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Polymerization of Cyclic Ethers

TAKEO SAEGUSA

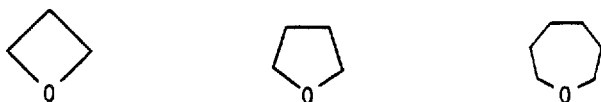
Department of Synthetic Chemistry
Kyoto University
Kyoto, Japan

ABSTRACT

In the present series of studies on the cationic polymerization of cyclic ethers, the reactivities of cyclic ethers were quantified and the effect of the catalyst upon the polymerization kinetics was revealed. These kinetic analyses were successfully performed by means of our "phenoxy end-capping method." The change of the reactivity by the ring size of the monomer was interestingly demonstrated. In addition, it is emphasized that the frequency factor as well as the activation energy influence the rate constant of propagation. As to the effect of catalyst upon the polymerization kinetics, the most important conclusion is that the rate constant of propagation changes very little according to the changes of the catalyst components. Variation of the conversion rate by a change of catalyst is due to differences in the rates of the initiation and the termination reactions.

Ring-opening polymerization of heterocyclic compounds involves a great variety of monomers, catalysts, polymerization mechanisms, and product polymers. In the chemistry of ring-opening polymerization, the quantification of the reactivities of monomers and the characterization of polymerization catalysts are the most fundamental problems. So far as we know, little systematic work has been done in this area. In the present series of studies, the cationic polymerization

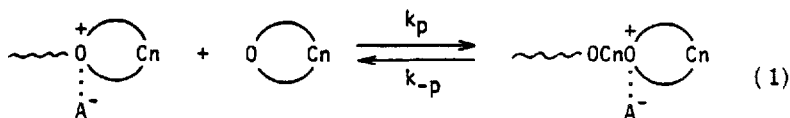
of cyclic ethers has been adopted for study because the structure of monomers and the propagation mechanisms are simple. First, a method of kinetic analysis was established, which was based upon the determination of the concentration of propagating species. Then, the following two subjects were quantitatively analyzed by means of a new method: 1) The polymerization reactivities of four-, five-, and seven-membered cyclic ethers, and 2) the effect of the catalyst nature



upon the kinetics of cationic polymerization of tetrahydrofuran (THF).

The results of the analysis of the first problem afford important information about the relationship between the ring size and the polymerization reactivity of cyclic ether. The values of the rate constants of propagation as well as initiation and termination of the cyclic ether's polymerization are given here for the first time, and the results will contribute effectively towards the true understanding of ring-opening polymerization.

The polymerization of cyclic ether is shown to be an S_N2 reaction between the cyclic oxonium of propagating species (electrophile) and monomer (nucleophile) (Eq. 1), where A^- is the counteranion derived



from the catalyst. As an S_N2 reaction, this type of propagation reaction is characterized by the combination of a strong electrophile and a weak nucleophile. The polymerization is sometimes reversible, and Eq. (2) represents the kinetics of the cationic propagation of cyclic ethers.

$$-dM/dt = k_p[P^*][M] - k_{-p}[P^*] \quad (2)$$

where $[P^*]$ is the concentration of propagating species, and k_p and k_{-p} are the rate constants of the propagation and depropagation

reactions, respectively. At the polymerization-depolymerization equilibrium,

$$k_p [P^*][M]_e = k_{-p} [P^*]$$

Therefore

$$k_p [M]_e = k_{-p}$$

Then, Eq. (2) becomes

$$-dM/dt = k_p [P^*] \{ [M] - [M]_e \} \quad (3)$$

When the polymerization is irreversible, $k_{-p} = 0$ and $[M]_e = 0$. Hence the kinetic equation becomes

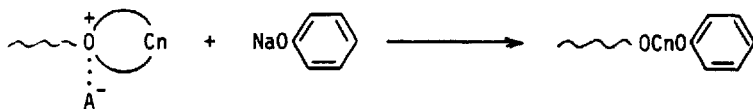
$$-dM/dt = k_p [P^*][M] \quad (4)$$

For the determination of k_p according to Eqs. (3) and (4), it is essential to know the $[P^*]$ value. The instantaneous value of $[P^*]$ during the cationic polymerization of cyclic ethers is determined by our new technique, the "phenoxy end-capping method" [1].

RESULTS AND DISCUSSION

Determination of Concentration of Propagating Species by Phenoxy End-Capping Method [1]

The phenoxy end-capping method is based on the quantitative conversion of the propagating species into the corresponding phenyl ether by treatment with sodium phenoxide, and the phenoxy group at polymer end is analyzed by means of uv spectroscopy.

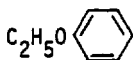


At a designed time of reaction, excess sodium phenoxide solution in THF was added to the polymerization system, and the short-stopping mixture was stirred for 1 hr at room temperature to ensure the end-capping reaction. Then the mixture was treated with a large excess of 1 N aqueous sodium hydroxide and extracted with CH_2Cl_2 . The extract was dried over anhydrous K_2CO_3 , centrifuged, and subjected to uv measurement.

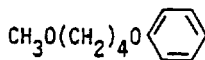
For this analysis, the following three problems should be solved.

1) The value of the molar extinction coefficient of the phenyl ether group at the polymer end should be known. 2) The quantitiveness of the end-capping reaction should be guaranteed. 3) side reaction leading to the formation of the phenyl ether group should be absent.

The molar extinction coefficient of phenyl ether at the polymer end was reasonably determined from the coefficients of two model compounds phenethole (I) and 4-methoxybutyl phenyl ether (II). In CH_2Cl_2



I

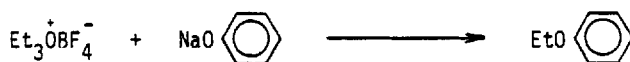


II

and Et_2O , these phenyl ethers showed uv absorption spectra of the same shape with λ_{max} at 272 $\text{m}\mu$ with the same extinction coefficient, $\epsilon_{\text{max}} = 1.93 \times 10^3$ liters/mole-cm (Fig. 1).

It is clear that the ϵ_{max} value of phenyl alkyl ether is not affected by the nature of the alkyl group. The presence of ether linkage in the alkyl group does not exert any noticeable effect on the uv spectrum. In addition, the uv spectra of polymers of three cyclic ethers having the phenyl ether end group strongly resembled the spectra of the two model compounds. From these results the ϵ_{max} value of the model compounds, 1.93×10^3 liter/mole-cm, was reasonably adopted as the ϵ_{max} value of the phenyl ether group at the polymer end.

Second, the conversion of cyclic oxonium ions of the propagating species into the corresponding phenyl ether should be quantitative for the determination of $[\text{P}^*]$. The quantitiveness was substantiated by a reference experiment in which triethyloxonium tetrafluoroborate (III) [2] was used as a model compound of the propagating species and was subjected to the phenoxy end-capping reaction under the same conditions as those of the treatment of polymerization (room temperature, 1 hr). The production of phenetole in this model reaction was shown to be quantitative and instantaneous [1]. The cyclic trialkyloxonium species at the propagating end is strained and its reactivity towards the phenoxide ion is considered to be higher than the reactivity of the triethyloxonium ion. Therefore, it is reasonable to conclude that the phenoxy end-capping reaction is quantitative.



