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Kinetic Studies on the Cationic Ring-Opening Polymerization of Tetrahydrofuran Initiated by Superacid Esters[1]

Shiro KOBAYASHI, Hidenori DANDA, and Takeo SAEGUSA
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606

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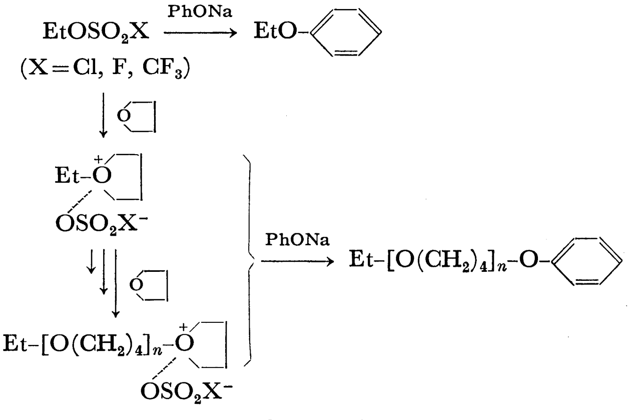
The present paper descibes kinetic studies on the cationic ring-opening polymerization of tetrahydrofuran (THF) initiated by superacid esters such as ethyl fluorosulfate ($EtOSO_2F$), chlorosulfate ($EtOSO_2Cl$), and trifluoromethanesulfonate ($EtOSO_2CF_3$). The phenoxyl end-capping method was found to de applicable to kinetic analyses of the THF polymerization initiated by superacid esters. Also, the rate constants of propagation (k_p) and of initiation (k_i) were determined directly by NMR spectroscopic method. Rate constants determined by these two methods were in good agreement within experimental error. As a polymerization mechanism it was established that the propagation proceeds *via* cyclic oxonium species. The k_p values of superacid esters varied depending upon the nature of the counter anion, OSO_2X^-, *e.g.*, k_p at 0 °C in CH_2Cl_2: 0.66×10^{-3} (X=F), 1.4×10^{-3} (X=Cl), and 1.7×10^{-3} ($X=CF_3$) l/mol·sec, respectively. These magnitudes, however, were at least lower than one half of those of typical Lewis acid initiators. Initiation by superacid ester is a dipole-diple reaction, and k_i values were about 1/10—1/20 of the corresponding value of triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$). Activation parameters were calculated for both the propagation and initiation reactions. In order to compare the present systems with those of superacid initiators, model reactions were examined by NMR spectroscopy.

In the last decade chemistry of superacid systems has widely been developed especially in the field of cationic reactions.[2] Thus, it has become possible to observe directly a variety of cationic species in such superacid media.[2a,b] Superacids are, according to Gillespie[2c] more acidic than 100% sulfuric acid, the most frequently used strong acid solvent. With this respect fluorosulfuric, chlorosulfuric and trifluoromethanesulfonic acids are the well-known among superacids.

It has been reported preliminarily in our recent presentation[3] that ester derivatives of fluorosulfuric and chlorosulfuric acids are very effective initiators for the cationic ring-opening polymerization of tetrahydrofuran (THF), oxetane, β-propiolactone, 2-oxazoline, epichlorohydrin, and propylene oxide. At almost the same time with our presentation,[3] Simith and Hubin[4] have reported semi-quantitative studies of the THF polymerization initiated by superacid derivatives including methyl trifluoromethanesulfonate. In the present paper we wish to report kinetic studies on the ring-opening polymerization of THF initiated with superacid esters. The superacid esters employed were ethyl fluorosulfate ($EtOSO_2F$), chlorosulfate ($EtOSO_2Cl$), and trifluoromethanesulfonate ($EtOSO_2CF_3$). The kinetic analyses were made on the basis of our "phenoxyl end-capping" method[5,6] which enabled the determination of the concentration of the propagating species [P*]. Furthermore, the kinetic analyses were also performed by NMR spectroscopy. Thus, rate constants were determined, for the first time, directly by NMR spectroscopic method.

Results and Discussion

Determination of [*P**]. In the ring-opening polymerization of THF by superacid ester initiators the phenoxyl end-capping procedure is shown in Scheme 1. For the determination of [P*], the modification of the original procedure was made; *i.e.*, phenetole produced directly from the initiator was successfully separated from the polymer phenyl ether by vacuum distillation with the aid of Decalin as the distillation entrainer.[7]



Scheme 1.

In Scheme 1, the reaction of sodium phenoxide with the propagating species and with the unreacted initiator should be quantitative in producing the polymer phenyl ether and phenetole, respectively. It has already been established that the propagating cyclic oxonium could be quantitatively converted into the polymer phenyl ether.[5] In the present study, the reactions of sodium phenoxide with superacid esters were examined. $EtOSO_2F$ and $EtOSO_2Cl$

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[1] "Superacids and Their Derivatives," Part I.

