M^{-1}\cdot s^{-1}$.

This, in our opinion, is because the simple equation

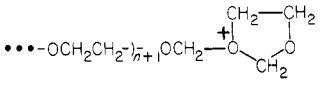
$$d[M]/dt = k_p[M][\text{active species}] \qquad (20)$$

used by all workers in this field, who also assumed [initiator]$_0$ = [active species], cannot be valid for the complicated actual system of parallel and competing reactions, even provided that initiator is quantitatively converted into various growing cations.

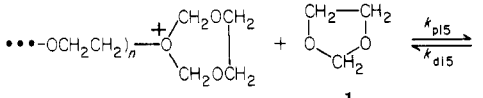
Let us assume, on the basis of relative concentrations and reactivities of carbenium and oxonium cations found in the model studies (cf. eq 18) that the whole system is reduced to two kinds of active species, namely, **7** and **15**. Such a propagating scheme reads as follows:



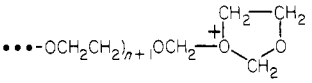
7 **1**



7 (21a)



15 **1**



7 (21b)

In reaction 21b the thermodynamically more stable ion **15** (dominating, according to the model studies, in the equilibrium **7** ⇌ **15**) is transformed into the less stable ones. Thus the equilibrium constant of reaction 21b should be smaller than that of reaction 21a.[41] This means that propagation on active species **15** is to a much higher degree compensated by depropagation than propagation on species **7**. The experimentally observed values k_p and k_d, determined from the simple equation $-d[M]/dt = k_p([M] - [M]_e)[P^*]$ (where [P*] is the sum of all of the growing species, including **7** and **15**) and $k_d = k_p[M]_e$, are functions of the corresponding individual rate constants and concentrations of the related growing species as shown in eq 21.

If **15** highly predominates and fast addition of monomer to these species is almost counterbalanced during all of the polymerization by a nearly equally fast depropagation, then the tiny amount of **7** would be responsible for consumption of monomer in propagation, whereas **15**, although highly active in adding and throwing away monomer molecules, would be equivalent to a dormant species. Then, of course, k_p calculated from eq 20 would be as many times higher than the reported values as many times lower is the concentration of the active species responsible for the chain growth.

7. Conclusions

It has been shown recently and is summarized in this paper that polyacetals, particularly poly(1,3-dioxolane), can be prepared as mostly cyclic or mostly linear polymers. Two groups of reasons were analyzed. The first comes from the thermodynamics of the ring–chain equilibria, requiring that in the equilibrated system the sum of the concentrations of all of the cyclics in the solution of the mixture of cyclic and linear macromolecules is constant. Thus the higher the total concentration of polymer at equilibrium (the highest is in the bulk), the lower the proportion of cyclics. Every polymer giving the ring–chain equilibrium has its own characteristic total concentration of cyclics, depending on the chain flexibility. For poly(1,3-dioxolane) this is close to 0.8 mol/L (expressed in monomer units). Thus any polymerization of this monomer conducted at or below a monomer concentration such that 0.8 mol/L (or less) polymer is produced should lead to almost exclusively cyclic product. Increasing the polymer concentration at the monomer–polymer equilib-

rium decreases the proportion of rings, the lowest attainable proportion being $100 \times 0.8/13.5 = 6$ mol % (assuming complete conversion of $[M]_0$(bulk) = 13.5 mol/L).

When polymer with shorter chains is considered and when the initial (end) group reacts faster with the cationic active center than the acetal oxygen atoms within a chain, end-to-end closure may become the predominant mechanism of cyclization. At these kinetically controlled conditions, the thermodynamic treatment, based on Jacobson–Stockmayer theory, does not hold any more. This can be particularly well observed in the stepwise polymerization with increasing degree of polymerization. Living linear dimers have a high tendency to give living cyclic dimers, which can form trimers and higher oligomers until the probability of two ends meeting becomes small and monomer addition to a given linear living oligomer becomes more probable than its cyclization. Thus the shorter living chains are hardly observed and mostly their living cyclic counterparts can be detected, although the former are responsible for the chain growth.

In the second part of this review, the structure of the active species is discussed. Recent studies of the reactions with linear and cyclic acetals of $CH_3OCH_2^+SbF_6^-$, modeling one of the alleged structures of the active species, revealed that the carboxonium ions can exist in the polymerizing mixtures, but at very low concentrations. It has also been shown that the predominant species are tertiary oxonium ions, either cyclic (e.g., involving monomer molecule) or linear branched ones. Various structures coexist in dynamic equilibrium, with one becoming predominant in the chain growth, depending on the monomer structure and the polymerization conditions. In the polymerization of 1,3-dioxolane the back-biting process gives also the isomerized active species, namely, cationated seven-membered ring at the growing chain end. This species reacts fast with monomer but depropagates at a comparable rate, playing kinetically the role of a dormant species. Therefore the rate constant of addition of 1,3-dioxolane to the active species contributing to the growth (e.g., as proposed by Jaacks, tertiary oxonium ion involving monomer molecule) is much higher than the experimentally determined apparent rate constant of propagation. In the polymerization of the seven-membered 1,3-dioxepane these experimentally determined rate constants are much closer to the real ones because the active species do not give the nine-membered cationated species that could have played the role of a dormant species.

In this connection Plesch's results of k_p for 1,3-dioxepane, which could not have been explained till now, are of paramount importance.[44] It has been found that k_p(1,3-dioxepane) is close to 10^4 $M^{-1} \cdot s^{-1}$, much higher than the values reported for 1,3-dioxolane and approaching our values of k_{ox}, i.e., for reaction of oxonium ion with an acetal, as in eq 19b.