III

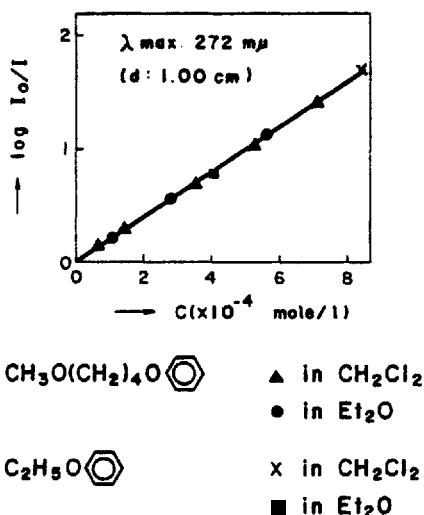


FIG. 1. Extinction coefficient of phenyl alkyl ethers.

The third requisite, i.e., the absence of a side reaction leading to the formation of phenyl ether was examined by a series of reference experiments. In the cases of all monomers and catalysts except for the triethyloxonium salts catalysts, phenyl ether was found to be formed exclusively from the propagating species at the polymer end. Any other reaction components as well as the reaction solvent (CH_2Cl_2) did not give phenyl ether under the prescription conditions. In the case of triethyloxonium salts catalysts, the phenoxy end-capping of an early polymerization system gave phenetole which was derived from the unreacted catalyst (see Fig. 1).

The phenoxy end-capping method was further verified in a living polymerization system of THF in which the number of propagating species was equal to that of the polymer molecule. Therefore, the concentration of propagating species could be determined from the amount of polymer and its number-average molecular weight. As a catalyst for the living polymerization of THF, the $\text{AlEt}_3\text{-H}_2\text{O}$ -epichlorohydrin (ECH) system [3, 4] was employed. [P*] was

determined at several reaction times by the phenoxyl end-capping method and also from the number-average molecular weights (Table 1). In the phenoxyl end-capping procedure, $[P^*]$ was determined from the production of phenyl ether and the consumption of sodium phenoxide.

There is remarkable agreement between the $[P^*]$ values determined by the above two procedures of the phenoxyl end-capping method. Furthermore, the $[P^*]$ values by the phenoxyl end-capping method agree well with the values calculated from the average molecular weights. These results are taken as showing the validity of the phenoxyl end-capping method.

Polymerization Reactivities of Four-, Five-, and Seven-Membered Cyclic Ethers

The relation between the reactivity and ring size of a cyclic monomer is one of the most fundamental problems in ring-opening polymerization. In the present study, the cationic polymerization reactivities of oxetane (four-membered), THF (five-membered), and oxepane (seven-membered) were examined and compared on the basis of their propagation rate constants and the corresponding activation parameters. For the purpose of comparison, solution polymerization in CH_2Cl_2 with BF_3 catalyst was carried out with all three monomers. In the cases of THF and oxepane, ECH was used as promoter in combination with BF_3 .

The propagation reactions of these monomers have been generalized by Eq. (1), and the rate equation of a bimolecular S_N2 reaction with or without the backward reaction of depolymerization has been given (Eqs. 3 and 4). Kinetic analyses of these polymerizations were performed on the basis of the $[P^*]$ determination by the phenoxyl end-capping method. As has been described before, three requirements for the phenoxyl end-capping method have been shown to be fulfilled in the polymerizations of these monomers.

THF Polymerization

The THF polymerization was first examined because the moderate reactivity of the monomer was suited for kinetic analysis. For the comparison of reactivity with other monomers, only polymerization by the BF_3 -ECH system is described here. ECH was used as the promoter, and its function is described in the section of these studies dealing with catalyst characterization. The THF polymerizations by several other catalysts are also described later.

Figure 2 shows the $[P^*]$ -time profile (Curve 1) and the $\ln \{ [M]_0 - [M]_e / [M]_t - [M]_e \}$ vs time plot (Curve 2) of the THF polymerization

TABLE 1. Polymerization of Tetrahydrofuran by $\text{AlEt}_3\text{-H}_2\text{O}$ (1:0.5) and ECH: Concentration of Propagating Species^a

Polymerization time (hr)	Polymer yield (%)	$[\text{P}^*] \times 10^{-3}$ (mole/l)		From $\Delta[\text{PhONa}]^c$	$[\text{P}^*]_{\text{os}} \times 10^{-3}$ (mole/l)	from \bar{M}_n	$\bar{M}_n \times 10^{-4}$
		From $[\text{PhOR}]^b$	From				
First stage							
10 min			1.23	-	-	-	-
0.5	1.0		1.48	1.40	-	-	-
1	2.5		1.63	1.52	-	-	-
Second stage							
2	5.6		1.87	1.80	-	-	-
3	8.7		1.84	1.60	-	-	-
4	13.2		2.15	2.02	2.39	2.39	4.69
5	18.3		1.96	2.03	2.15	2.15	7.85
6	21.7		1.98	2.03	2.04	2.04	10.4

^aPolymerization conditions: THF, 0.125 M ($[\text{M}]_0 = 12.6$ moles/l; AlEt_3 , 1.78×10^{-3} M ($[\text{AlEt}_3]_0 = 0.178$ mole/l); ECH, 2.02×10^{-4} M ($[\text{ECH}]_0 = 0.020$ mole/l); bulk polymerization at 0°C.

^bAmount of phenyl ether group of polymer, i.e., concentration of propagating species.

^cAmount of sodium phenoxide consumed.

^dNumber-average molecular weight determined by osmometry.

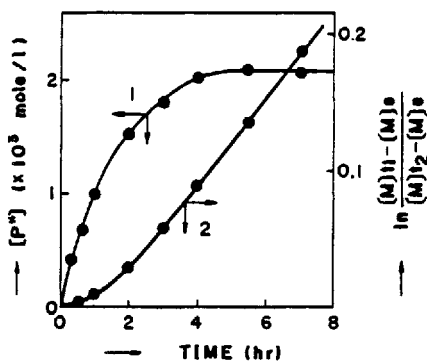


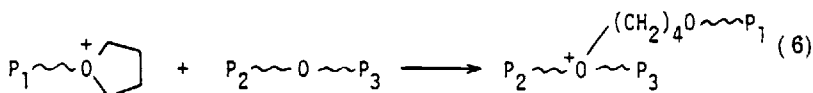
FIG. 2. Bulk polymerization of tetrahydrofuran by BF_3 -ECH system (0°C) $[\text{M}]_0$ 12.6 mole/liter, $[\text{BF}_3]_0$ 0.011 mole/liter, $[\text{ECH}]_0$ 0.010 mole/liter, and $[\text{M}]_e$ 1.7 mole/liter.

