creases gradually in the range of 0.80–0.50. These results agree well with the values of H_r and H_p calculated from specific rotations.

These structural analyses of DL copolymers combined with our kinetic analyses may be suggested that *dl*-Ni catalyst has a stereoselectivity for DL-NCA higher than other catalysts. This highly stereoselective capacity of *dl*-Ni catalyst suggests the asymmetric carbon atom in the acyloxy moiety of this catalyst contributes mainly to this property, because that of $Ni(OAc)_2 \cdot 4H_2O$-*n*-Bu_3P and of benzylamine is similar to each other and differs from that of nickel *dl*-2-methylbutyrate catalyst.

III. An Example of Highly Stereoregular Polymer Obtained from DL-NCA. DL-BG-NCA was polymerized in 5 wt % dioxane solution at 30° for 72 hr with the *dl*-Ni catalyst (molar ratio, NCA:Ni:P = 4:1:11.8) after aging at 30° for 25 min. The polymer obtained in 79.5% yield had a molecular weight of 5.98×10^4 and was composed of the regular and perturbed helixes in a ratio of 90:10. This value of chain conformation is independently supported quantitatively by the surface pressure *vs.* surface area relationship obtained by the monolayer methods using our samples.[24] Highly stereoregular polyalanine was also obtained from DL-Ala-NCA with the *dl*-Ni catalyst in 5 wt % anisole solution.

The stereoselective polymerization of DL-BG- and of DL-Ala-NCA with *dl*-Ni catalyst was extended to the stereoelective (or asymmetric) polymerization of DL-BG- and of DL-Ala-NCA with *d*-Ni catalyst. This extension gave optically active polymers fully supporting our evidence, and will appear in a subsequent paper.

References and Notes

(1) (a) Faculty of Pharmaceutical Science, Tokushima University, Shomachi, Tokushima 770, Japan; (b) Technical Institute, Asahi Chemical Co., Nobeoka, Miyazaki, Japan; (c) Technical Development Institute, Asahi Chemical Co., Fuji, Shizuoka, Japan.
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Superacids and Their Derivatives. IV.[1] Kinetic Studies on the Ring-Opening Polymerization of Tetrahydrofuran Initiated with Ethyl Trifluoromethanesulfonate by Means of ^{19}F and ^{1}H Nuclear Magnetic Resonance Spectroscopy. Evidence for the Oxonium–Ester Equilibrium of the Propagating Species

Shiro Kobayashi, Hidenori Danda, and Takeo Saegusa*

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan.

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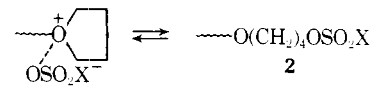
ABSTRACT: Kinetic studies on the ring-opening polymerization of tetrahydrofuran (THF) initiated with ethyl trifluoromethanesulfonate ($EtOSO_2CF_3$) were performed by means of ^{19}F and ^{1}H nmr spectroscopy. The equilibrium between the oxonium (**3**) and ester (**4**) species of propagation was directly observed by ^{19}F nmr spectroscopy. Solvent effect on the polymerization was examined in five solvents of CCl_4, $CHCl_3$, CH_2Cl_2, benzene, and nitrobenzene. The fraction of the oxonium ion concentration, $[O^+]$, was increased in polar solvents, and *vice versa*. Rate constants of initiation (k_i) and propagation due to **3** ($k_{p(i)}$) and apparent rate constants of propagation ($k_{p(ap)}$) were determined on the basis of the direct determination of the instantaneous concentrations of **3**, **4**, and monomer by ^{19}F and ^{1}H nmr spectroscopy. Rate constants of propagation due to the ester **4** ($k_{p(e)}$) were estimated to be very small compared with $k_{p(i)}$. The activation parameters of the elementary reactions were determined in CCl_4 solvent.

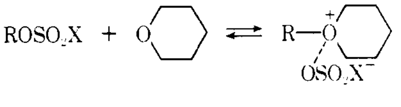
Very recently we have reported kinetic studies on the cationic ring-opening polymerization of tetrahydrofuran (THF) initiated by superacid esters[2] and anhydrides.[3] In these studies, the oxonium–ester equilibrium of propagating species (eq 1) has been discussed.[2]



(1)

1 ($X = CF_3, F, Cl$)

In addition, such equilibrium has already been established in the reactions of superacid esters with tetrahydropyran (eq 2).[1,4]



(2)

In the previous study by proton nmr (^{1}H nmr) spectroscopy,[2] however, it was very difficult to verify directly the

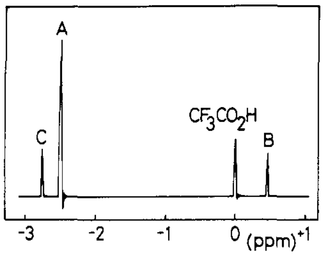


Figure 1. ^{19}F nmr spectrum of the THF polymerization mixture by $EtOSO_2CF_3$ initiator in CCl_4 after 48 min at 13°.