[2] For review see a) G. A. Olah and C. U. Pittman, Jr., *Adv. Phys. Org. Chem.*, **4**, 305 (1966); b) G. A. Olah, *Angew. Chem.*, **85**, 183 (1973); c) R. J. Gillespie, *Accounts Chem. Res.*, **1**, 202 (1968); d) R. J. Gillespie and T. E. Peel, *Adv. Phys. Org. Chem.*, **9**, 1 (1971).

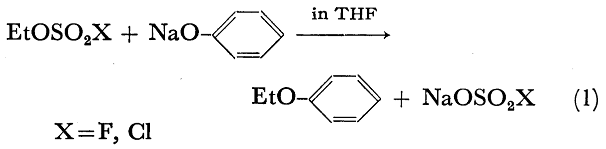
[3] T. Saegusa and S. Kobayashi, presented at the 21st Annual Meeting of the Society of Polymer Science, Japan, May, 1972.

[4] S. Smith and A. J. Hubin, "Polymer Preprints," Vol. 13, p. 66 (1972).

[5] T. Saegusa and S. Matsumoto, *J. Polym. Sci., Part A-1*, **6**, 1559 (1968).

[6] T. Saegusa and S. Matsumoto, *Macromolecules*, **1**, 442 (1968).

[7] T. Saegusa and S. Matsumoto, *J. Macromol. Sci. Chem.*, **A4**, 873 (1970).

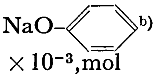


(1)

X=F, Cl

were allowed to react with sodium phenoxide in THF at room temperature, and the reaction mixture was treated in a similar manner as that for the polymerization system. The amount of phenetole produced was determined by UV spectroscopy. Reaction (1) has been regarded as quantitative (in Table 1). Thus, the phenoxyl end-capping method has been shown valid for the kinetic analysis of the THF polymerization initiated by superacid esters as in the case of the $Et_3O^+BF_4^-$ initiator system.[7]

Table 1. Reactions of $EtOSO_2F$ and $EtOSO_2Cl$ with sodium phenoxide at room temperature

$EtOSO_2X$[a] × 10^{-3}, mol	X	NaO- [b] × 10^{-3},mol	Reaction time (min)	Yield[c] (%)
0.99	F	4.0	10	96
0.59	F	2.9	30	95
1.15	Cl	3.5	5	93

a) Solution in 3 ml of THF.
b) Solution in 6 ml of THF.
c) Based on $EtOSO_2X$. Determined by UV analysis.

Polymerization by Superacid Esters. Figure 1 shows the [P*]-time (Curve A) and conversion-time (Curve B) relationships in the THF polymerization initiated by $EtOSO_2F$. Throughout the polymerization, [P*] continued to increase. After 20 hr, [P*] reached to 63% of the initial concentration of the initiator. The induction period was observed in the conversion-time relationship and then, monomer was consumed monotonously. These observations indicate a slow initiation followed by a fast propagation.

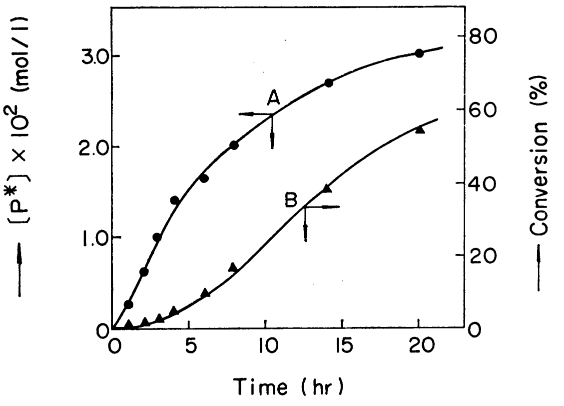
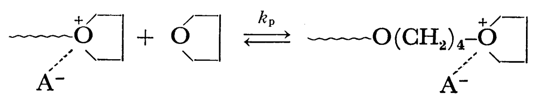


Fig. 1. Polymerization of THF by $EtOSO_2F$ at 0 °C. [P*]-time (Curve A) and monomer conversion-time (Curve B) relationships: $[I]=4.8\times10^{-2}$ mol/l, $[M]_0=9.80$ mol/l in CH_2Cl_2 solution.

It has been already established that in the cationic polymerization of THF the propagation reaction can be expressed by



(2)

On the basis of S_N2 mechanism the rate equation of propagation is given by

$$-\frac{d[M]}{dt}=k_p[P^*]\{[M]-[M]_e\} \tag{3}$$

where $[M]$ and $[M]_e$ represent the instantaneous and equilibrium monomer concentrations, respectively, and k_p is the rate constant of propagation. Integration of Eq. (3) with respect to time gives

$$\ln\frac{[M]_{t_1}-[M]_e}{[M]_{t_2}-[M]_e}=k_p\int_{t_1}^{t_2}[P^*]dt \tag{4}$$

where $[M]_{t_1}$ and $[M]_{t_2}$ represent the monomer concentrations at time t_1 and t_2, respectively.