by the BF_3 -ECH system at 0°C [5]. It is seen that $[\text{P}^*]$ increases in the first stage of polymerization and remains unchanged in the subsequent stage. The first stage is designated as the induction period in which the propagating species are continuously formed. The induction period of Curve 1 corresponds to that given by Curve 2 of the first-order plot of the monomer concentration according to Eq. (3). The polymerization-depolymerization equilibrium in THF polymerization has long been known [6, 7]. The propagation rate constant was conveniently determined in the following way, using the $[\text{P}^*]$ -time curve.

$$\ln \frac{[\text{M}]_{t_1} - [\text{M}]_e}{[\text{M}]_{t_2} - [\text{M}]_e} = k_p \int_{t_1}^{t_2} [\text{P}^*] dt \quad (5)$$

Integration of Eq. (3) yields Eq. (5). The value of $\int_{t_1}^{t_2} [\text{P}^*] dt$ is obtained by graphical integration on the $[\text{P}^*]$ -time curve. The plot of $\ln \{ [\text{M}]_{t_1} - [\text{M}]_e / [\text{M}]_{t_2} - [\text{M}]_e \}$ vs the integrated $[\text{P}^*]$ is expected to be linear and, if this is so, the slope of the straight line will correspond to k_p .

In the THF polymerization, the oxonium exchange may possibly occur between the propagating cyclic oxonium ion and the ether linkages in polymer molecule (Eq. 6). The reactive oxonium species



are converted by this exchange into the polymeric open-chain oxonium of the so-called "dormant" nature. Consequently, the oxonium exchange reaction may affect the polymerization. However, in the present study, because the basic strength of the THF monomer is much stronger than that of the open-chain ethers, and because the conversion percentages in the present study have been confined to below 30%, the effect of the oxonium exchange is taken to be quite small under the conditions of kinetics.

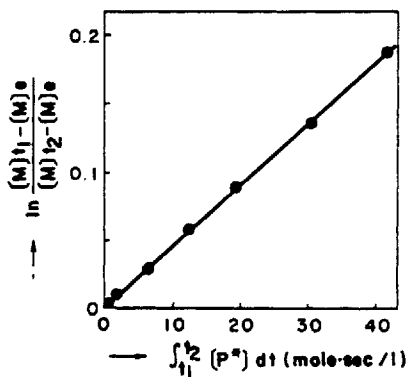


FIG. 3. Polymerization of tetrahydrofuran by BF_3 -ECH system. (The conditions are given in Fig. 2).

Figure 3 shows a linear plot of Eq. (5) in which $t_1 = 0$, $t_2 =$ variable, and $[M]_e = 1.7$ mole/l at 0°C [8]. The straight line passing through the origin may be taken to support the assumptions made for the procedures of kinetic analysis. The slope of the straight line gives the k_p value.

The THF polymerization was also carried out at -10 and $+10^\circ\text{C}$ in solution ($[M]_0 = 6.3$ mole/l, in CH_2Cl_2) by the same catalyst ($[\text{BF}_3]_0$ and $[\text{ECH}]_0$, each 0.01 mole/l) [9]. Similarly to the polymerization at 0°C (Figs. 2 and 3), the polymerization at -10°C proceeded without noticeable termination. On the other hand, at $+10^\circ\text{C}$ a decrease

of $[P^*]$ by termination was observed in a later stage of polymerization. By the same procedure and using the $[M]_e$ values reported by Ofstead [8], k_p was determined at -10 and $+10^\circ\text{C}$ (Table 2). The Arrhenius plot of k_p values at three temperatures gave a straight line (Fig. 4) from which the activation parameters were obtained; $\Delta E_p^\ddagger = 12$ kcal/mole and $A_p = 1.1 \times 10^7$ liters/mole-sec. These values were similar to the corresponding parameters of the THF polymerization by the AlEt_3 - H_2O (2:1)-ECH system, i.e., $\Delta E_p^\ddagger = 12$ kcal/mole and $A_p = 5.3 \times 10^7$ liters/mole-sec [4].

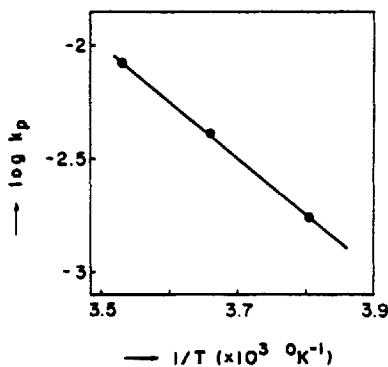


FIG. 4. Arrhenius plot of propagation rate constant in the polymerization of tetrahydrofuran by BF_3 -ECH system.

Oxetane Polymerization [10]

Oxetane was polymerized in CH_2Cl_2 at -27.8 , -22.6 , -10.4 and 0°C by BF_3 catalyst without promoter. The initial concentrations of the monomer and the catalyst were 3.1 mole/l and 3 mole/l, respectively. $[P^*]$ was about 80% of the molar concentration of BF_3 in this temperature range. Figure 5 shows the $[P^*]$ -time profile of the oxetane polymerization at -10.4°C .

The polymerization of oxetane has been known to suffer from a complication of the formation of a small amount of cyclic tetramer, a sixteen-membered cyclic ether [11].

In the kinetic treatment of the present study, the mixture of linear

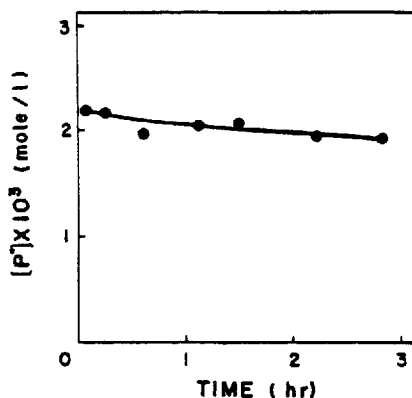
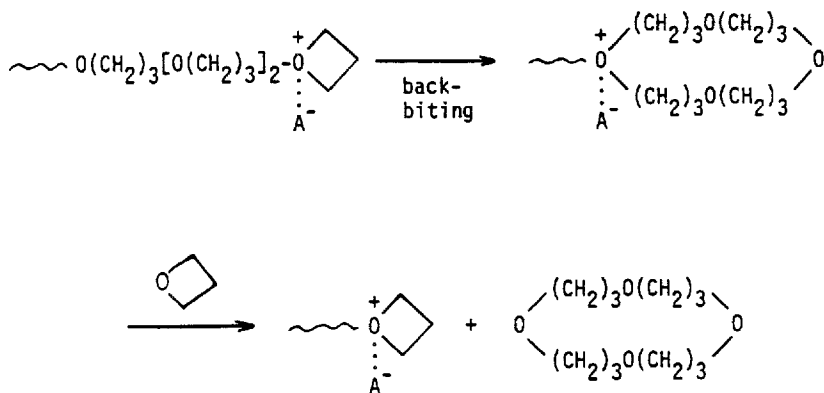


FIG. 5. Solution polymerization of oxetane in CH_2Cl_2 by BF_3 catalyst. -10.4°C . $[\text{M}]_0$ 1.5 mole/liter and $[\text{BF}_3]_0$ 0.003 mole/liter.



polymer and a small amount of cyclic tetramer was taken to be the polymeric material. The oxonium exchange reaction as depicted by Eq. (6) may occur with the polymer ether linkage as well as with the cyclic tetramer. However, the oxonium exchange does not cause any considerable error because 1) the oxetane monomer is a strong base, and 2) the polymerization temperatures of the present study were low, where the formation of cyclic tetramer was quite small. It is safe to assume that the concentrations of the oxonium ions of polymer ether and of cyclic tetramer are very small.