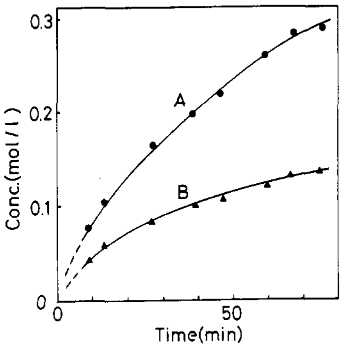
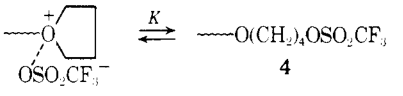


Figure 2. Polymerization of THF with $EtOSO_2CF_3$ monitored by ^{19}F nmr spectroscopy in CCl_4 at 13°. Relationships of ($[O^+]$ + [E])-time (curve A) and of $[O^+]$-time (curve B): $[M]_0 = 5.30$ mol/l., $[I]_0 = 1.05$ mol/l.

equilibrium of eq 1 probably due to the limitation of the sensitility and resolution of ^1H nmr spectroscopy. Therefore, the elucidation of the equilibrium has been an important unsolved problem in several studies[2-6] upon the THF polymerization catalyzed by superacids and their derivatives. In the present study, we used fluorine-19 nmr (^{19}F nmr) spectroscopy and succeeded in direct observation of both the cyclic oxonium ion (**3**) and ester (**4**) species during the kinetic run of the THF polymerization initiated by ethyl trifluoromethanesulfonate ($EtOSO_2CF_3$). Then, kinetic studies of the THF polymerization were carried out in five solvents by means of ^{19}F as well as ^1H nmr spectroscopy. Thus, clear-cut evidence for the equilibrium of eq 3 was given. The equilibrium constant (K = **4**/**3**) was very dependent upon the solvent employed.


$$\xrightleftharpoons{K} \sim O(CH_2)_4OSO_2CF_3 \quad (3)$$

3 **4**

Results and Discussion

^{19}F nmr Spectroscopy. Figure 1 illustrates the ^{19}F nmr spectrum of the THF polymerization system initiated by $EtOSO_2CF_3$, which was taken after 48 min at 13°. The molar ratio of monomer to initiator was 5:1. The ^{19}F chemical shifts are given in parts per million from the external standard of CF_3CO_2H capillary. Peak A at −2.52 ppm is due to $EtOSO_2CF_3$. Peak B at +0.46 ppm is assigned to the oxonium counter anion of **3** ($OSO_2CF_3^-$) of the propagating species. Finally, peak C at −2.80 ppm is reasonably ascribed to the ester type species of **4** ($\sim CH_2OSO_2CF_3$). Peak C appears at lower field than peak A, since the polymer alkyl group of **4** is more electron withdrawing than ethyl group of $EtOSO_2CF_3$ due to the inductive effect of 4-alkoxy group in the polymer alkyl. No other peaks were detected in the ^{19}F nmr spectrum. Thus, the ^{19}F nmr spectroscopy provides a new method for the direct determination of the instantaneous concentrations of initiator and the oxonium and ester species of propagation.

Table I
The ^{19}F Chemical Shift Data[a] in the THF Polymerization in Five Solvents at 0°

Solvent	Initiator ($EtOSO_2CF_3$)	Oxonium ($OSO_2CF_3^-$)	Ester ($\sim CH_2OSO_2CF_3$)
CCl_4	−2.52	+0.46	−2.80
C_6H_6	−1.99	+0.67	−2.24
$CHCl_3$	−2.62	+0.43	−2.91
CH_2Cl_2	−2.48	+0.71	−2.73
$C_6H_5NO_2$	−2.20	+0.32	−2.41

[a] In parts per million from the external standard of CF_3CO_2H capillary.

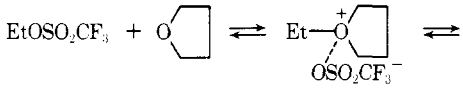
Similarly, the kinetics were carried out in four other solvents. Signals due to initiator, **3**, and **4** appeared separately in all cases. The ^{19}F chemical shifts varied according to the solvent used (Table I).

Oxonium–Ester Equilibrium. Figure 2 shows the variations of ($[O^+]$ + [E]) (curve A) and of $[O^+]$ with time (curve B) during the THF polymerization in CCl_4 at 13°, where $[O^+]$ and [E] denote the concentrations of the oxonium ion (**3**) and the ester (**4**) species, respectively. At the end of the kinetic run (after 76 min) 28% of the initial feed of initiator has been reacted. The molar ratio of $[O^+]$ to [E] reached to a constant value of 46:54 after about 30 min. This indicates that the equilibrium of eq 3 is actually present in the THF polymerization initiated by $EtOSO_2CF_3$.