Based on the data in Fig. 1, the plot of Eq. (4) was made (Fig. 2). The slope of the straight line gave a k_p value of 0.66×10^{-3} l/mol·sec at 0 °C.

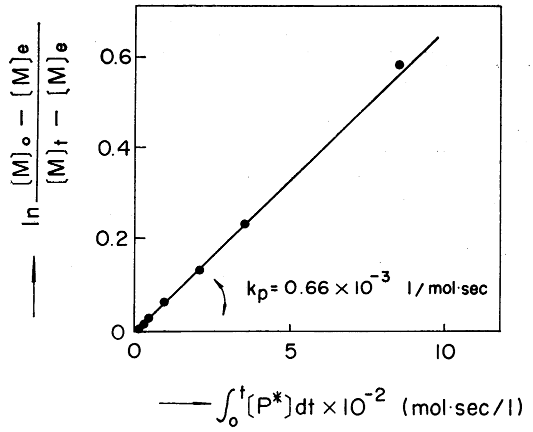
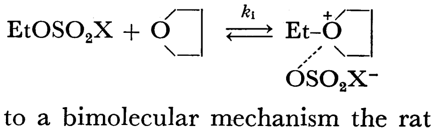


Fig. 2. Polymerization of THF by $EtOSO_2F$ at 0 °C: $[I]_0=4.8\times10^{-2}$ mol/l, $[M]_0=9.80$ mol/l in CH_2Cl_2 solution. $[M]_e=1.7$ mol/l.[8]

The initiation reaction can be formulated as



(5)

According to a bimolecular mechanism the rate equation of initiation is given by

$$-\frac{d[I]}{dt}=k_i[I][M] \tag{6}$$

Integration of Eq. (6) gave

$$\ln\frac{[I]_{t_1}}{[I]_{t_2}}=k_i\int_{t_2}^{t_1}[M]dt \tag{7}$$

where k_i is the rate constant of initiation and $[I]_{t_1}$ and $[I]_{t_2}$ are the instantaneous concentrations of the unreacted initiator at time t_1 and t_2, respectively.

Figure 3 shows the plot of Eq. (7) on the reasonable assumption that the amount of the reacted initiator corresponds to [P*] of Curve A in Fig. 1. The slope of the straight line of Fig. 3 gave the initiation rate constant, 0.33×10^{-5} l/mol·sec at 0 °C.

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[8] E. A. Ofstead, "Polymer Preprints," Vol. 6, p. 674 (1965).

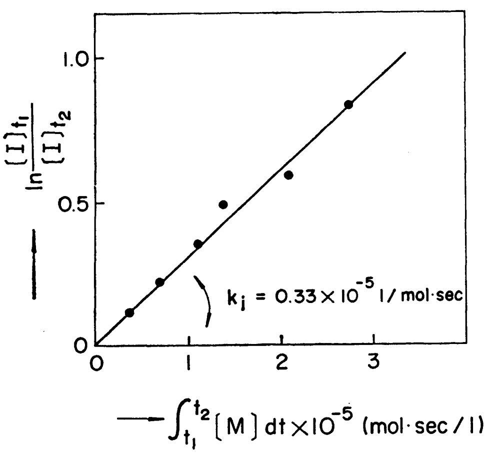


Fig. 3. Plots of Eq. (7) in the THF polymerization by EtOSO$_2$F in CH$_2$Cl$_2$ at 0 °C. $t_1=1.0$ hr.

In a similar manner k_p and k_i values were determined at other temperatures. Furthermore, kinetic analyses were carried out on the THF polymerizations initiated by EtOSO$_2$Cl and EtOSO$_2$CF$_3$. These results are summarized in Table 2.

TABLE 2. RATE CONSTANTS OF PROPAGATION (k_p) AND INITIATION (k_i) OF THE THF POLYMERIZATION[a)]

Initiator	Temp (°C)	$10^3\cdot k_p$ (l/mol·sec)	$10^5\cdot k_i$ (l/mol·sec)
EtOSO$_2$F	8.4	1.4	0.67
	0	0.66	0.33
	−8.0	0.32	0.13
EtOSO$_2$Cl	6.5	2.2	0.50
	0	1.4	0.38
	−4.5	0.89	0.19
	−11.9	0.45	0.09
EtOSO$_2$CF$_3$	9.5	3.0	1.6
	0	1.7	0.80
	−7.8	0.76	0.45

a) Solution polymerization in CH$_2$Cl$_2$. $[M]_0=9.80$ mol/l, $[I]_0=0.048$ mol/l.