The equilibrium monomer concentration in the kinetic analysis was taken to be zero since the oxetane polymerization was shown

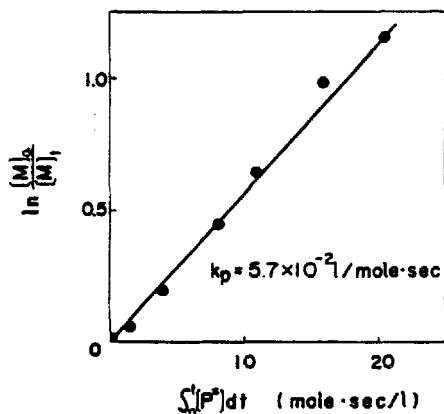


FIG. 6. Polymerization of oxetane by BF_3 catalyst. (The conditions are given in Fig. 5.)

to be irreversible [11]. Integration of Eq. (4) gives

$$\ln [M]_{t_1} / [M]_{t_2} = k_p \int_{t_1}^{t_2} [P^*] dt \quad (7)$$

The plot of Eq. (7) gave a straight line passing the origin at four temperatures. Figure 6 shows an example of the plot of Eq. (7). From the slope of the straight line, k_p was determined (Table 2), and the activation parameters were obtained by the Arrhenius plot (Fig. 7) of the k_p values at four temperatures (Table 2).

Oxepane Polymerization [12, 13]

Prior to kinetic analysis of oxepane polymerization, the method of preparation of pure oxepane had to be established [12]. Several methods have been reported for the preparation of oxepane. In the dehydration of hexamethyleneglycol by H_2SO_4 or by acidic metal oxide [14], the product mixture contains several undesirably by-products such as 2-methyltetrahydropyran and 2-ethyltetrahydrofuran which could not be readily separated from oxepane by fractional distillation. The production of these inseparable by-products is due to the unavoidable side reactions of the isomerization of carbonium ion intermediate, which is a perplexing problem in these procedures.

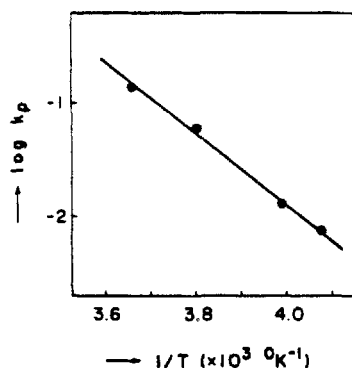
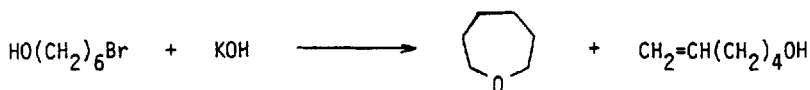


FIG. 7. Arrhenius plot of propagation rate constant in the polymerization of oxetane by BF_3 .

The method of alkaline ring-closure of bromohydrin [15] was found to be suited for the preparation of pure oxepane:






The only by-product was 5-hexenol which was readily separable from oxepane after treatment with bromine water. Repeated fractional distillation on sodium metal gave oxepane with a purity above 99.9% [12].

Oxepane was found to be polymerized by various cationic catalysts such as $\text{Et}_3\text{O}^+\text{BF}_4^-$, $\text{Et}_3\text{O}^+\text{SbCl}_6^-$, BF_3/ECH , and SbCl_5/ECH [12]. A kinetic study was made of polymerization by the catalyst system of BF_3 -ECH at a temperature range of -10 to 30°C . The polymerization rate was generally quite slow, and a long reaction time, e.g., 75~100 hr at room temperature, was required for sizable conversion percentages. In a long reaction time, the occurrence of termination became noticeable even at 0°C in the $[\text{P}^*]$ -time profile (Fig. 8).

The oxepane polymerization was found to be reversible. The $[\text{M}]_e$ values were obtained by the depolymerization of purified polymer with $\text{Et}_3\text{O}^+\text{SbCl}_6^-$ and by the ultimate conversion of polymerization with the same initiator. The two values agreed with each other, and the $[\text{M}]_e$ values were obtained at 10 and 30°C (Table 3).

TABLE 2. Rate Constants and Activation Parameters

			
$k_p \times 10^3$ (liter/mole-sec) ^a			
-27.8	7.5	-	-
-22.6	13	-	-
-10	57 (at -10.4)	1.7	0.0033
0	140	4.1	0.015
10	-	8.4	0.031
20	-	-	0.091
30	-	-	0.43
ΔF_p^\ddagger (kcal/mole) (at 0°C)	17	22	27
ΔE_p^\ddagger (kcal/mole)	14	12	18
$10^{-7} A_p$ (liter/mole-sec)	5300	1.1	190
ΔF^b (kcal/mole)	21.2	2	4.9
pK_b	1.80 ^{c,d}	2.08 ^d	2.02 ^d

^aSolution polymerization in CH_2Cl_2 . The initial feeds were as follows,

oxetane: $[M]_0 = 3.1$ mole/l, $BF_3 \cdot THF = 0.008$ mole/l.

THF: $[M]_0 = 6.3$ mole/l, $BF_3 \cdot THF$, ECH = 0.01 mole/l.

oxepane: $[M]_0 = 2.9$ mole/l, $BF_3 \cdot THF$, ECH = 0.057 mole/l.

^bFree energy of hypothetical polymerization of the corresponding cycloalkane [16].

^cS. Iwatsuki, N. Takigawa, M. Okada, Y. Yamashita, and Y. Ishii, *Kogyo Kagaku Zasshi*, **67**, 1236 (1964).

^dE. M. Arnett and C. Y. Wu, *J. Amer. Chem. Soc.*, **84**, 1684 (1962).

The $[M]_e$ value of the oxepane polymerization is much smaller than that of the THF polymerization. This fact indicates that oxepane is more strained than THF. The ring strain of oxepane is due to the trans-annular interaction of repulsions of the pseudo-axial hydrogens (Fig. 9).

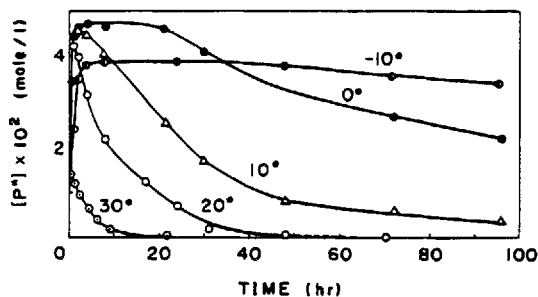


FIG. 8. Solution polymerization of oxepane in CH_2Cl_2 by BF_3 -ECH system. $[M]_0$ 2.9 mole/liter, $[\text{BF}_3]_0$ and $[\text{ECH}]_0$ each 5.7×10^{-2} mole/liter ($-10 \sim 20^\circ\text{C}$) and 2.9×10^{-2} mole/liter (30°C).