Such an equilibrium was observed also in CH_2Cl_2 solvent. In this case, however, the ratio of $[O^+]$ to [E] became a constant value of 89:11 after about 30 min at 0°. This finding is taken to support our previous conclusion that "the contribution of **4** to the propagation is, if any, very small during the THF polymerization in CH_2Cl_2."[2] Namely, the polymerization proceeded mostly *via* the oxonium propagating species in CH_2Cl_2.

Similarly the THF polymerization was monitored by ^{19}F nmr spectroscopy in three other solvents. In $CHCl_3$ and benzene solvents, the fractions of $[O^+]$ were 85 and 75% at 0°, respectively, after the equilibrium was reached. In nitrobenzene, however, the [E] fraction was very small, *e.g.*, below 2% at 0°, throughout the polymerization.

The equilibrium was also examined under the reaction conditions where the monomer concentration was below that of the polymerization equilibrium, $[M]_e$. Figure 3 shows the relationships of ($[O^+]$ + [E]) *vs.* time (curve A) and $[O^+]$ *vs.* time (curve B) in CH_2Cl_2 at 35°. The initial THF concentration was 1.02 mol/l., which is much lower than $[M]_e = 4.00$ mol/l. at 35°.[7] The ratio of $[O^+]$ to [E] was in a constant ratio of 90:10 after 50 min. This ratio was not changed even after 7 hr at 35°. With the aid of ^1H nmr spectroscopy it was concluded that the following reaction mainly took place to produce the cyclic oxonium (**5**) and ester species (**6**). The value of **5**/**6** = 90/10 at 35° is very close to that of **3**/**4** = 89/11 in the THF polymerization at 0° in CH_2Cl_2.



5

$$\rightleftharpoons EtO(CH_2)_4OSO_2CF_3 \quad (4)$$

6

At a reaction time of 7 hr when the equilibrium of eq 4 was already reached, the concentrations of $EtOSO_2CF_3$, **5**, and **6** were respectively 0.61, 0.42, and 0.05 mol per l., *i.e.*,

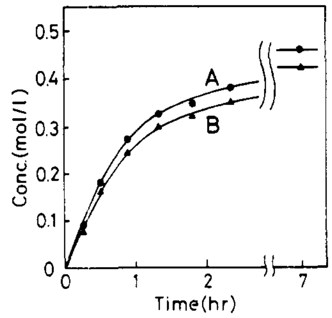
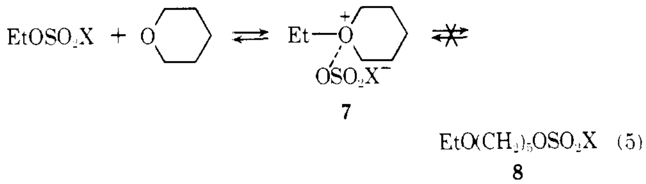


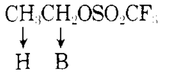
Figure 3. A molar reaction of THF with $EtOSO_2CF_3$ monitored by ^{19}F nmr spectroscopy in CH_2Cl_2 solution at 35°. Relationships of ($[O^+] + [E]$)-time (curve A) and of $[O^+]$-time (curve B): $[THF]_0 = 1.02$ mol/l., $[EtOSO_2CF_3]_0 = 1.08$ mol/l.

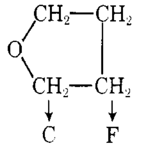
the cyclic oxonium species **5** was in equilibration not only with ester species of $EtOSO_2CF_3$ but also with 4-ethoxybutyl trifluoromethanesulfonate (**6**). It is interesting to compare this result with the result of the ^1H nmr study on the reaction of $EtOSO_2X$ with tetrahydropyran (eq 5) in CH_2Cl_2, in which the cyclic oxonium species **7** was in equilibration only with the starting ester species of $EtOSO_2X$, but not with a 5-ethoxypentyl-type ester (**8**).[1]

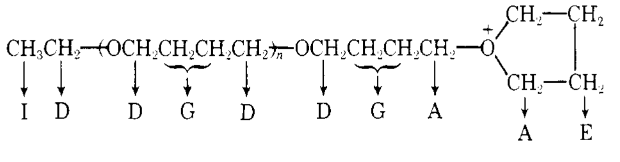


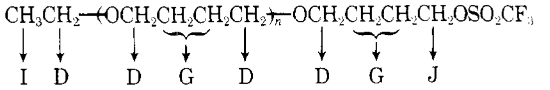
(5)

^1H Nmr Spectroscopy. Figure 4 shows a ^1H nmr spectrum of the THF polymerization system in CCl_4 by $EtOSO_2CF_3$ initiator, which was taken at the same reaction time and temperature as those of ^{19}F nmr spectrum shown in Figure 1. The signal pattern is just the same as that of the ^1H nmr spectrum previously reported, whose signal assignments were already made.[2] Therefore, only the results of the assignment of signals A–J of Figure 4 are given here as follows.