In all cases Arrhenius plots were linear, and the activation parameters were calculated (Table 3). For the purpose of comparison the k_p and k_i values at 0 °C are listed again, and the data with triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$) initiator are also given in Table 3. The k_p value of EtOSO$_2$F initiator is extremely small, *e.g.*, about 1/6 of that of $Et_3O^+BF_4^-$ initiator. The k_p values of EtOSO$_2$Cl and EtOSO$_2$CF$_3$ initiators are between those of EtOSO$_2$F and $Et_3O^+BF_4^-$. In the THF polymerization initiated by various Lewis acids such as BF$_3$, SnCl$_4$, EtAlCl$_2$, and Et$_3$Al–H$_2$O systems, the k_p values were determined by us using the phenoxyl end-capping methods.[11)] The k_p values are in a narrow range between 3.7 and 9.9×10^{-3} l/mol·sec at 0 °C in CH$_2$Cl$_2$. Therefore, the k_p values by superacid esters of the present study are 1/15—1/2.2 for those of Lewis acid initiators. Since the activation parameters ($\Delta H_p^{\ddagger}$ and $\Delta S_p^{\ddagger}$) of EtOSO$_2$X are very close to those of $Et_3O^+BF_4^-$, it is evident that the propagation of the polymerizations by superacid esters proceeds *via* an oxonium mechanism as shown in Eq. (2). Significant difference in k_p values between superacid esters and Lewis acids initiators may reasonably be attributed to the difference in the nature of the counter anions, A^- of Eq. (2). A recent report has revealed that the THF polymerization by $Et_3O^+BF_4^-$ proceeds *via* two species, *e.g.*, the free-ion and the ion-pair.[12)] It may be likely that the effect of the counter anion on k_p is attributed partly to the different contribution of above two species toward k_p. Elucidation of this point must await further studies.

The initiation is a dipole-dipole reaction producing an oxonium ion (Eq. (5)). With this respect the initiation is similar to Menschutkin reaction in which an ammonium ion is formed from amine and alkyl halide (Eq. (8)). The initiation rate constant, k_i is at

$$R_3N + R'Y \longrightarrow R_3R'\overset{+}{N}Y^- \qquad (8)$$

least 2×10^2 times smaller than k_p in superacid ester systems. The k_i values of superacid esters are 1/20—1/10 of k_i of $Et_3O^+BF_4^-$. The activation parameters of the initiation exhibited relatively low $\Delta H_i^{\ddagger}$ and

TABLE 3. ACTIVATION PARAMETERS OF PROPAGATION AND INITIATION IN THE THF POLYMERIZATION BY SUPERACID ESTERS AND OXONIUM SALT IN CH$_2$Cl$_2$

Initiator	EtOSO$_2$F[a)]	EtOSO$_2$Cl[a)]	EtOSO$_2$CF$_3$[a)]	$Et_3O^+BF_4^-$ [b)]
Propagation				
$10^3\cdot k_p$ at 0 °C (l/mol·sec)	0.66	1.4	1.7	3.7
$\Delta H_p^{\ddagger}$ (kcal/mol)	13.0	11.8	11.6	12
$\Delta S_p^{\ddagger}$ (e.u.)	−26	−28	−29	−26
Initiation				
$10^5\cdot k_i$ at 0 °C (l/mol·sec)	0.33	0.38	0.80	6.1[c)]
$\Delta H_i^{\ddagger}$ (kcal/mol)	13.5	12.8	10.5	16.4
$\Delta S_i^{\ddagger}$ (e.u.)	−34	−37	−44	−16

a) Present work.
b) Taken from Refs. 7, 9, and 10.
c) Data at 2.5 °C; see Ref. 10.

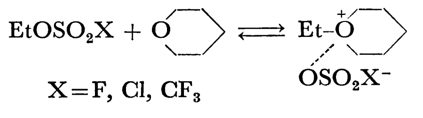
[9)] T. Saegusa, S. Matsumoto, M. Motoi, and H. Fujii, *Macromolecules*, **5**, 236 (1972).

[10)] T. Saegusa, Y. Kimura, H. Fujii, and S. Kobayashi, *ibid.*, in press.

[11)] a) T. Saegusa, *J. Macromol. Sci. Chem.*, **A6**, 997 (1972); b) T. Saegusa and S. Kobayashi, "Progress in Polymer Science, Japan," Vol. 6, Kodansha Scientific, Tokyo, 1973.

[12)] J. M. Sangster and D. J. Worsfold, *Macromolecules*, **5**, 229 (1972).

also, low (unfavorable) $\Delta S_i^{\neq}$ values. This is in accordance with a dipole-dipole S_N2 mechanism (Eq. (5)) as seen in Menschutkin reaction.[13] Similar results have been obtained also in the molar reactions between superacid esters and tetrahydropyran (Eq. (9)).[14]



(9)