TABLE 3. Equilibrium Monomer Concentration of Oxepane Polymerization^a

	Time (days)	Monomer/polymer at equilibrium ^b	$[M]_e \times 10^2$ (mole/l)
At 30°C			
From monomer ^c	38	2.7/97.3	9.3
From polymer ^d	18	2.4/97.6	7.0
			av 8
At 10°C			
From monomer ^c	38	2.1/97.9	7.2
From polymer ^d	18	1.6/98.4	4.9
			av 6

^aPolymerization and depolymerization were carried out with $\text{Et}_3\text{O}^+\text{SbCl}_6^-$ (2 mole %) in CH_2Cl_2 .

^bThe monomer concentration in the system was determined by glpc analysis using 1,1,2,2-tetrachloroethane as the internal standard.

^c $[M]_0 = 3.45$ moles/l.

^dThe initial concentration of the monomeric units in polymer was 2.87 moles/l.

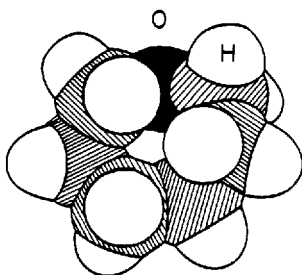


FIG. 9. Molecular model for oxepane.

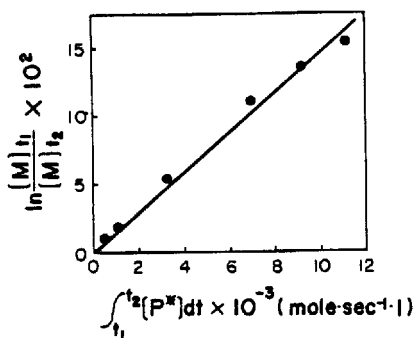


FIG. 10. Polymerization of oxepane (0°C). (The conditions are given in Fig. 8.) $t_1 = 1$ hr.

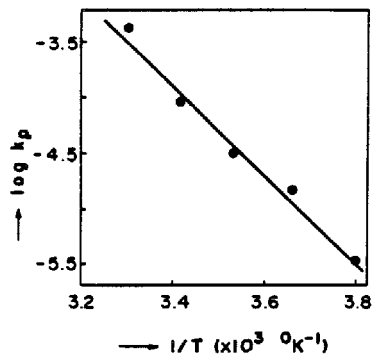


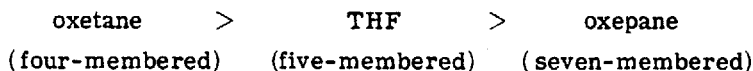
FIG. 11. Arrhenius plot of propagation rate constant in the polymerization of oxepane by BF_3 -ECH system.

In the practical treatment of kinetics according to Eq. (5), however, the $[M]_e$ term could be neglected because the $[M]_e$ value is very small in comparison with $[M]$ in the present study. The plot of Eq. (7) was linear at five temperatures listed in Table 2. Figure 10 is the linear plot at 0°C. The Arrhenius plot of k_p was also linear (Fig. 11), from which the activation parameters were calculated (Table 2).

Comparison of Rate Constants and Activation Parameters

The fundamental data of the kinetics and the thermodynamics of the polymerizations of three cyclic ethers are summarized in Table 2. It is the first time a set of rate constants of propagation of cyclic ethers having different ring sizes have been given and compared.

The order of reactivities as expressed by the propagation rate constant at 0°C is



At 0°C, oxetane is about 35 times as reactive as THF, and THF in turn is about 270 times as reactive as oxepane. The order of this reactivity is not in agreement with the order of the magnitudes of the ring strains of monomers, i.e., oxetane > oxepane > THF, which has reasonably been estimated from the $[M]_e$ values. Also, the same order of ring strain is given in the free energy changes of the hypothetical ring-opening polymerizations of cycloalkanes of the respective ring sizes [16]. Oxepane is more strained than THF, but the k_p value of oxepane is much smaller than that of THF.

The basic strengths of these monomers are expressed by their pK_b values (Table 2), which might be considered to be parallel to the inherent reactivities of monomer as nucleophile, and is possibly one of factors governing the reactivity. However, the order of basic strength, oxetane > oxepane \approx THF, can not account for the big reactivity difference between THF and oxepane. Thus the consideration of basic strength of monomer is not enough to explain the reactivity difference. In general, the rate constant of propagation of a S_N2 reaction is to be governed not only by the nucleophilic reactivity of the monomer but also by the reactivity of the cyclic

oxonium ion of the propagating species and the steric hindrance in the transition state of propagation.

It now seems worthwhile to examine the activation parameters. The higher k_p value of oxetane in comparison with that of THF is mainly due to the higher value of the frequency factor (Table 2). The activation energy of the oxetane polymerization is even higher than that of the THF polymerization. This fact is taken to indicate that the orientation of the cyclic oxonium ion and the monomer is looser in the S_N2 transition state of the oxetane polymerization (Fig. 12).

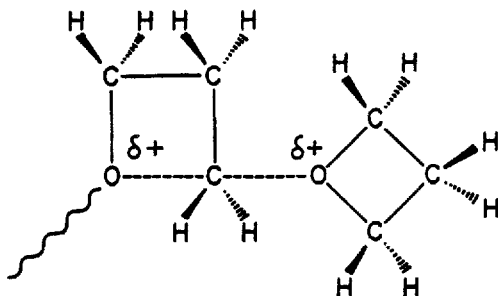
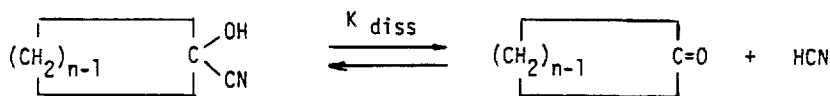
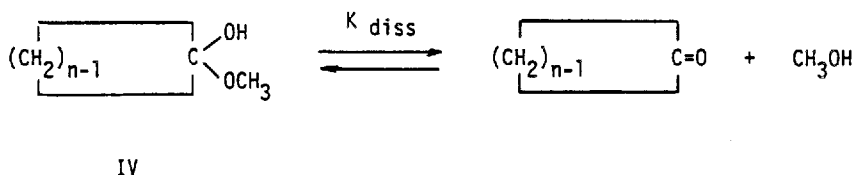


FIG. 12. Transition state of the propagation of the oxetane polymerization.

