conditions. No indication of resonance broadening, which could be attributed to the presence of chemical shift nonequivalence, was apparent.

In light of this evidence, one must conclude that a mixture of meso and racemic configurations is not present and that the observed resonances can be attributed to only one type of structure (I or II above). In view of the isospecific nature of the catalyst employed, it is logical to assume that only structure I is present. Without suitable model studies, however, no absolute choice between I and II can be made. With the above-mentioned assumption in mind, our results here strongly support the conclusion that steric control is maintained by the asymmetric catalytic site, and not by the last unit of the growing polymer chain.

Acknowledgments. We thank Dr. Bruce Hawkins of Bruker Instruments, Inc., U.S.A., and Dr. David Axelson of Florida State University for obtaining 67.9-MHz ^{13}C spectra of propylene–ethylene copolymer.

References and Notes

(1) L. F. Johnson, F. Heatley, and F. A. Bovey, *Macromolecules*, **3**, 175 (1970).
(2) Y. Inoue, A. Nishioka, and R. Chujo, *Makromol. Chem.*, **168**, 163 (1973).
(3) A. Zambelli, D. E. Dorman, A. I. R. Brewster, and F. A. Bovey, *Macromolecules*, **6**, 925 (1973).
(4) J. C. Randall, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 703 (1974).
(5) A. Zambelli, P. Locatelli, G. Bajo, and F. A. Bovey, *Macromolecules*, **8**, 687 (1975).
(6) C. Wolfsgruber, G. Zannoni, E. Rigamonti, and A. Zambelli, *Makromol. Chem.*, **176**, 2765 (1975).
(7) J. C. Randall, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1693 (1976).
(8) J. C. Randall, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 2083 (1976).
(9) W. O. Crain, A. Zambelli, and J. D. Roberts, *Macromolecules*, **4**, 330 (1971).
(10) A. Zambelli, "NMR, Basic Principles and Progress", Vol 4, P. Diehl, E. Fluck, and R. Kosfeld, Ed., Springer-Verlag, New York, N.Y., 1971.
(11) A. Zambelli, G. Gatti, C. Sacchi, W. O. Crain, and J. D. Roberts, *Macromolecules*, **4**, 475 (1971).
(12) C. J. Carman and C. E. Wilkes, *Rubber Chem. Technol.*, **44**, 781 (1971).
(13) Y. Tanaka and K. Hatada, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 2057 (1973).
(14) C. E. Wilkes, C. J. Carman, and R. A. Harrington, *J. Polym. Sci., Polym. Symp.*, **No. 43**, 237 (1973).
(15) F. A. Bovey, M. C. Sacchi, and A. Zambelli, *Macromolecules*, **7**, 752 (1974).
(16) K. F. Elgert and W. Ritter, *Makromol. Chem.*, **177**, 2781 (1976).
(17) R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, **48**, 3831 (1968).
(18) R. Freeman, H. D. W. Hill, and R. Kaptein, *J. Magn. Reson.*, **7**, 327 (1972).
(19) D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964).
(20) D. E. Axelson, L. Mandelkern, and G. C. Levy, *Macromolecules*, **10**, 557 (1977).
(21) A. Zambelli and C. Tosi, *Adv. Polym. Sci.*, **15**, 31 (1974).

^1H-NMR Studies of the 1,3-Dioxolan–$(C_2H_5)_3O^+SbF_6^-$ System. End Groups and Structure of the Active Species[1]

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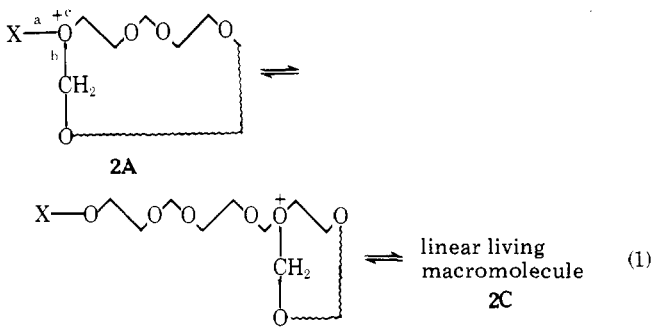
ABSTRACT: The Fourier pulse transform (FPT) ^1H-NMR method was used to study the structure of the growing macrocations in the polymerization of 1,3-dioxolan (1) and perdeuterated 1,3-dioxolan (1-d_6) initiated with $(C_2H_5)_3O^+SbF_6^-$ in CD_3NO_2 solvent. Analysis of 300-MHz ^1H-NMR spectra revealed that the $(C_2H_5)_3O^+$ cation is quantitatively transformed during initiation into $(C_2H_5)_2O$ and C_2H_5–O–. . . polymer end group. No C_2H_5-$O^+<$ cations, other than these from unreacted initiator, were detected; this fact indicates that the presence of the macrocyclic growing cations of the type C_2H_5-$O^+<$ can be neglected. In the studies of the kinetics of cationation of 1,3-dioxolan with $(C_2H_5)_3O^+SbF_6^-$ it was found that this reaction is slow ($k_{iM} = 1 \times 10^{-4}$ mol^{-1} L s^{-1}, 35 °C, CH_3NO_2 solvent) in comparison with propagation ($\bar{k}_p \sim 10^2$ mol^{-1} L s^{-1} at the same conditions). This, however, does not influence the kinetics of $(C_2H_5)_3O^+SbF_6^-$ disappearance because the rate constant (k_{iP}) of the reaction of $(C_2H_5)_3O^+SbF_6^-$ with dimethoxymethane used as a model of polymer segment is close to k_{iM} ($k_{iP} = 0.95 \times 10^{-4}$ mol^{-1} L s^{-1}, 35 °C, CH_3NO_2 solvent). Termination of the living poly-1,3-dioxolan-d_6 (after initiation is completed) with $(CH_3)_3N$ gave predominantly linear macromolecules of the following structure: $CH_3CH_2(-OCD_2CD_2OCD_2-)_nN^+(CH_3)_3$. Both end groups were identified in the FPT ^1H-NMR spectra of the isolated polymers, the ratio of the end groups, determined from integration, being close to 1:1. Degrees of polymerization (DP_n) calculated from end-group analysis were found to be close to the DP_n calculated for the living conditions assuming that one molecule of initiator gives one macromolecule.