NMR Studies. It has already been presented that the kinetics of the THF polymerization by superacid esters could be studied by means of NMR spectroscopy as well as the phenoxyl end-capping method.[15] In order to compare the kinetic data obtained by two different methods, the THF polymerization by superacid esters was examined also by NMR spectroscopy. A mixture of THF–$EtOSO_2CF_3$ (5: 1 molar ratio) in CH_2Cl_2 solution was introduced into an NMR sample tube at −78 °C. The tube was sealed and then the course of the reaction was followed by the change of NMR spectrum of the system. Figure 4 shows an example NMR spectrum of the reaction system which was taken after 20 min at 0 °C. Signals C and D are due to α-methylene protons of THF monomer and of linear polymer, respectively. Peak F is due to β-methylene protons of THF monomer, while signal G due to β-methylene protons of polymer is overlapping with peaks F and H. A sharp quartet (B) and triplet (H) are due to methylene and methyl protons, respectively, of the initiator. Signals A (δ 4.72) and E (δ 2.32) are reasonably assigned to α- (six protons) and β- (four protons) methylene protons of cyclic oxonium of the propagating species. This assignment coinsides with that of our previous work[10] in which the formation of cyclic oxonium ions was clearly shown by NMR in the reaction of $Et_3O^+BF_4^-$ with cyclic ethers. Finally, a triplet (peak I) can be assigned to methyl protons of ethoxy group at polymer end. A quartet due to methylene protons of the ethoxy group is overlapping with peak D. Table 4 summarizes the chemical shift assignments.

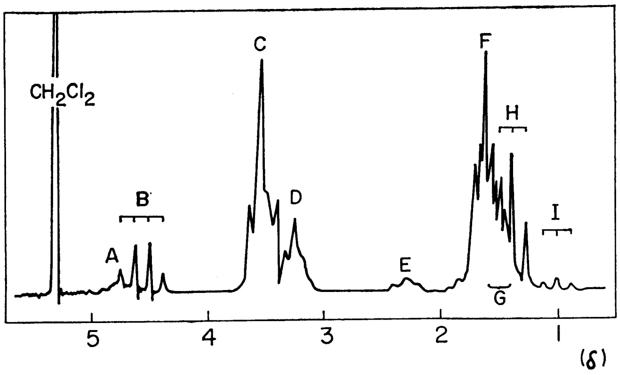
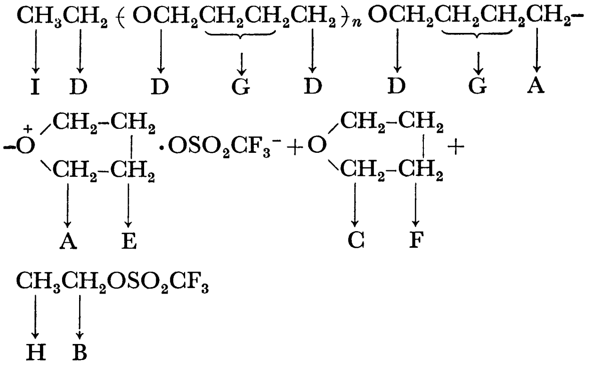


Fig. 4. NMR spectrum of the THF polymerization mixture by $EtOSO_2CF_3$ in CH_2Cl_2 after 20 min at 0 °C.

TABLE 4. SIGNAL ASSIGNMENTS IN THE POLYMERIZATION MIXTURE OF THF BY $EtOSO_2CF_3$



Signal	Chemical shift in ppm (fromMe_4Si)[a]
A	4.72(m)
B	4.55(q)
C	3.52(m)
D	3.28(m)
E	2.32(t)
F	1.67(m)
G	1.50(m)
H	1.40(t)
I	1.02(t)

a) Multiplicity: m=multiplet, q=quartet, and t=triplet.

The concentrations of monomer, the initiator consumed and P* were determined by integration of signals C, I, and E, respectively. Thus, the kinetic analysis could be made in a similar way to that of the phenoxyl end-capping method. Figure 5 shows the variations of [P*]-time (Curve A) and of monomer conversion-time (Curve B), respectively. The molar concentration of cyclic oxonium species (obtained from the signal E) was equal to that of ethoxy group at the polymer end (obtained from the signal I) throughout the polymerization, *i.e.*, the system was of living character without termination. Therefore, the concentration of P* could be determined by either the

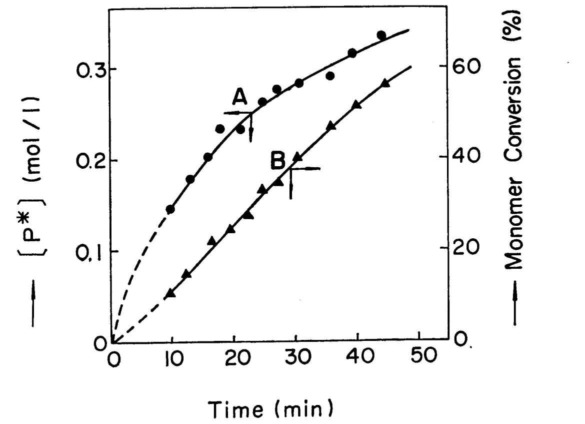


Fig. 5. Polymerization of THF with $EtOSO_2CF_3$ monitored by NMR spectroscopy. Solution polymerization at 0 °C. [P*]-time (Curve A) and monomer conversion-time (Curve B) relationships: $[I]_0$=1.27 mol/l, $[M]_0$=7.70 mol/l.

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[13] K. Wiberg, "Physical Organic Chemistry," John-Wiley & Sons, Inc., New York (1966), p. 379.