One of possible explanations is as follows. The angle of a four-membered ring is smaller than that of a five-membered ring. Both the ether oxygen and the α -methylene carbon atom of oxetane are more exposed in comparison with the corresponding atoms of THF. Owing to the decreased steric hindrance by the hydrogens on the adjacent carbon atoms of the propagating cyclic oxonium ion and monomer, the transition state of oxetane polymerization will have a higher freedom as depicted in Fig. 12. On the other hand, the much lower k_p value of oxepane in comparison with that of THF is ascribed to the higher activation energy. The frequency factor of the oxepane propagation is even a little higher than that of the THF propagation. The higher value of activation energy is explained by the decreased activity (increased stability) of the seven-membered oxonium ion of the propagating species. Oxepane molecule has a puckered structure, and in its oxonium ion the strain arising from the tri-valent oxygen will be readily relieved by the small deformations

of the angles of the other bonds. In the cases of oxetane and THF, the cyclic oxonium ions of the propagating species are planar and rigid, and the strains of the tri-valent oxygens of their oxonium are hardly relieved. In relation to the case of the relief of the strain caused by the bond-angle deformation in seven-membered ether, the dissociations of cyclic hemiacetals [17] (IV) and cyclic cyanohydrins [18] (V) into the corresponding cyclic ketones are to be cited.



In both of the above dissociations, the sp^3 carbon atoms of the adducts of IV and V are converted into the sp^2 carbons of carbonyl compounds. The dissociation constants of the seven-membered adducts are much higher than those of the respective five-membered ones. These facts have been explained as follows: the strain caused by the conversion of sp^3 carbon to sp^2 is relieved more easily in the seven-membered adducts than in the five-membered ones.

Effect of Catalyst Nature upon Kinetics of THF Polymerization

Several representative catalyst systems of the THF polymerization were examined with respect to the $[\text{P}^*]$ change during the reaction and the rate constant of propagation.

[P*]-Time Profile

AlEt₃-H₂O-ECH System. As has been mentioned before, this catalyst system has been shown to be a catalyst of living polymerization of THF [1]. Figure 13 shows the [P*]-time profile (Curve 1) and $\ln \{ [M]_0 - [M]_e / [M]_t - [M]_e \}$ vs time plot. As in the case of the BF₃-ECH catalyst (Fig. 2), [P*] increases in the induction period, and then it remains unchanged. Also, the induction period shown by Curve 1 corresponds to that shown by Curve 2. It is also important to note here that the final value of [P*] is only about 1% of the concentration of AlEt₃ which has been used in the preparation of the catalyst system. In other words, the efficiency of the production of active species is very low. In the case of the BF₃-ECH system, the efficiency was 19% (Fig. 2).

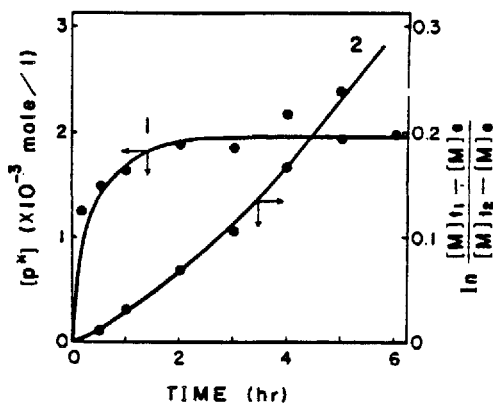


FIG. 13. Bulk polymerization of tetrahydrofuran by AlEt₃-H₂O (2:1)-ECH system (0°C). [M]₀ 12.6 mole/liter, [AlEt₃]₀ 0.178 mole/liter, [ECH]₀ 0.02 mole/liter, and [M]_e 1.7 mole/liter.

Lewis Acid-ECH Systems [5]. The three combinations of Lewis acids and ECH were examined. BF₃, SnCl₄, and EtAlCl₂ were employed as the Lewis acid component. The BF₃-ECH system has been described in the preceding section. ECH plays a role of the so-called "promoter" in these systems. The concept of promoter has been originated and rationalized by us [4, 19, 20]). Promoters are reactive small-ring compounds whose cationic ring-opening reactions

The $[P^*]$ -time curves of the THF polymerizations by the SnCl_4 -ECH and EtAlCl_2 -ECH systems at 0°C are shown in Figs. 14A and B, respectively. In both cases the $[P^*]$ -time profile (Curve 1) is quite different from the corresponding curves by the BF_3 -ECH (Fig. 2, Curve 1) and AlEt_3 - H_2O -ECH systems (Fig. 13, Curve 1). Only a rapid decrease of $[P^*]$ is seen in Fig. 14A. In Fig. 14B a period for the increase of $[P^*]$ was observed at a very early stage of polymerization, showing that the initiation is a little slower. The rapid decrease of $[P^*]$ means that there is a rapid termination reaction, which accords with the early cessation of polymerization producing low molecular weight polymers (Curve 2 in Figs. 14A and B).

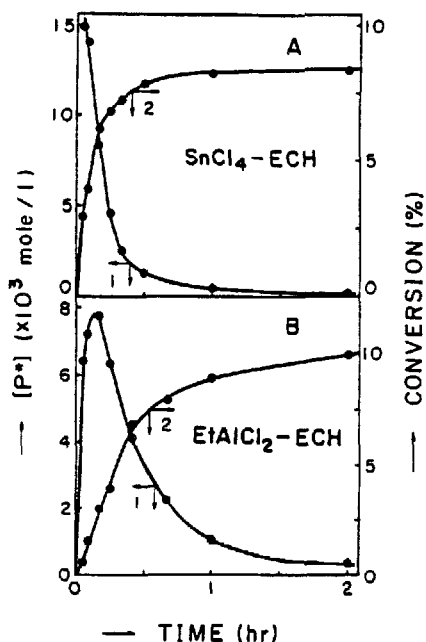
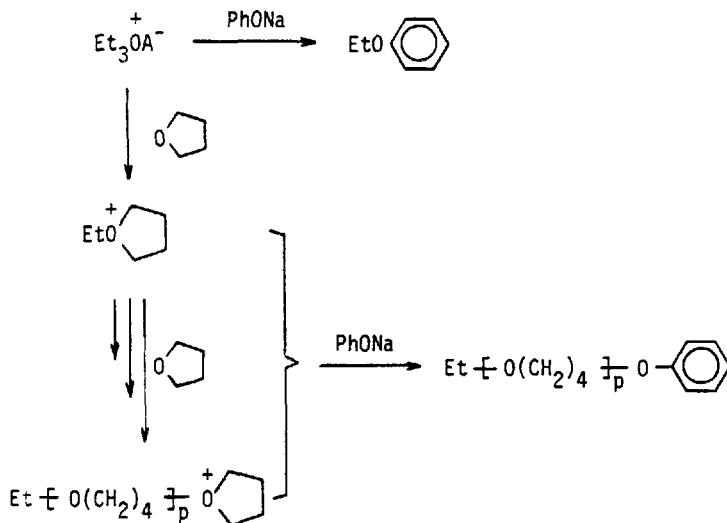


FIG. 14. Bulk polymerization of tetrahydrofuran (0°C). A: $[\text{SnCl}_4]_0$ 0.055 mole/liter and $[\text{ECH}]_0$ 0.053 mole/liter. B: $[\text{EtAlCl}_2]_0$ 0.053 mole/liter and $[\text{ECH}]_0$ 0.051 mole/liter.