It has been shown in our previous paper that poly-1,3-dioxolans (poly-1) prepared with stable oxocarbenium and trialkyloxonium cations as initiators ($C_6H_5CO^+SbF_6^-$ and $(C_2H_5)_3O^+SbF_6^-$) and terminated with C_2H_5ONa, $(C_6H_5)_3P$, $(n\text{-}C_4H_9)_3P$, and $(CH_3)_3N$ are predominantly linear.[2] Macromolecules were found to contain two end groups, one coming from initiator and the second one from the terminating agent. Polymerization degrees ($\overline{DP}_n$) of these polymers are close to the calculated ones, i.e., to the ratio of concentration of reacted monomer to that of reacted initiator. This is what could be expected for a living system, like polymerization of tetrahydrofuran.[3,4]

On the other hand, poly-1 prepared with $HClO_4$ had, according to Plesch,[5,6] $\overline{DP}_n$ rather independent of this ratio and dominated by transfer. These polymers were claimed to contain mostly cyclic macromolecules of low polymerization degrees. These findings were assumed as the basis of an idea of the "ring-expansion" growth of poly-1.[5]

However, in our opinion, neither linear nor cyclic structures of the isolated, killed macromolecules are straightforward arguments by themselves for the linear or cyclic growth of the living macromolecules.

Indeed, let us consider a general equilibrium between a cyclic and linear living poly-1:



2A

2B

linear living macromolecule
2C

(1)

In this equilibrium (eq 1) cyclic living macromolecules **2A** and **2B** are results of back biting (**2B**) or back biting leading to end-to-end closure (**2A**). The probability of the latter process to occur is enhanced when the oxygen atom in the *initial end group* (e.g., oxygen atom in the ether end group) is much more nucleophilic than any other oxygen atom in the acetal bonds along the chain.

Let us now examine the reaction of a killing agent with these living macromolecules. The *linear living* macromolecules will give their *linear dead* replica, but the *cyclic living* ones may give either *cyclic dead* or *linear dead* macromolecules, depending on the initiator used and, therefore, on a structure of X in **2A.**

In the living cyclic structure **2A,** with two ends (initial and final units) coupled together, there are three nonequivalent bonds, a, b, and c, that can be broken upon the attack of the killing agent.

If X equals, e.g., CH_3 or C_2H_5 (initiation with esters of strong acids or with trialkyloxonium salts), then there are in **2A** two rather stable bonds a and c and one much less stable acetal bond b. Thus, even if cyclic **2A** were a predominant structure of the living macromolecules, then their reaction with a nucleophilic killing agent would give mostly linear dead macromolecules.

Thus, the results of our previous work,[2] in which we observed practically exclusive formation of the linear high molecular weight poly-1, with end groups of a structure and with concentration as predicted for a living system by the structure and the concentration of the initiator used, is not a sufficient argument to assume that chain growth proceeded by linear living macromolecules.

In order to distinguish between the extreme structures **2A** and **2C,** as predominant *during* a chain growth, it is therefore necessary to observe directly the position of X; in **2A** it is adjacent to the positively charged oxygen atom and in **2C** it is a part of the ether chain end. If X = CH_3CH_2, then the differences in the chemical shifts of the CH_3CH_2 triplet in the ion (**2A**) and in an ether (**2C**) are sufficiently large to be distinguished and permit, on this basis, the distinguishing between **2A** and **2C** as the dominating structures of the ionic species. In the present paper we report on the ^{1}H-NMR studies of the 1,3-dioxolan–$(C_2H_5)_3O^+SbF_6^-$ system.