[14] S. Kobayashi, T. Ashida, and T. Saegusa, presented at the 22nd Annual Meeting of the Society of Polymer Science, Japan, May, 1973.

[15] T. Saegusa, S. Kobayashi, and H. Danda, presented at the 21st Symposium of the Society of Polymer Science, Japan, November 1972.

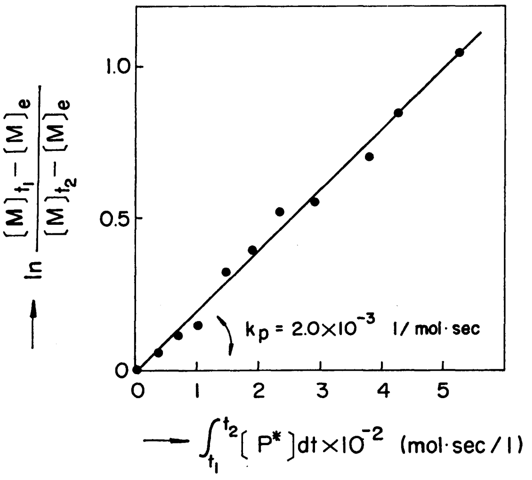


Fig. 6. Polymerization of THF by $EtOSO_2CF_3$ in CH_2Cl_2 at 0 °C: $[I]_0=1.27$ mol/l, $[M]_0=7.70$ mol/l, $[M]_e=1.7$ mol/l[8], $t_1=10$ min.

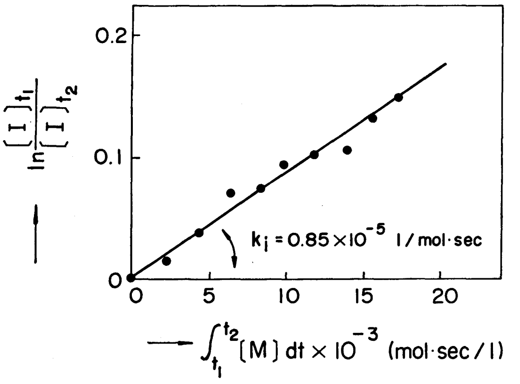


Fig. 7. Plots of Eq. (7) in the THF polymerization by $EtOSO_2CF_3$ in CH_2Cl_2 at 0 °C. $t_1=13$ min

signal E or I.

Based on the data in Fig. 5 the plots of Eq. (4) gave a straight line. From the slope a k_p value was obtained as 2.0×10^{-3} l/mol·sec at 0 °C (Fig. 6). On the basis of the relationship that the concentration of the propagating species is equal to that of the initiator consumed, the [P*]-time relationship in Fig. 5 was plotted according to Eq. (7) as shown in Fig. 7. Then, a k_i value was obtained as 0.85×10^{-5} l/mol·sec at 0 °C from the slope of the straight line.

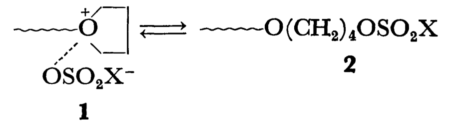
In an analogous manner k_p and k_i values were determined by NMR spectroscopy for the systems of $EtOSO_2F$ and $EtOSO_2Cl$ initiators (in Table 5). It can be seen that the rate constant values by NMR spectroscopy and by phenoxyl end-capping method (Tables 5 and 2) are in good agreement within experimental error.

TABLE 5. RATE CONSTANTS OF PROPAGATION (k_p) AND INITIATION (k_i) OF THE THF POLYMERIZATION DETERMINED BY NMR SPECTROSCOPY IN CH_2Cl_2 SOLUTION AT 0 °C[a)]

Initiator	$10^3\cdot k_p$ (l/mol·sec)	$10_5\cdot k_i$ (l/mol·sec)
$EtOSO_2F$	0.8	0.5
$EtOSO_2Cl$	1.5	0.6
$EtOSO_2CF_3$	2.0	0.85

a) $[M]_0=7.70$mol/l, $[I]_0=1.27$ mol/l.

In all systems of three initiators, the polymerization proceeded *via* oxonium propagating species in accordance with the mechanism of Scheme 1. An equilibrium of oxonium-ester species (Eq. (10)) may come into play during the polymerization.

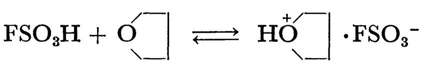


1 **2** (10)

If the ester type species **2** were involved in the system, a peak should have appeared which is a characteristic signal of the α-methylene protons of an ester type $\sim\!\sim CH_2OSO_2X$. However, any peak was not detected in the region of τ 4.25 throughout the THF polymerization initiated by a series of superacid esters under NMR measurement conditions. This indicates that the contribution of **2** to the propagation is, if any, very small during the THF polymerization where monomer is present in large excess, although the molar reaction of superacid ester and tetrahydropyran (Eq. (9)) has been proved to be an equilibrium system.[14)]

Very recently, Pruckmayr and Wu have reported NMR studies on the THF polymerization initiated by superacids such as FSO_3H.[16)] However, they did not determine the rate constants of such polymerization systems, in which "acidic" proton was present in a significant amount. Consequently, such proton made the polymerization systems complicated, bringing about termination, chain-transfer, the breaking of the polyether chain, the proton-proton exchange and so forth. Unlike these systems, the present reaction of superacid ester initiator is quite clean, since no "acidic" proton is involved. Therefore, NMR spectra were simple in all cases as shown in Fig. 4. So far as we know the present study is the first case that the initiation and propagation rate constants in the THF ploymerization were determined directly by means of high resolution NMR spectroscopy.