Based on the above assignments the instantaneous concentration of THF monomer could be determined by integration of peaks C and D, as previously carried out in the THF polymerization by $EtOSO_2CF_3$ initiator.[2] Figure 5 shows the monomer conversion–time relationship under the same conditions as those of Figure 2.

Kinetics. The following scheme of reactions explains the course of the THF polymerization initiated by $EtOSO_2CF_3$.

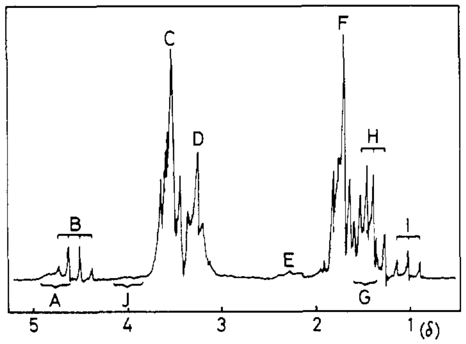


Figure 4. ^1H nmr spectrum of the THF polymerization mixture by $EtOSO_2CF_3$ initiator in CCl_4 after 48 min at 13°.

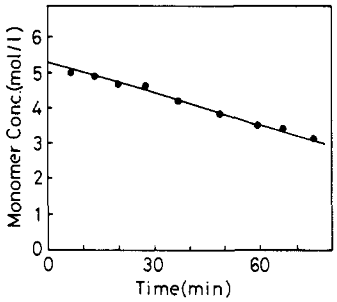
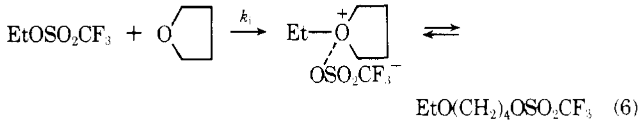
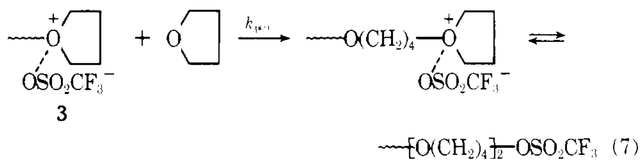


Figure 5. The monomer concentration–time relationship in the polymerization of THF with $EtOSO_2CF_3$ monitored by ^1H nmr spectroscopy in CCl_4 at 13°: $[M]_0 = 5.30$ mol/l., $[I]_0 = 1.05$ mol/l.



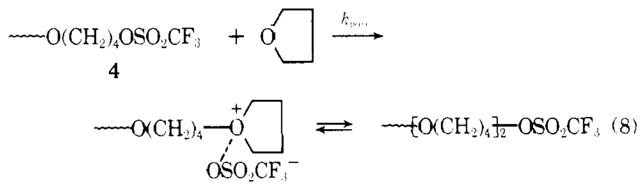
(6)

Propagation



(7)

and



(8)

On the basis of a bimolecular mechanism (eq 6) the rate equation of initiation is given by

$$-d[I]/dt = k_i[I][M] \qquad (9)$$

Integration of eq 9 gave

$$\ln \frac{[I]_0}{[I]} = k_i \int_0^t [M]dt \qquad (10)$$

where k_i is the rate constant of initiation, and $[I]_0$ is the initial feed concentration of $EtOSO_2CF_3$.

The rate equation of propagation is expressed as

$$-d[M]/dt = k_{p(ap)}[P^*]\{[M] - [M]_e\} \qquad (11)$$

Table II
Rate Constants, Activation Parameters, and the $[O^+]$ Fraction in the THF Polymerization Initiated by $EtOSO_2CF_3$ in CCl_4[a]

Temp (°C)	$k_i \times 10^5$ (l./(mol sec))	$k_{p(ap)} \times 10^3$ (l./(mol sec))	$k_{p(i)} \times 10^3$ (l./(mol sec))	$[O^+]$ Fraction[b] (%)
0	0.80	0.84	2.2	45
13	2.1	1.6	3.6	46
25	3.9	3.0	5.7	47
ΔH^* (kcal/mol)	20	16	13	
ΔS^* (eu)	−5	−12	−24	

[a] Solution polymerization in CCl_4. $[M]_0$ = 5.30 mol/l., $[I]_0$ = 1.05 mol/l. [b] At a later stage of polymerization where the equilibrium of eq 3 was reached.

where, [M] and $[M]_e$ are the instantaneous and equilibrium monomer concentrations, $k_{p(ap)}$ is the apparent rate constant of propagation, and [P*] represents the total concentration of the propagating species.