Experimental Section

Preparation and purification of 1,3-dioxolan-d_6 and purification of CD_3NO_2 and CH_3NO_2 solvents was described earlier.[2]

$C_6H_5CO^+SbF_6^-$ salt was prepared from C_6H_5COF and SbF_5 in liquid SO_2 as described.[2]

$(C_2H_5)_3O^+SbF_6^-$ salt was prepared, according to the method developed by us,[7] from $C_6H_5CO^+SbF_6^-$ salt and an excess of $(C_2H_5)_2O$ in liquid SO_2.

CH_3OCH_2–$N^+(CH_3)$ SbF_6^- salt was prepared by mixing equimolar amounts of CH_3OCH_2Cl and $(CH_3)_3N$ in Freon 113. Precipitated salt CH_3OCH_2–$N^+(CH_3)_3Cl^-$ was dissolved in liquid SO_2 and an equimolar amount of $(C_2H_5)_3O^+SbF_6^-$ was added. Exchange of anions leads to the formation of an easily decomposing $(C_2H_5)_3$ O^+Cl^-:

$$CH_3OCH_2\text{–}N^+(CH_3)_3Cl^- + (C_2H_5)_3O^+SbF_6^- \rightarrow CH_3OCH_2\text{–}N^+(CH_3)_3SbF_6^- + \{(C_2H_5)_3O^+Cl^-\} \rightarrow C_2H_5Cl + (C_2H_5)_2O$$

C_2H_5Cl, $(C_2H_5)_2O$, and solvent were removed by evaporation and the remaining salt (white solid) showed no presence of Cl^- ions (silver salt test). The purity of the salt, obtained after crystallization from C_2H_5OH, was >95% (based on the ^{1}H-NMR spectrum). CH_3OCH_2–$N^+(CH_3)_3SbF_6^-$ is quite stable; the ^{1}H-NMR spectrum does not show any decomposition after heating for 6 h in boiling water. In the ^{1}H-NMR spectrum the following signals appear (CD_3NO_2 solvent):

δ	4.65 (s)	O-CH_2–$N^+<$
δ	3.70 (s)	CH_3–O–
δ	3.05 (s)	–N(CH_3)$_3$

From the integration the ratio of signals is equal to 2:3:8.1.

CH_3–CH_2–$N^+(CH_3)_3$ $SO_3CF_3^-$ salt was prepared by mixing equimolar amounts of CH_3–CH_2–OSO_2CF_3 and $(CH_3)_3N$ in CH_3NO_2 solvent at room temperature. After 2 h, solvent was evaporated and the remaining salt (white solid) was dissolved in CD_3CN.

δ	3.38 (q)	–CH_2–$N^+<$
δ	3.05 (s)	–$N^+(CH_3)_3$
δ	1.35 (t)	CH_3–CH_2–$N^+<$

From integration the ratio of signals is equal to 2:8.6:3.05.

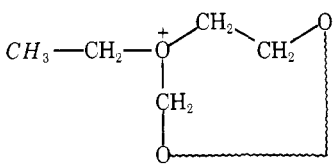
Polymerizations and kinetic experiments were carried out in sealed in vacuo NMR tubes.

^{1}H-NMR spectra were recorded with a Jeol FX 60 FT NMR Spectrometer, (60 MHz) coupled with a JFA 100 data processing system and with a 300 MHz Varian apparatus.

Results and Discussion

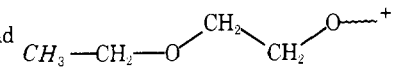
In this paper we describe the differentiation between cyclic (**2A**) and linear (**2C**) growing species, without going into details as to what is the actual structure of **2C.** In our earlier papers we already took a position that linear active species are tertiary polymeric oxonium ion.[8]

If X = C_2H_5, the structures **2A** and **2C** are as follows:



2A

and



(2)

2C

Chemical shifts of protons of CH_3 and CH_2 groups being a part of the CH_3-CH_2-$O^+<$ group in **2A** should be close to those of $(CH_3$–$CH_2)_3O^+$ because of the similarity in structure. $(CH_3$–$CH_2)_2O$ may be used on the same basis as a model for **2C.**

Thus, the chemical shifts according to the data listed in ref 7 are close to those given below:

CH_3–CH_2–O^+: CH_3 δ 1.75 (t); –CH_2– δ 4.80 (q)

CH_3–CH_2–O–: CH_3 δ 1.15 (t); –CH_2– δ 3.50 (q)

Quartets of –CH_2– protons appear in the region of 1 and poly-1 absorptions, and their observation is consequently difficult. Triplets of CH_3 groups appear, however, in the region of the spectrum which is free from any other signals, the difference between chemical shifts of the CH_3 group in **2A** and **2C** being large enough ($\Delta\delta$ = 0.6 ppm) to permit an independent observation of both species.