Triethyloxonium Salts [21]. Triethyloxonium salts such as $\text{Et}_3\text{O}^+\text{BF}_4^-$, $\text{Et}_3\text{O}^+\text{SbCl}_6^-$, and $\text{Et}_3\text{O}^+\text{SbF}_6^-$ are known as a group of powerful catalysts of the cationic polymerization of cyclic ethers [21-23].

In the present study, $\text{Et}_3\text{O}^+\text{BF}_4^-$ and $\text{Et}_3\text{O}^+\text{AlCl}_4^-$ were examined. The procedure of the phenoxy end-capping method was to be modified in these cases because the phenoxy end-capping reaction produces phenetole from the unreacted catalyst, if it is present, in addition to the polymer phenyl ether from the propagating species.



Phenetole should be separated from the polymer phenyl ether before uv analysis. The separation was accomplished successfully by vacuum distillation with the aid of decalin as the distillation entrainer (at room temperature, 0.2-0.3 mm Hg). In this distillation, phenetole was completely distilled out, and the polymer phenyl ether from the propagating species, even the species having a degree of polymerization of 1 ($p = 1$) in the scheme shown), was not evaporated. These essential facts were confirmed by reference experiments using mixtures of poly-THF and one of two phenyl ethers, phenetole and $\text{CH}_3\text{O}(\text{CH}_2)_4\text{OC}_6\text{H}_5$. In the phenoxy end-capping analysis of the polymerization system, the amount of phenetole in the distillate corresponds to the amount of the remaining catalyst of triethylxonium salt, and the amount of phenyl ether in the distillation residue is equal to that of the propagating species. Thus the concentrations of the propagating species and the remaining catalyst were determined separately. Figure 15 shows the changes of $[P^*]$ (Curve 1) and $[\text{Et}_3\text{O}^+\text{BF}_4^-]$ (Curve 2) during the THF polymerization by $\text{Et}_3\text{O}^+\text{BF}_4^-$. The initiation is fast as is indicated by the rapid

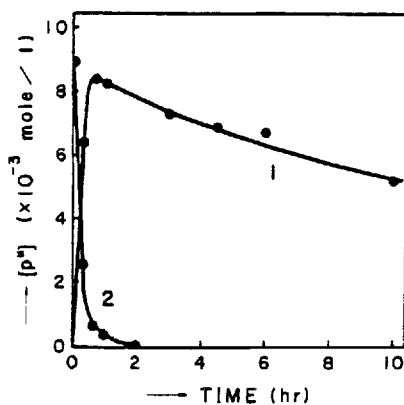


FIG. 15. Solution polymerization of tetrahydrofuran by $\text{Et}_3\text{O}^+\text{OBF}_4^-$ (0°C) Curve 1: $[\text{P}^*]$ vs. time. Curve 2: $[\text{Et}_3\text{O}^+\text{OBF}_4^-]$ vs. time. $[\text{M}]_0$ 6.3 mole/liter and $[\text{Et}_3\text{O}^+\text{OBF}_4^-]_0$ 895×10^{-3} mole/liter.

decrease of the concentration of the oxonium salt. After about 1 hr, $[\text{P}^*]$ attained the maximum value that was about 90% of the initial molar concentration of the catalyst. The catalyst efficiency was found very high. The so-called "high catalyst activity" of this catalyst is ascribed to the high efficiency of the production of $[\text{P}^*]$, but not to the k_p value. After $[\text{P}^*]$ attained the maximum value, a slow decrease of $[\text{P}^*]$ started, which shows the presence of slow termination. Thus, strictly speaking, this polymerization is not a living one. Termination in this polymerization was demonstrated more clearly at 30°C [22].

$\text{Et}_3\text{O}^+\text{AlCl}_4^-$ is not a good catalyst. Even in an early stage of polymerization, $[\text{P}^*]$ is quite low. In the subsequent stage, $[\text{P}^*]$ remained very small, too (Fig. 16, Curve 1). Correspondingly, the consumption rate of monomer was very small, and the product was a liquid of low molecular weight. The end group of the liquid product was examined by using a sample prepared with a large amount of catalyst. The product was shown to be a mixture of chloride-terminated oligomers, $\text{Et}-(\text{O}(\text{CH}_2)_4)_n\text{Cl}$ ($n = 3 \sim 4$).

In Figs. 2, 13, 14, and 15, it is seen that the $[\text{P}^*]$ -time profile of the THF polymerization varies considerably according to the nature of catalysts. The variation of the $[\text{P}^*]$ -time profile is due to the differences of the rates of the P^* production (initiation) and of the P^* disappearance (termination). As will be shown in the following section, the rate constant of propagation changes very little according to the nature of the catalyst.

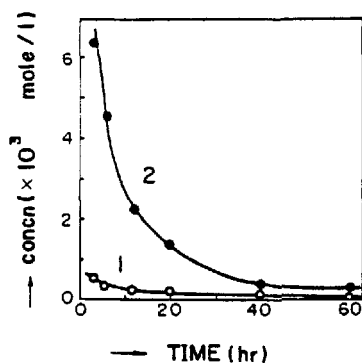


FIG. 16. Solution polymerization of tetrahydrofuran by $\text{Et}_3^+\text{OAlCl}_4^-$ in CH_2Cl_2 (0°C). Curve 1: $[\text{P}^*]$ vs. time. Curve 2: $[\text{Et}_3^+\text{OAlCl}_4^-]$ vs. time. $[\text{M}]_0$ 6.3 mole/liter and $[\text{Et}_3^+\text{OAlCl}_4^-]$ 5.7×10^{-2} mole/liter.

Rate Constant of Propagation of THF Polymerization [5, 21, 23]

The effect of catalyst nature on the rate constant of propagation in the THF polymerization was examined on the basis of the $[\text{P}^*]$ -time curve. The method of kinetic analysis has been shown in the THF polymerization by the BF_3 -ECH system (Figs. 2 and 3). The plot of Eq. (5) was made with the catalyst systems AlEt_3 - H_2O (2:1)-ECH, SnCl_4 -ECH, EtAlCl_2 -ECH, AlEt_3 - H_2O (2:1)-propylene oxide (PO), AlEt_3 - H_2O (2:1)- β -propiolactone (BPL), and $\text{Et}_3\text{O}^+\text{BF}_4^-$ at 0°C . Similarly to the case of the BF_3 -ECH system (Fig. 3), the plot of Eq. (5) gave a straight line passing the origin. Even in the polymerization with the EtAlCl_2 -ECH system, where the $[\text{P}^*]$ changes considerably during the polymerization, the plot of Eq. (5) gave a straight line (Fig. 17). k_p values of various catalysts were successfully obtained from these linear plots. Table 4 lists the summary of the k_p values at 0°C . Table 4 discloses the important fact that the k_p value varies very little according to the nature of catalyst. In the first three catalyst systems of Table 4, the Lewis acid component was changed. As has been described previously, the monomer conversion rate and the molecular weight of product polymer vary greatly according to the nature of the Lewis acid component. But it is shown that k_p values fall in a narrow range. Therefore the variations are ascribed to differences in the rates of initiation and termination.