Integration of eq 11 gave

$$\ln \frac{[M]_0 - [M]_e}{[M]_t - [M]_e} = k_{p(ap)} \int_0^t [P^*] dt \tag{12}$$

where $[M]_0$ is the initial feed concentration of THF. Now, [P*] is given by

$$[P^*] = [O^+] + [E] \tag{13}$$

The ester species **4** is not dead, but is thought to be inherently capable of propagation, since the ester of $EtOSO_2CF_3$ initiates the THF polymerization. [P*] is equal to the amount of the reacted initiator. Therefore, the following relationship is derived

$$k_{p(ap)} = k_{p(i)}X_i + k_{p(e)}X_e \tag{14}$$

where $k_{p(i)}$ and $k_{p(e)}$ represents the rate constants of propagation due respectively to the oxonium ion **3** and ester **4** species, and X_i and X_e are the molar fractions of $[O^+]$ and [E], respectively, *e.g.*, $X_i + X_e = 1$. It is reasonable to assume that the magnitude of $k_{p(e)}$ must be at least smaller than that of k_i which was about 140–280 times smaller than that of $k_{p(i)}$ as shown in Tables II and III (*vide infra*), *e.g.*, $k_{p(i)} \gg k_{p(e)}$. Furthermore, X_e was not so large, *e.g.*, below 0.55 in all cases (Tables II and III). Therefore, eq 14 becomes

$$k_{p(ap)} \simeq k_{p(i)}X_i \tag{15}$$

Consequently, eq 12 is converted to

$$\ln \frac{[M]_0 - [M]_e}{[M]_t - [M]_e} = k_{p(i)} \int_0^t [O^+] dt \tag{16}$$

The integrated value of [M] in eq 10 was given by graphical integration on the [M]-time curve in Figure 5. The value of $\ln [I]_0/[I]$ was obtained from curve A in Figure 2. Thus, a plot of eq 10 gave a straight line, whose slope gave the k_i value, $k_i = 2.1 \times 10^{-5}$ l./(mol sec) in CCl_4 at 13°.

Then, $k_{p(ap)}$ and $k_{p(i)}$ were determined. The ∫(from 0 to *t*)[P*]d*t* value was calculated by integration on curve A in Figure 2. A plot of eq 12 is shown in Figure 6A, whose slope corresponds to $k_{p(ap)}$, $k_{p(ap)} = 1.6 \times 10^{-3}$ l./(mol sec) in CCl_4 at 13°. The integrated value of $[O^+]$ in eq 16 was obtained also by graphical integration on curve B in Figure 2.

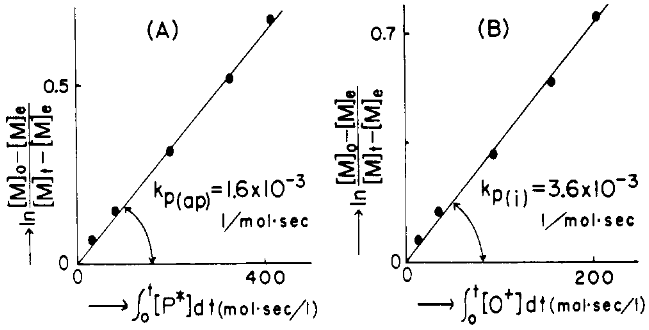


Figure 6. Plots of eq 12 (A) and of eq 16 (B) in the THF polymerization by $EtOSO_2CF_3$ in CCl_4 at 13°: $[M]_0$ = 5.30 mol/l., $[I]_0$ = 1.05 mol/l., $[M]_e$ = 2.3 mol/l.[7]

Figure 6B shows a linear plot of eq 16. From the slope of the straight line passing the origin, the value of $k_{p(i)}$ was determined, $k_{p(i)} = 3.6 \times 10^{-3}$ l./(mol sec) in CCl_4 at 13°. Similarly the $k_{p(ap)}$ and $k_{p(i)}$ values were determined at 0 and 25°. The rate constants and the activation parameters as well as the $[O^+]$ fraction (%) at equilibrium are shown in Table II.