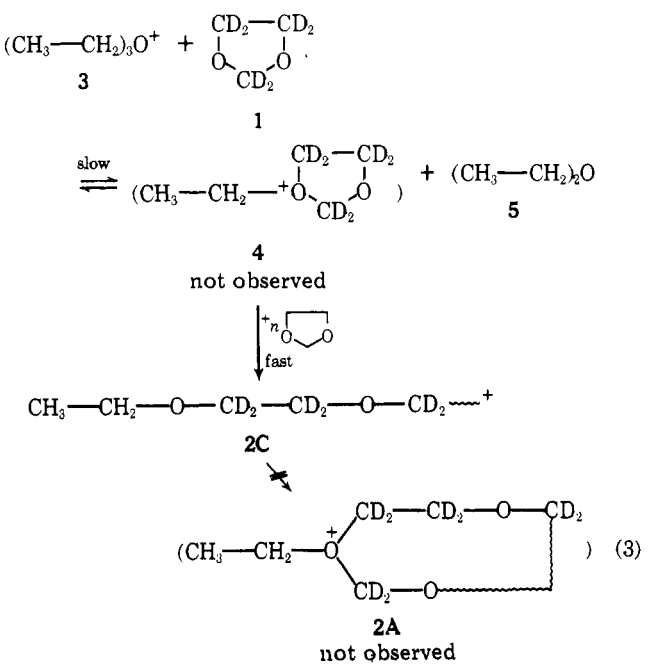
^{1}H-NMR Studies of the 1,3-Dioxolan–$(CH_3CH_2)_3O^+SbF_6^-$ System. ^{1}H-NMR Spectra at the Early Stage of Polymerization. Polymerization of 1 initiated by **3** was

studied by the Fourier pulse transform (FPT) ^{1}H-NMR method (60-MHz apparatus) and by conventional CW technique (300-MHz apparatus[11]). Small concentration of the end groups could be observed because perdeuterated 1,3-dioxolan (1-d_6) and perdeuterated solvent (CD_3NO_2) were used throughout this work. The reaction was studied at a concentration of 1-d_6 above its ceiling concentration and at a concentration of 3 low enough (close to 10^{-3} mol L^{-1}) to permit a formation of high molecular weight polymers.

^{1}H-NMR spectra (300 MHz) of the reaction mixture (δ 1.0–2.0 region) taken after 3.6×10^3 and 7.2×10^3 s are shown in Figures 1a and 1b, respectively. Three separate signals due to the presence of three distinct CH_3 groups can be identified: there is one in the region of the CH_3–CH_2–$O^+<$ group and two others in the region of the CH_3–CH_2–O group. A triplet close to δ 1.75 has to be attributed to the CH_3–CH_2–$O^+<$ group in the triethyloxonium salt, which at this stage of the reaction is not completely used up. One of the two triplets close to δ 1.15 comes from diethyl ether. Thus, the only ethyl group chemically bonded to the growing macromolecule gives a signal (triplet) in the region of the CH_3–CH_2–O group absorption; no CH_3-CH_2-$O^+<$ groups, other than those from $(CH_3$–$CH_2)_3O^+$ cation, could be detected.

The intensity of the δ 1.75 triplet gradually decreases while the intensity of both triplets close to δ 1.15 parallely increases; the ratio of the area under the lower field triplet to the area under the higher field one is close to 1:2 (1:1.8 and 1:1.7 on spectra a and b, respectively).

The following reaction scheme may account for the observed changes of the spectrum (anions omitted):



The net effect, which is observed during initiation, is a quantitative transformation of the ionic CH_3-CH_2-$O^+<$ groups into the CH_3–CH_2–O end groups and $(CH_3CH_2)_2O$:

$$(CH_3\text{–}CH_2)_3O^+ + n(1 - d_6) \rightarrow CH_3\text{–}CH_2\text{–}O\text{–}CD_2\text{–}CD_2\text{–}O\text{–}CD_2 \sim\sim^+ + (CH_3\text{–}CH_2)_2O$$

The difference between chemical shifts of triplets of CH_3 groups in **2C** and **5** is caused by an additional deshielding effect of a nearest oxygen atom of the polyacetal chain, and the signal of one CH_3 group of **2C** appears at lower field then signals of two CH_3 groups of **5**. Thus, one could expect that if structure **2A** were present in the reaction mixture, a similar effect should make possible a separate observation of CH_3–CH_2–$O^+<$ groups in **2A** and **3**.

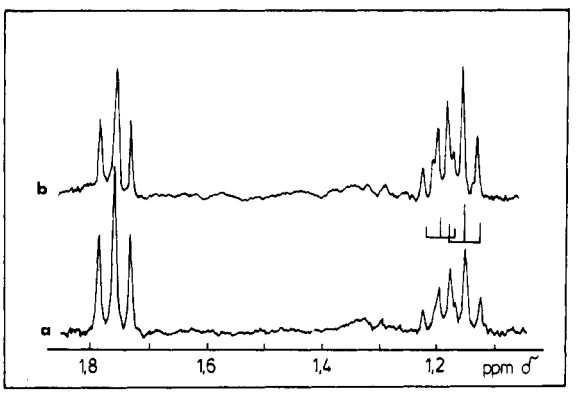
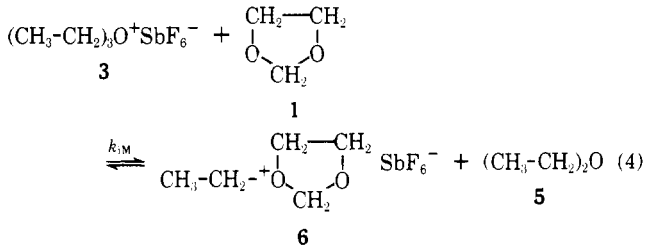