As to NMR spectral assignments Pruckmayr and Wu[16)] ascribed a peak at δ 4.25 to α-methylene protons of cyclic trialkyloxonium in benzene. For a peak at δ 4.65 they assigned it to α-methylene protons of cyclic dialkyloxonium ion. Their assignment of cyclic trialkyloxonium ion, however, is not compatible with that of the present work. It is unlikely that cyclic dialkyloxonium ion (the protonated THF, **3**) was observed as a long-lived species at their NMR measurement conditions, since proton exchange reaction (Eq. (11)) is very fast. We attempted to observe **3** directly by NMR spectroscopy.



3 (11)

However, the direct observation of **3** as a long-lived species was unsuccessful in FSO_3H–benzene at 0 °C or in FSO_3H–CH_2Cl_2 solution even at lower temperature of −50 °C. Rapid proton exchange still took place at

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16) G. Pruckmayr and T. K. Wu, *Macromolecules*, **6**, 33 (1973).

−50 °C. This rapid proton exchange is suggested from their observations[16] that the signal of α-methylene protons of monomer THF was shifted downfield to δ 3.75 in the presence of "acidic" protons[16] from δ 3.52 of free THF in the absence of such protons (Table 4) whereas the peak of α-methylene protons of polymer chain were less affected.

On the basis of above findings we think that a peak at δ 4.65 is due to α-methylene protons of cyclic trialkyloxonium ion (propagating species) and that a peak at δ 4.25 must be due to another species. For such species we propose here a polymer alkyl ester species of superacid as given by **2**. To support this,

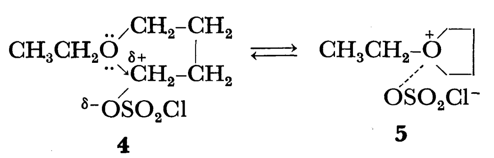
$$\sim\!\sim\!\sim CH_2OSO_2X$$

$$\mathbf{2}\ (X{=}F)$$

a model compound (**4**) was prepared from 4-ethoxy-1-butanol and sulfuryl chloride according to Eq. (12). **4** is recognized as a 1 : 1 adduct of $EtOSO_2Cl$ and THF. The reaction of alcohol and sulfuryl chloride is probably the best one to prepare alkyl chlorosulfate.[17) Figure 8 shows NMR spectra of the reaction mixture of Eq. (12). At 30 min after the addition of sulfuryl chloride to the above ether alcohol a peak (A) due to α-methylene protons of OSO_2Cl group appeared at δ 4.25 (spectrum I in Fig. 8). After the reaction mixture was concentrated under reduced pressure with bubbling of dry nitrogen at 0 °C a spectrum of II (Fig. 8) was obtained. Additionally two peaks appeared at δ 4.70 (B) and δ 2.35 (C). They are assigned to α-(B) and β-(C) methylene protons of cyclic trialkyloxonium ion (**5**). This indicate that 30% of **4** (from integration) underwent an intramolecular cyclization to produce **5**. It should be added here that the chemical shifts are not changed by the nature of X (X= F, Cl, or CF_3) of OSO_2X in **4** or **5**.[18]

$$CH_3CH_2O(CH_2)_4OH + SO_2Cl_2 \xrightarrow{\text{in } CH_2Cl_2} CH_3CH_2O(CH_2)_4OSO_2Cl + HCl \qquad (12)$$

$$\mathbf{4}$$



(13)

4 **5**

All of these findings are taken to substantiate our assignments, *i.e.*, peaks at δ 4.65 and δ 4.25 are respectively due to α-methylene protons of cyclic trialkyloxonium ion (propagating species, **1**) and to α-methylene protons of superacid ester (**2**, X=F) of polymer chain. By the same reason, β-methylene protons of **1** corresponds to a peak at δ 2.40, which was assigned to β-methylene protons of **3**.[16] As to our assignment, the production of **2** is explained reasonably. For example, the initiator reacts with hydroxyl group at the polymer end to produce a polymer alkyl ester of fluorosulfuric acid as shown by Eq. (14). This kind of reaction, *i.e.*, a reaction of alcohol and superacid, provides a good synthetic method of superacid ester.[19] Another possibility of the production of **2** is a reaction of the propagating species given by Eq. (10), in which the counter anion, OSO_2X^-, attacks nucleophilically the α-carbon atom of cyclic oxonium ion **1**. This type of reaction (Eq. (10)) may be facilitated in the presence of "acidic" protons. Thus, propagating cyclic trialkyloxonium ion **1** will eventually convert into species **2** according to Eq. (10). This agrees with the observation that peaks at δ 4.65 and 2.40 disappeared and instead a peak at δ 4.25 appeared at a long reaction time.[16]

$$FSO_3H + \sim\!\sim\!\sim CH_2OH \longrightarrow \sim\!\sim\!\sim \underset{\mathbf{2}}{CH_2OSO_2F} + H_2O \qquad (14)$$