The activation parameters of initiation, in which a dipole–dipole reaction between $EtOSO_2CF_3$ and THF produces a cyclic onium species (eq 6), are relatively large in CCl_4 (ΔH^* = 20 kcal/mol, ΔS^* = −5 eu). In a polar solvent of CH_2Cl_2, both parameter values were much smaller.[2] This is not unreasonable because such tendency has been already observed in the same type of reaction of eq 2, *i.e.*, both the ΔH^* and ΔS^* values were increased in a less polar solvent of CH_2Cl_2 in comparison with those in a more polar solvent of nitrobenzene.[1]

It is seen that the activation parameters of $k_{p(ap)}$ are slightly different from those of $k_{p(i)}$. This is due to different values between ∫(from 0 to *t*)[P*]d*t* of eq 12 and ∫(from 0 to *t*)$[O^+]$d*t* of eq 16 depending upon the reaction temperature during kinetic runs. It should be noted, however, that the $[O^+]$ fraction in [P*] was not changed at the reaction temperatures of 0, 13, and 25°, after the equilibrium of the oxonium-ester propagating species has been reached at a later stage of the THF polymerization, as shown in the last column in Table II.

Similarly, on the basis of the combined data of ^{19}F and ^1H nmr spectroscopy kinetic analyses were successfully performed in the other four solvents. These are given in Table III.

It is worth while to note that the order of the $[O^+]$ fraction at equilibrium coincides with that of the dielectric constant (ε) of the polymerization mixture, which is also given in Table III. Namely, the cyclic oxonium is stabilized more strongly in highly polar media than in less polar ones.

The k_i values were generally increased in polar solvents, *e.g.*, the rate of initiation was about four times faster in a polar solvent of nitrobenzene than in a nonpolar solvent of CCl_4. Similar results have been observed in many dipole–dipole reactions producing onium ions such as the reaction of eq 2[1] and Menschutkin reactions (eq 17).[9]

$$R_3N + R'X \longrightarrow R_3R'N^+X^- \tag{17}$$

In CCl_4 the value of $k_{p(ap)}$ was 2.6 times smaller than that of $k_{p(i)}$. In a highly polar solvent of nitrobenzene, however, both the $k_{p(ap)}$ and $k_{p(i)}$ values were identical since the $[O^+]$ fraction was higher than 98% throughout the kinetic run. Interestingly, the $k_{p(i)}$ values did not vary so much in the five solvents; they are in a narrow range of 2.0–4.4 × 10^{-3} l./(mol sec) at 0°, irrespective of a big change of the dielectric constants of the system. The reason may be explained as follows. The propagating chain end probably

Table III
Rate Constants and the [O+] Fraction in the THF Polymerization by $EtOSO_2CF_3$ Initiator in Five Solvents at 0°[a]

Solvent	ϵ[b] of Solv.	ϵ of the Mix.[c]	$k_i \times 10^5$ (l./(mol sec))	$k_{p(ap)} \times 10^3$ (l./(mol sec))	$k_{p(i)} \times 10^3$ (l./(mol sec))	[O+] Fraction[d] (%)
CCl_4	2.24	4.5	0.80	0.84	2.2	45
C_6H_6	2.28	4.5	1.1	1.7	2.7	75
$CHCl_3$	4.81	6.0	1.1	1.8	2.2	85
CH_2Cl_2	8.93	8.3	1.2	1.7	2.0	89
$C_6H_5NO_2$	34.8	23.4	3.1	4.4	4.4	>98

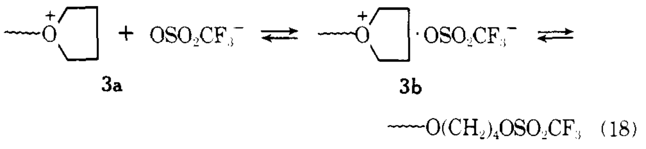
[a] $[M]_0$ = 5.30 mol/l., $[I]_0$ = 1.05 mol/l. [b] Dielectric constant taken from ref 8. [c] Calculated by assuming the molar additivity in the dielectric constant value of solvent and THF. ϵ of THF = 7.58.[8] [d] At equilibrium.

Table IV
Rate Constants in the THF Polymerization with $EtOSO_2CF_3$ Initiator Determined by ^1H nmr Spectroscopy in Five Solvents at 0°[a]

Solvent	$k_i \times 10^5$ (l./(mol sec))	$k_{p(ap)} \times 10^3$ (l./(mol sec))	$k_{p(i)} \times 10^3$ (l./(mol sec))
CCl_4	0.6	1.0	~4[b]
C_6H_6	0.8	*c*	~2.8[b]
$CHCl_3$	1.0	1.9	~3.1[b]
CH_2Cl_2	1.1	2.1	2.1
CH_2Cl_2	(0.85)[d]		(2.0)[d]
$C_6H_5NO_2$	3.9	4.3	4.3

[a] $[M]_0$ = 5.30 mol/l., $[I]_0$ = 1.05 mol/l. [b] Quantitative determination could not be made in these solvents due to the broadness of peak E, and also due probably to the relatively low [O+] value. [c] Could not be determined because the triplet signal I at the polymer end was overlapped with that of $EtOSO_2CF_3$ in benzene. [d] Taken from ref 2. $[M]_0$ = 7.70 mol/l., $[I]_0$ = 1.27 mol/l.