Figure 1. ^{1}H-NMR spectrum (300 MHz) of 1,3-dioxolan-d_6 (1-d_6) polymerizing with $(C_2H_5)_3O^+SbF_6^-$ as initiator (1–2 ppm δ region). [1-d_6] = 3.0 mol L^{-1}, $[(C_2H_5)_3O^+SbF_6^-] = 1.6 \times 10^{-2}$ mol L^{-1}, solvent CD_3NO_2, 25 °C, reaction time (a) 3600 s and (b) 7200 s.

As it will be shown further on in this paper ionic groups CH_3–CH_2–$O^+<$ are eventually quantitatively converted into the nonionic ether end groups in a living system, before the killing agent is added, and are preserved in the dead macromolecules, after their isolation and purification, as it has been shown in our previous paper.[2]

Kinetics of Cationation of 1,3-Dioxolan by $(C_2H_5)_3O^+SbF_6^-$. The first reaction in the process of initiation of 1 polymerization by 3 is thus a formation of 1-ethyl-1,3-dioxolanium cation:



As it was shown in the previous section, in the presence of an excess of 1, oxonium ions 6 react fast giving a linear structure **1C**. Because the concentration of 1 is much higher than the concentration of 5 formed in reaction 4, cationation is practically irreversible.

Thus, the rate constant k_{iM} can simply be determined by measuring the rate of disappearance of 3.

The progress of cationation was followed by measuring the areas under the peaks at δ 1.75 and 1.15 (integration), which correspond to CH_3–CH_2–$O^+<$ and CH_3–CH_2–O groups, respectively. Because the sum of concentrations of both species at any stage of the reaction is equal to the starting concentration of 3 (if the concentration is expressed in terms of CH_3–CH_2–O groups concentration), the ratio $[3]_0/[3]_t$ may simply be expressed as:

$$[3]_0/[3]_t = (a + b)/a$$

where a = the area under the δ 1.75 peak and b = the area under the δ 1.15 peak, both in arbitrary units.

Thus, if a process is treated as a pseudo-first-order reaction, the rate constant k_{iM} may be determined from a simple equation:

$$k_{iM} = [\ln (a + b)/a][1]_0 t$$

The typical plot of $\ln ([3]_0/[3]_t)$ vs. time, for a cationation of 1 with 3, is given in Figure 2; the rate constant of cationation k_{iM} determined from this plot is equal to 1.0×10^{-4} mol^{-1} L s^{-1} (35 °C, CH_3NO_2 solvent).

From a dependence of $\ln k_{iM}$ on reciprocal of absolute

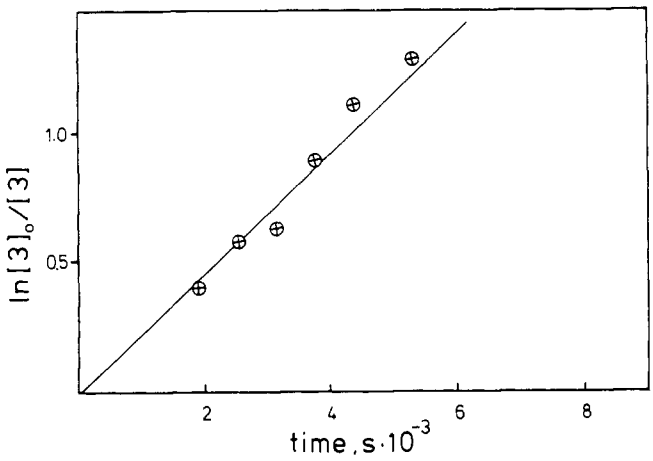


Figure 2. The pseudo-first-order kinetic plot of a reaction of 1,3-dioxolan (**1**) with $(CH_3CH_2)_3O^+SbF_6^-$ (**3**). $[1]_0$ = 2.30 mol L^{-1}, $[3]_0$ = 8.6 × 10^{-3} mol L^{-1}, CH_3NO_2 solvent, 35 °C.

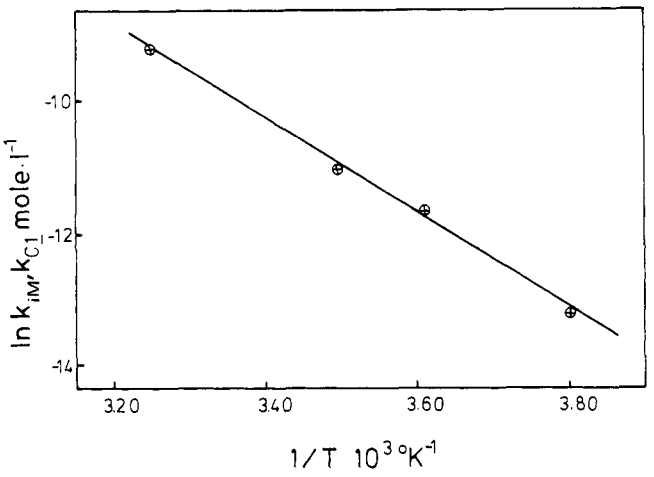


Figure 3. Dependence of ln k_{iM} on reciprocal of an absolute temperature.