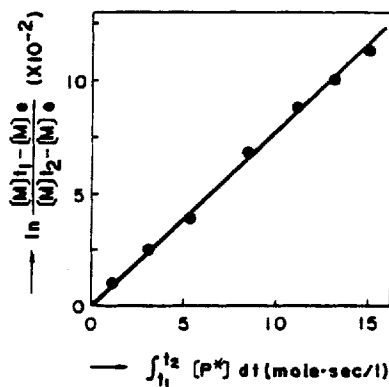


FIG. 17. Polymerization of tetrahydrofuran by EtAlCl_2 -ECH system (The conditions are given in Fig. 14B.)

TABLE 4. Polymerization of Tetrahydrofuran. Rate Constant of Propagation

Catalysts ^a	$k_p \times 10^3$ (liter/mole-sec)	Ref.
BF_3 -ECH	4.4	11
SnCl_4 -ECH	6.3	11
EtAlCl_2 -ECH	7.8	11
AlEt_3 - H_2O (2:1)-ECH	6.6	13
AlEt_3 - H_2O (2:1)-PO	6.0	13
AlEt_3 - H_2O (2:1)-BPL	6.7	13
$\text{Et}_3^+\text{OBF}_4^-$	3.6	12

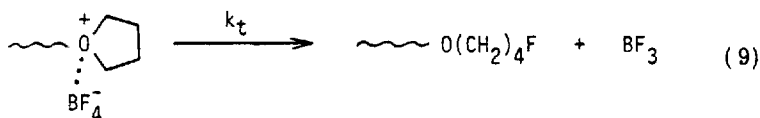
^aPromoters. ECH: epichlorohydrin. PO: propylene oxide. BPL: β -propiolactone.

The second group of catalysts in Table 2 are combinations of the AlEt_3 - H_2O (2:1) system, as the Lewis acid component, with three promoters, ECH, PO, and BPL [23]. In the case of PO as promoter, a part of the remaining PO reacted with sodium phenoxide to generate a small amount of a phenyl ether in the phenoxyl end-capping procedure. In this polymerization, therefore, the remaining PO was removed by vacuum distillation from the system at 10 min after the polymerization

was initiated. By a reference experiment, this modification was shown to be satisfactory to remove the side reaction producing erroneous phenyl ether. In the case of BPL, a reference experiment showed that the erroneous formation of phenyl ether from the remaining BPL was negligible. The three systems of $\text{AlEt}_3\text{-H}_2\text{O}$ (2:1)-promoter gave almost the same k_p values. This result is quite compatible with the concept of promoter [4, 19, 20], i.e., the function of a promoter is to generate the cationic propagating species but not to exert an influence upon the rate constant of propagation. The variation in the conversion rate through the nature of promoter has frequently been observed, and it is ascribed to the difference in $[\text{P}^*]$. In other words, the nature of promoter primarily affects the rate and the efficiency of the production of the oxonium propagating species.

Rate Constants of Initiation and Termination of THF Polymerization

In the THF polymerization catalyzed by triethyloxonium salt, the rate constants of initiation and termination could be roughly estimated [21]. In the case of Et_3OBF_4 catalyst, the rate of termination may be approximated to the rate of the $[\text{P}^*]$ decrease after 2 hr in Fig. 15, where the production of $[\text{P}^*]$ by initiation is almost negligible. The termination reaction has been formulated as being the self-decomposition of the propagating species (Eq. 9) [22].



On the basis of the first-order decomposition mechanism (Eq. 10), the rate constant of termination, k_t , was roughly estimated.

$$-d[\text{P}^*]/dt = k_t [\text{P}^*] \quad (10)$$

The plot of the first order of $[\text{P}^*]$ gave a straight line, and the k_t value was estimated to be about 1×10^{-5} (sec^{-1}) (Table 5).

The rate constant of initiation, k_i , of the $\text{Et}_3\text{O}^+\text{BF}_4^-$ catalyzed polymerization was determined from the $[\text{Et}_3\text{O}^+\text{BF}_4^-]$ -time curve (Curve 2 in Fig. 15) according to

$$-d[\text{Et}_3\text{O}^+\text{BF}_4^-]/dt = k_i[\text{Et}_3\text{O}^+\text{BF}_4^-][M] \quad (11)$$

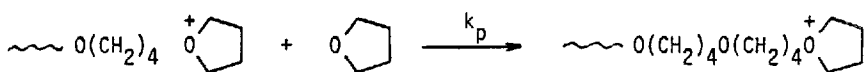
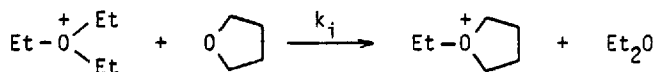
TABLE 5. Rate Constants of Initiation and Termination of Tetrahydrofuran Polymerization Catalyzed by Triethyloxonium Salt at 0°C^a

Catalyst	Concentration (10 ⁻² mole-liter)	k _t × 10 ⁵ (sec ⁻¹)	k _i × 10 ⁴ (liter/mole-sec)
Et ₃ O ⁺ BF ₄ ⁻	0.9	1	2
Et ₃ O ⁺ AlCl ₄ ⁻	5.7	~10 ³	4

^aSolution polymerization in CH₂Cl₂: [M]₀ = 6.3 moles/l, 0°C.

The value of k_i thus obtained (Table 5) was in good agreement with the value given by Tobolsky et al. [24] using ¹⁴C-labeled species of Et₃O⁺BF₄⁻.

Both the initiation and propagation are S_N2 reactions between an oxonium salt (electrophile) and THF (nucleophile). But k_i is smaller



than k_p. This difference may be explained by assuming that the cyclic trialkyloxonium ion, $\sim\overset{+}{\text{O}}\text{THF}$, is more reactive than Et₃O⁺ toward the THF monomer.

In the polymerization by Et₃O⁺AlCl₄⁻, the rate constants of initiation and termination were also determined on the basis of the [P*]-time and the [Et₃O⁺AlCl₄⁻]-time curves in Fig. 16. The rate of the [P*] increase is expressed by

$$d[P^*]/dt = - \frac{d[Et_3O^+AlCl_4^-]}{dt} - k_t [P^*] \quad (12)$$

Equation (12) is transformed into

$$k_t [P^*] = - \frac{d\{ [P^*] + [Et_3O^+AlCl_4^-] \}}{dt} \quad (13)$$

Through the use of Eq. (13), k_t was determined at several reaction times (Table 5). All values of k_t were of the order of 10^{-2} sec^{-1} . It is very important to note that the k_t value of the $Et_3O^+AlCl_4^-$ -catalyzed polymerization is much higher than that of the $Et_3O^+BF_4^-$ -catalyzed polymerization. The k_t value is taken as a measure of stability of the counterion, which is decisive on the duration of propagation. By a rough calculation based on the $[Et_3O^+AlCl_4^-]$ -time curve in Fig. 16, k_1 was determined. It did not differ much from that of $Et_3O^+BF_4^-$ (Table 5).

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