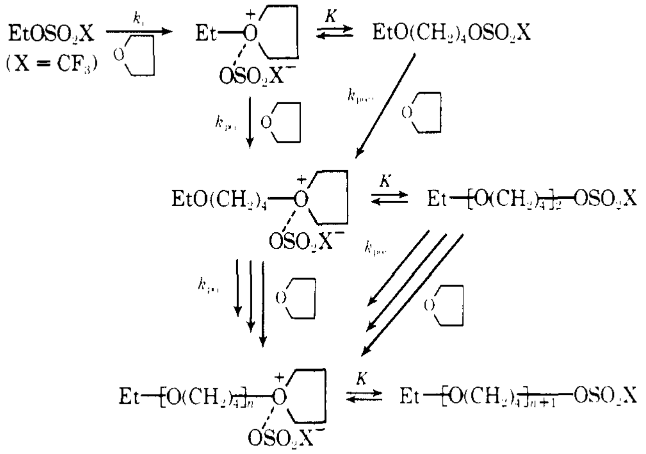
consists of three kinds of species in the THF polymerization by $EtOSO_2CF_3$ initiator, *i.e.*, the free ion (**3a**), ion pair (**3b**), and ester (**4**) species, respectively. This is very reasonable since Sangster and Worsfold[10] have recently reported that two kinds of the oxonium propagating species, the free ion and the ion pair, were involved in the THF polymerization initiated by triethyloxonium tetrafluoroborate ($Et_3O^+ \cdot BF_4^-$). Each species exhibited a different rate constant of propagation.[10] In eq 18 the combined concentration of **3a** and **3b** corresponds to the [O+] value in the present study. It is likely, therefore, that the variation of the polymerization solvent brings about the change not only in the [O+]/XE] ratio but also in the **3a**/**3b** ratio in the oxonium species. In addition, it is also very likely that the rate constants of propagation due to **3a** and **3b** may be varied with the change of the solvent.


3a **3b** **4** (18)

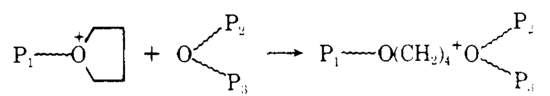
Thus, the present study provides a novel method which allows a determination of $k_{p(ap)}$ and $k_{p(i)}$ on the basis of the direct determination of the instantaneous concentrations of **3** and **4** by ^{19}F nmr spectroscopy. The instantaneous concentration of monomer was obtained with the aid of ^1H nmr spectroscopy.

The above results are taken to support the proposed mechanism (eq 6–8). All the processes of the THF polymerization by $EtOSO_2CF_3$ initiator can be given by Scheme I. In the scheme the interconversion between **3** and **4** was a faster process than propagation, *i.e.*, the equilibrium of eq 3 was attained during the kinetic run. The rate constant ($k_{p(e)}$) of the intermolecular oxonium formation of eq 8 was very small compared with $k_{p(i)}$. The value of $k_{p(e)}$ is probably around that of k_i. The precise determination of $k_{p(e)}$ value, however, is required for the further study. The ester-type species **4** is not dead, but is inherently capable of reacting with THF to produce oxonium species. In this sense, we propose to denote **4** as a *"sleeping species."*[11]

Scheme I

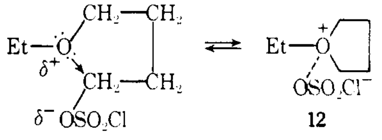


It is shown in the THF polymerization that the propagating cyclic oxonium ion (**9**) undergoes chain transfer with polymer alkyl ether to form a trialkyl oxonium ion (**10**) of the so-called "dormant" species.[12] The cyclic oxonium **10** is

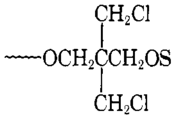

9 **10**

also not a dead species, and can regenerate the cyclic oxonium ion by the reaction with monomer. However, **10** should be discriminated from a *"sleeping species"* in a sense that **4** can *awake* into a cyclic oxonium ion of the propagating species (**3**) not only by the intermolecular reaction with monomer but also by the intramolecular cyclization of the so-called back-biting reaction.[12]

A similar type of back-biting reaction has already been observed by us,[2] *i.e.*, 4-ethoxybutyl chlorosulfate (**11**) cyclized intramolecularly to produce a cyclic oxonium ion (**12**).