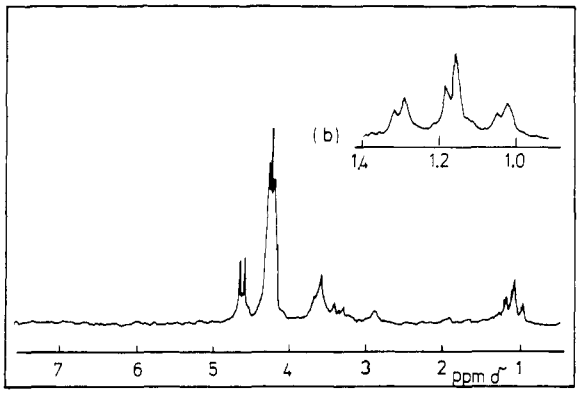


Figure 4. FPT ^{1}H-NMR spectrum (60 MHz) of 1,3-dioxolan-d_6 (**1**-d_6) polymerizing with $(C_2H_5)_3O^+SbF_6^-$ as initiator, taken after monomer–polymer equilibrium was established. Number of accumulated scans = 1600, [**1**-d_6] = 3.0 mol L^{-1}, $[(C_2H_5)_3O^+SbF_6^-]$ = 4.4 × 10^{-3} mol L^{-1}, solvent CD_3NO_2, 25 °C. (b) Expanded fragment of a spectrum in the region of ethereal CH_3–CH_2–O groups absorption.

temperature (Figure 3) the activation parameters of reaction were determined as equal to: $\Delta H^{\ddagger}_{iM}$ = 13.5 kcal mol^{-1}, $\Delta S^{\ddagger}_{iM}$ = −30 cal K^{-1} mol^{-1}. Using the same approach, the rate constant of cationation of dimethoxymethane, used as a model of one unit of polymer chain, was found equal to k_{iP} = 0.95 × 10^{-4} mol^{-1} L s^{-1} (35 °C, CH_3NO_2 solvent).

Chart I

4.70 (s)	–O–CD_2–O–	In **1**-d_6[d]
4.65 (s)	–O–CD_2–O–	In poly-**1**-d_6[d]
4.33 (s)	CD_3NO_2	Solvent[d]
3.75 (s)	–O–CD_2–CD_2–O–	In **1**-d_6[d]
3.65 (s)	–O–CD_2–CD_2–O–	In poly-**1**-d_6[d]
3.50 (q)[b]	CH_3–CH_2–O–	
2.90 (broad singlet)	unidentified	
1.15[c] (t)	CH_3–CH_2–O–	

[a] Two signals, due to monomer and polymer, are not completely resolved. [b] Partially hidden under δ 3.65 singlet. [c] Signal composed of two triplets in 1:2 integration ratio. [d] Due to the incomplete deuteration.

The values of the rate constants are slightly lower than those determined by Enikolopyan et al. for a similar system ($(C_2H_5)_5O^+BF_4^-$ was used as initiator and CH_2Cl_2 as a solvent) and equal to: k_{iM} = 2.0 × 10^{-4} mol^{-1} L s^{-1} (34 °C, CH_2Cl_2 solvent) and k_{iP} = 1.35 × 10^{-4} mol^{-1} L s^{-1} (34 °C, CH_2Cl_2 solvent).[9] Because the rate constant of reaction of an ion with a molecule should be higher in less polar solvent, providing that free ions–ion pairs equilibria does not complicate this simple picture, agreement between both sets of results is satisfactory, although it cannot be ruled out that higher rates observed for $(C_2H_5)_3O^+BF_4^-$ salt are due to the decomposition of tetrafluoroborate salt, being less stable than the corresponding hexafluoroantimonate salt.

In light of this agreement it is difficult to understand the results recently published by Black and Worsfold.[10] These authors claim that in reaction of $(C_2H_5)_3O^+PF_6^-$ (1.08 mol L^{-1}) with **1** (3.26 mol L^{-1}) at 0 °C in CH_2CL_2 solvent, after 7.86 × 10^4 s (~22 h), about 75% of the unreacted salt is still present in the system while, according to our results, reaction is almost complete (88% conversion) at this stage.

The conclusions coming from kinetic measurements are the following: the rate constant of cationation of dimethoxymethane, being a model of one segment of poly-**1** chain (k_{iP}), is very close to the rate constant of cationation of **1** (k_{iM}), thus the presence of polymer does not influence the kinetics of **3** disappearance; the rate constants of initiation (k_{iM} and k_{iP}) are much lower (approximately 10^5–10^6 times) than the rate constant of propagation.