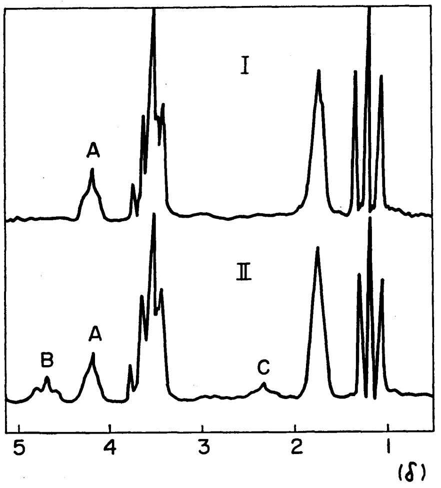


Fig. 8. NMR spectra of the reaction mixture of 4-ethoxy-1-butanol and sulfuryl chloride in CH_2Cl_2: (I) At 30 min after the addition of sulfuryl chloride at 0 °C; (II) After concentration at reduced pressure with bubbling of dry nitrogen at 0 °C.

Experimental

Materials. THF and solvents were purified as previously reported.[5,6] The THF solution of sodium phenoxide was prepared in a similar manner as reported.[5] Fluorosulfuric acid was prepared from hydrogen fluoride and fuming sulfuric acid, bp 69 °C/50 mmHg (lit,[20] 163 °C). $EtOSO_2F$ and $EtOSO_2CF_3$ were prepared by the reaction of diethyl sulfate with FSO_3H and with CF_3SO_3H, bp the former 88 °C/390 mmHg (lit,[19] 113 °C/752 mmHg) and the latter 55—58 °C/100 mmHg (lit,[20] 115 °C). $EtOSO_2Cl$ was prepared by the usual procedure[17] from sulfuryl chloride and ethanol, bp 58 °C/25 mmHg (lit,[17] 43 °C/10 mmHg). 4-Ethoxy-1-butanol was prepared from 1,4-butanediol, ethyl iodide and sodium, bp 70—72 °C/9 mmHg (lit,[21] 72 °C (8 mmHg)).

Polymerization Procedure. Polymerization was carried out under nitrogen. At a polymerization temperature 1.0 ml CH_2Cl_2 solution of the initiator (0.24 mmol) was added to 50 mmol of THF monomer, which resulted in the initial

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[17] E. Buncel and J. P. Millington, *Can. J. Chem.*, **43**, 556 (1964).

[18] S. Kobayashi and T. Saegusa, unpublished results.

[19] J. Meyer and G. Schramm, *Z. Anorg. Allg. Chem.*, **206**, 24 (1932).

[20] T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 173 (1956).

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monomer and catalyst concentrations of 9.80 mol/l and 0.048 mol/l, respectively. After a desired reaction time 1.5 ml THF solution of sodium phenoxide (0.5 mol/l) was added to stop the polymerization. The reaction mixture was stirred further for 30 min at room temperature. Then, it was treated with a large excess of 1M aqueous sodium hydroxide solution. The reaction mixture was extracted three times with 5 ml of CH_2Cl_2. The extracts were combined and dried over K_2CO_3 and centrifuged. The CH_2Cl_2 solution was diluted to 25 ml and the total amount of phenyl ether was determined by UV spectroscopy. A 1.0 ml portion of this CH_2Cl_2 solution was mixed with 4 ml of Decalin and the mixture was subjected to distillation at room temperature under reduced pressure (below 0.3 mmHg). The residue was dissolved in CH_2Cl_2 to the total volume of 20 ml. Then, the amount of phenyl ether at the polymer end was determined by UV analysis. Conversion percent was determined from the amount of the product polymer.

UV Measurements. All UV spectra were taken on Shimadzu UV-200 spectrometer in CH_2Cl_2 solution at room temperature.

NMR Measurements. Into 14.6 mmol of THF 2.4 mmol of $EtOSO_2CF_3$ in 0.40 ml CH_2Cl_2 was added slowly at -78 °C. After mixing a portion of the reaction mixture was transfered into an NMR sample tube, and then the tube was sealed at the same temperature. The extent of the reaction was negligible at -78 °C. The tube was then placed in the NMR probe insert which was kept constant at 0 °C. The time of the insertion was assumed to be the start of the reaction. Then, the reaction was followed. The instrument used was a Hitachi R-20B NMR spectrometer. The reaction temperature was kept constant within ± 1 °C and the experimental error of the integration was within $\pm 2\%$.

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