Registry No. 1,3-Dioxolane, 646-06-0; 1,3-dioxepane, 505-65-7; poly(1,3-dioxolane), 25067-64-5.

References and Notes

(1) Plesch, P. H.; Westermann, P. H. *J. Polym. Sci., Part C* **1968**, *16*, 3837.
(2) Gresham, W. F. U.S. Patent 2 394 910, 1946.
(3) Jaacks, V.; Boehlke, K.; Eberius, E. *Makromol. Chem.* **1968**, *118*, 354.
(4) Andrews, J. M.; Semlyen, J. A. *Polymer* **1942**, *13*, 142.
(5) Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 1600.
(6) Nysenko, Z. N.; Berman, E. L.; Ludvig, E. B.; Klimow, A. P.; Ponomarenko, W. A.; Isagulanz, G. W. *Vysokomol. Soedin.* **1976**, *18*, 1696.
(7) Schulz, R. C.; Albrecht, K.; Rentsch, C.; Tran Thi, Q. V. In *ACS Symp. Ser.* **1977**, *No. 59*, 77.
(8) Yamashita, Y.; Kawakami, Y. In *ACS Symp. Ser.* **1977**, *No. 59*, 99.
(9) Plesch, P. H. *Pure Appl. Chem.* **1976**, *48*, 287.
(10) Kubisa, P.; Penczek, S. *Makromol. Chem.* **1979**, *180*, 1821.
(11) Schweitzer, C. E.; MacDonald, R. N.; Punderson, J. O. *J. Appl. Polym. Sci.* **1959**, *1*, 158.
(12) Jaacks, V.; Kern, W. *Makromol. Chem.* **1963**, *62*, 1.
(13) Jaacks, V.; Frank, H.; Grünberger, E.; Kern, W. *Makromol. Chem.* **1968**, *115*, 290.
(14) Jaacks, V. *Makromol. Chem.* **1966**, *99*, 300.
(15) Firat, Y.; Jones, F. R.; Plesch, P. H.; Westermann, P. H. *Makromol. Chem.* **1975**, *Suppl. 1*, 203.
(16) Plesch, P. H. *IUPAC Int. Symp. Macromol. Chem., Budapest, 1969*, p 213.
(17) Kelen, T.; Schlotterbeck, D.; Jaacks, V. *XXIII IUPAC Cong., Boston, 1971*, Vol. II; p 649.
(18) Kubisa, P.; Penczek, S. *Macromolecules* **1977**, *10*, 1216.
(19) Kubisa, P.; Penczek, S. *Makromol. Chem.* **1978**, *179*, 445.
(20) Brzezinska, K.; Chwiałkowska, W.; Kubisa, P.; Matyjaszewski, K.; Penczek, S. *Makromol. Chem.* **1977**, *178*, 2491.
(21) Boehlke, K.; Weyland, P.; Jaacks, V. *XXIII IUPAC Cong., Boston, 1971*, Vol. II, p 641.
(22) Penczek, S. *Makromol. Chem.* **1974**, *175*, 1217.
(23) Enikolopyan, N. S. *J. Macromol. Sci.* **1972**, *A6*, 1053.
(24) Ponomarenko, W. A. *Vysokomol. Soedin.* **1977**, *19*, 1670.
(25) Kuhn, W. *Kolloid.-Z.* **1934**, *68*, 2.
(26) Flory, P. J. *Macromolecules* **1974**, *7*, 381.
(27) Flory, P. J.; Semlyen, J. A. *J. Am. Chem. Soc.* **1966**, *88*, 3209.
(28) Schulz, R. C.; Albrecht, K.; Hellermann, W.; Kane, A.; Tran Thi, Q. V. *Pure Appl. Chem.* **1981**, *53*, 1763.
(29) Matyjaszewski, K.; Zielinski, M.; Kubisa, P.; Słomkowski, S.; Chojnowski, J.; Penczek, S. *Makromol. Chem.* **1980**, *181*, 1469.
(30) Rosenberg, B. A.; Irzhak, W. I.; Enikolopyan, N. S. "Interchain Exchange Reactions in Polymers" (Russian); Khimia: Moscow, 1975.
(31) Yokoyama, Y.; Okada, M.; Sumimoto, H. *Makromol. Chem.* **1977**, *178*, 529.
(32) Berman, E. L.; Ludvig, E. B.; Ponomarenko, W. A.; Medvedev, S. S. *IUPAC Int. Symp. Macromol. Chem., Budapest, 1969*, Vol. I, p 269.
(33) Kucera, M.; Pichler, J. *Vysokomol. Soedin.* **1965**, *7*, 3.
(34) Cordes, E. H. In *Prog. Phys. Org. Chem.* **1967**, *4*, 1.
(35) Kreevoy, M.; Taft, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 3146.
(36) Penczek, S.; Matyjaszewski, K. *J. Polym. Sci., Polym. Symp.* **1976**, *No. 56*, 255.
(37) Boehlke, K.; Frank, H.; Jaacks, V. *IUPAC Int. Symp. Macromol. Chem., Budapest, 1969*, Vol. I, p 299.
(38) Penczek, S.; Szymański, R. *Polym. J.* **1980**, *12*, 617.
(39) Szymański, R.; Penczek, S. *Makromol. Chem.* **1982**, *183*, 1587.
(40) Olah, G. A.; Bollinger, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 2992.
(41) Penczek, S.; Kubisa, P.; Matyjaszewski, K.; Szymanski, R., in preparation.
(42) Jones, F. R.; Plesch, P. H. *Chem. Commun.* **1969**, 1230.
(43) Kubisa, P. *J. Macromol. Sci.* **1977**, *A11*, 2247.
(44) Plesch, P. H. *Adv. Polym. Sci.* **1971**, *8*, 137.