^{1}H-NMR Spectra of the Living Poly-1,3-dioxolan at Equilibrium. The final spectrum of the **1**–d_6–$(CH_3CH_2)_3O^+SbF_6^-$ system in CD_3NO_2 solution, taken after initiation had been finished and monomer–polymer equilibrium had been established, is shown in Figure 4.

The signals in Chart I appear in the spectrum (chemical shifts are given in ppm δ from TMS ±0.027 ppm accuracy).

Analysis of the spectrum confirms that the δ 1.75 signal, observed in the spectrum of the reaction mixture in which unreacted triethyloxonium salt is still present, is due exclusively to this compound and disappears completely after initiation is finished. The only signals at the region of CH_3–CH_2 absorption are those of CH_3–CH_2–O groups in **2C** and **5**, although in the 60-MHz spectrum both triplets are not completely resolved (Figure 4b) even if this region is expanded.

Identification of the Polymer End Groups. Further evidence for the proposed reaction scheme comes from an analysis of ^{1}H-NMR spectra of poly-**1**-d_6 initiated with $(CH_3CH_2)_3O^+SbF_6^-$ and terminated with trimethylamine.

Reaction mixture, composed of 3.0 mol L^{-1} of **1**-d_6 and 4.4 × 10^{-3} mol L^{-1} of **3** in CD_3NO_2 solvent, was kept in a sealed vessel until initiation was completed (time calculated on the basis of k_{iM} determined in the previous paragraph) and monomer–polymer equilibrium was established, then fivefold molar excess over **3** of trimethylamine solution in benzene was added to terminate the reaction. All volatile compounds were

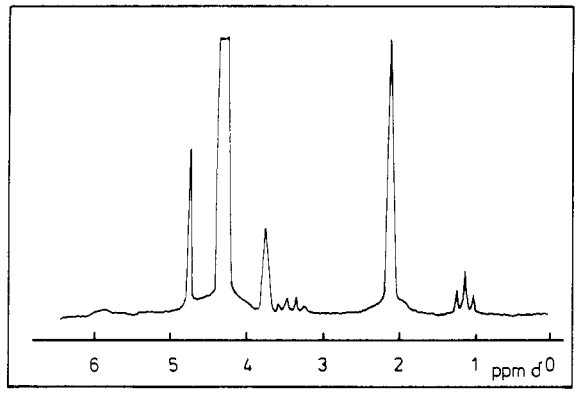


Figure 5. FPT ^{1}H-NMR spectrum (60 MHz) of a volatile fraction obtained after polymerization of 1,3-dioxolan-d_6 (1-d_6) initiated with $(C_2H_5)_3O^+SbF_6^-$, terminated with a solution of $N(CH_3)_3$ in benzene in fivefold excess (over initiator). Polymerization conditions: [1-d_6] = 3.0 mol L^{-1}; $[(C_2H_5)_3O^+SbF_6^-]$ = 4.4 × 10^{-3} mol L^{-1}, solvent CD_3NO_2, 25 °C. Number of accumulated scans = 1800.

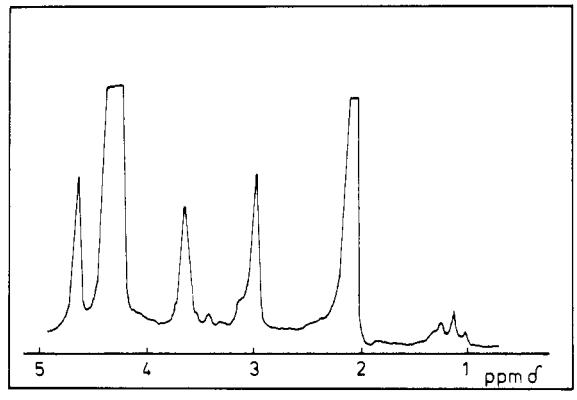


Figure 6. FPT ^{1}H-NMR spectrum (60 MHz) of poly-1-d_6 initiated with $(C_2H_5)_3O^+SbF_6^-$ and terminated with $N(CH_3)_3$ in CD_3NO_2 solution. Polymerization conditions: [1-d_6] = 3.0 mol L^{-1}, $[(C_2H_5)_3O^+SbF_6^-]$ = 4.4 × 10^{-3} mol L^{-1}, solvent CD_3NO_2, 25 °C. Number of accumulated scans = 1600.

distilled off and a solid polymer after drying for several hours on a vacuum line was again dissolved in CD_3NO_2.

^{1}H-NMR spectra of volatile fraction and of a polymer solution are given on Figures 5 and 6, respectively.

Analysis of the spectrum indicates that the volatile fraction is a mixture of **1**, **5**, trimethylamine, and solvent. The assignments of signals are the following (chemical shifts are given in ppm δ from TMS):

4.70 (s) and 3.75 (s)	–O–CD_2–O– and –O–CD_2–CD_2–O– in 1-d_6
4.33 (s)	CD_3NO_2
2.10 (s)	$(CH_3)_3N$
1.15 (t) and 3.50 (q)	CH_3 and –CH_2– in **5**

In the spectrum of polymer the following signals appear:

4.65 (s) and 3.65 (s)	–O–CD_2–O– and –O–CD_2–CD_2–O– in poly-1-d_6
4.33 (s)	CD_3NO_2
3.05 (s)	$N^+(CH_3)_3$
2.10 (s)	$(CH_3)_3N$ (not completely removed from the polymer sample)
1.15 (t)	CH_3–CH_2–O

A quartet from the CH_3–CH_2–O group (δ 3.50) is only partially visible, because two of its arms are hidden under a large signal δ 3.65.