11 **12**

In relation to the ester species **4**, we have found that the ester (**13**) is actually the only propagating species in the polymerization of 3,3-bis(chloromethyl)oxacyclobutane by $EtOSO_2CF_3$ initiator.[13]



$$\sim\!\sim OCH_2\overset{CH_2Cl}{\underset{CH_2Cl}{C}}CH_2OSO_2CF_3$$

13

Penczek *et al.*[6] have presented a kinetic study on the THF polymerization by $EtOSO_2CF_3$ under the conditions where the initial concentration of initiator was as low as 0.122 mol/l. They assumed that the average rate constant of propagation ($\bar{k}_p$) is independent on the nature of the counteranion in the THF polymerization initiated by Lewis acid catalysts, which cannot produce ester-type species. Thus, a big change in $\bar{k}_p/k_{p(ap)}$ values was observed with the variation of solvents, *e.g.,* 23.0 in CCl_4, 2.45 in CH_2Cl_2, and 1.07 in nitromethane at 25°. They ascribed the variation of $\bar{k}_p/k_{p(ap)}$ to the change of the fraction of the ester species in different solvents. However, they determined directly the concentrations of neither **3** nor **4**. From the present results, their observation can not be ascribed entirely to the ester species, because the values of $([O^+] + [E])/[O^+]$ are in a narrow range between 2.2 (in CCl_4) and 1.0 (in nitrobenzene) at 0° under the present polymerization conditions (Table III). In addition, it is likely that even k_p of the oxonium propagation is changed depending on the nature of the counteranion, since our previous studies revealed that rate constants of propagation varied with initiators employed, *i.e.,* 0.66–9.9 l./(mol sec) at 0° in CH_2Cl_2.[2,12a,b]

Kinetics by ^1H Nmr Spectroscopy. It has already been established that kinetics of the THF polymerization by superacid esters could be performed by ^1H nmr spectroscopy alone.[2] Since the THF polymerization by $EtOSO_2CF_3$ was found to be of living character without termination, kinetic analyses could be made as follows.[2] The instantaneous concentration of P* was obtained by the integration of peak I (Figure 4), from which k_i and $k_{p(ap)}$ values were determined according to eq 10 and 12, respectively. With monitoring peak E, $k_{p(i)}$ values were obtained according to eq 16. However, signal J could not be observed as a fine peak even in CCl_4 where a large amount of [E] should be involved. These results are summarized in Table IV.

The values of rate constants in CH_2Cl_2 and nitrobenzene are in good agreement with the corresponding values in Table III. The same values between $k_{p(ap)}$ and $k_{p(i)}$ were obtained in these solvents. This indicates that the contribution of the ester type to $k_{p(ap)}$ is very small, as already pointed out.[2] In the other three solvents, CCl_4, $CHCl_3$, and benzene, k_i and $k_{p(ap)}$ values are in good agreement with the corresponding values of Table III. In these three solvents, however, peak E was very broad and $[O^+]$ values were relatively low, which did not allow good quantitative measurement of the integrated value of $[O^+]$ in eq 16. Therefore, $k_{p(i)}$ values thus obtained may not be reliable in these solvents.

The above observations indicate that there is a limitation in ^1H nmr spectroscopy in the determination of $k_{p(i)}$. Since signal J due to the methylene protons of $\sim\sim CH_2OSO_2CF_3$ cannot be detected as a peak in ^1H nmr spectra, the kinetic analysis becomes less reliable in less polar systems in which the [E] fraction was increased. However, it is safe to say that ^1H nmr spectroscopy is still a useful method to perform kinetics on the THF polymerization by superacid esters especially in polar solvents such as CH_2Cl_2 or nitrobenzene, in which only a low concentration of the ester type is involved in the propagation species.

Experimental Section

Materials. THF and solvents were purified as previously reported.[1] $EtOSO_2CF_3$ was prepared by the reaction of diethyl sulfate with CF_3SO_3H, bp 55–58° (100 mm) (lit.[14] 115°).

Kinetic Procedures. Kinetic reactions were carried out under nitrogen. Into an nmr sample tube containing 0.20 ml of solvent, 2.44 mmol of THF and 0.482 mmol of $EtOSO_2CF_3$ were introduced at −78° by using a microsyringe (the initial concentrations of $[M]_0 = 5.30$ mol/l. and $[I]_0 = 1.05$ mol/l., respectively). Then, the tube was sealed and stirred at the same temperature. The extent of the reaction was negligible at −78°. The tube was placed in the nmr probe insert which was kept at a constant temperature. The reaction was then monitored by ^{19}F nmr or ^1H nmr spectroscopy. The instrument used was a Hitachi R-20B nmr spectrometer equipped with radiofrequency units for proton (60 MHz) and fluorine-19 (56.456 MHz) nuclei. The reaction temperature was kept constant within ±1° and the experimental error of the integration was within ±2%.

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