Table I
Comparison of $\overline{DP}_n$ (calcd) and $\overline{DP}_n$ (found) from ^{1}H-NMR End-Group Analysis of Poly-1-d_6 Initiated with $(C_2H_5)_3O^+SbF_6^-$ or $C_2H_5OSO_2CF_3$ and Terminated with $(CH_3)_3N$ after the Monomer–Polymer Equilibrium was Established (25 °C, CD_3NO_2 Solvent)

[1-d_6]$_0$, mol L^{-1}	[3]$_0$ × 10^3, mol L^{-1}	$\overline{DP}_n$ (calcd) ([1]$_0$ – [1]$_e$)/[3]$_0$	$\overline{DP}_n$ (found) from ^{1}H-NMR [CH_3CH_2O]	[CH_3CH_2O]/[$N^+(CH_3)_3$]
3.0	4.4[a]	340	330	1.1
3.0	9.5[b]	160	120	0.8

[a] 3.9 × 10^{-3} mol L^{-1} of $(CH_3CH_2)_2O$ was recovered as a component of a volatile fraction. [b] $CH_3CH_2OSO_2CF_3$ was used as initiator instead of **3**.

The assignment of a signal at δ 3.05 is based on the comparison with the spectrum of an independently prepared model compound: CH_3OCH_2–$N^+(CH_3)_3$ SbF_6^-, in which for the $N^+(CH_3)_3$ group a singlet at δ 3.05 (cf. Experimental Section) appears.

The spectrum of polymer solution is consistent with a proposed structure of growing species. A position of the CH_3 group absorption, which is the same as in the living system, indicates that the CH_3–CH_2 group does not participate in reaction with trimethylamine but remains as CH_3–CH_2–O end group (CH_3CH_2–$N^+(CH_3)_3$ protons would absorb at δ 1.35, cf. Experimental Section), while quaternary ammonium salt is formed at the other end:

$$CH_3\text{–}CH_2(\text{–}OCD_2CD_2OCD_2\text{–})_nN^+(CH_3)_3\ SbF_6^-$$

The molar ratio of both end groups CH_3–CH_2–O and $N^+(CH_3)_3$, determined from the corresponding peak areas (integration), is close to 1:1. The mole fractions of H atoms in positions C_2 and $C_4(C_5)$ in the deuterated 1 are known.[2] Thus,[2] the proportion of the end groups in poly-1-d_6 may be calculated, allowing the determination of $\overline{DP}_n$. This is compared with $\overline{DP}_n$ calculated as ([1]$_0$ – [1]$_e$)/[3]$_0$, assuming that one molecule of initiator forms one macromolecule (Table I).

The data of Table I indicate that the chain transfer we observed previously to proceed at the early stages of polymerization[8] does not influence considerably the polymerization degree, given by a ratio of reacted monomer to reacted initiator, and that the concentration of the cyclic macromolecules (formed by back-biting and by the end-to-end closure) is in this system sufficiently low to not influence considerably the equality of $\overline{DP}_n$ (calcd) and $\overline{DP}_n$ (found) from the end groups (Table I).

References and Notes

(1) Part 6 of the series: Kinetics and Mechanism of the Polymerization of Cyclic Acetals. Presented in part at the 4th International Symposium on Cationic Polymerization, Akron, Ohio, June 1976.
(2) P. Kubisa and S. Penczek, *Makromol. Chem.*, accepted for publication.
(3) P. Dreyfuss and M. P. Dreyfuss, *Fortschr. Hochpolym. Forsch.*, **4**, 528 (1967).
(4) S. Smith and A. J. Hubin, *J. Macromol. Sci., Chem.*, **7**, 1399 (1973).
(5) P. H. Plesch and P. H. Westermann, *J. Polym. Sci., Part C*, **16**, 3837 (1968).
(6) Y. Firat, F. R. Jones, P. H. Plesch, and P. H. Westermann, *Makromol. Chem., Suppl.*, **1**, 203 (1975).
(7) R. Szymanski, H. Wieczorek, P. Kubisa, and S. Penczek, *Chem. Commun.*, 33 (1976).
(8) S. Penczek, *Makromol. Chem.*, **175**, 1217 (1974).
(9) I. S. Morozowa, W. W. Iwanow, M. A. Markewitch, R. D. Sabirowa, and N. S. Enikolopian, *Dokl. Akad. Nauk SSSR*, **215**, 641 (1974).
(10) P. E. Black and D. J. Worsfold, *J. Macromol. Sci., Chem.*, **9**, 1533 (1975).
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