Superacids and Their Derivatives. V.[1] Kinetics and Mechanism of the Cationic Polymerization of 3,3-Bis(chloromethyl)oxacyclobutane Initiated by Ethyl Trifluoromethanesulfonate. Evidence for Ester Type Propagating Species

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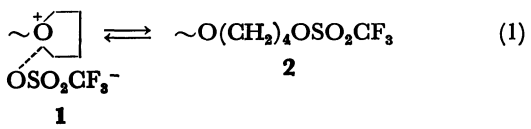
Kinetic analysis of the cationic ring-opening polymerization of 3,3-bis(chloromethyl)oxacyclobutane (BCMO) initiated by ethyl trifluoromethanesulfonate ($EtOSO_2CF_3$) was carried out by direct determination of the instantaneous concentrations of monomer, initiator, and propagating species by means of ^1H and ^{19}F NMR spectroscopy. It was established that the polymerization of BCMO proceeds *via* an ester type propagating species (**4**). The propagating species of the first (P_1^*) and subsequent propagations (P_n^*, $n \geqq 2$) were directly observed. The rate constants of initiation (k_i) and propagations of the first (k_{p1}), second (k_{p2}) and subsequent steps (k_{pn}, $n \geqq 3$) were determined. Activation parameters as well as the solvent effect supported the proposed mechanism, in which the rate-determining step is a dipole-dipole reaction between monomer and propagating ester species to form the intermediate cyclic oxonium ions (**7**, **8**, and **10**) as unstable transient species.

In a series of our studies on the reaction of superacid derivatives with cyclic ethers, we have reported kinetic studies on the cationic ring-opening polymerization of tetrahydrofuran (THF) initiated by superacid esters[1,2] and by pyrosulfuryl chloride,[3] and on the oxonium formation from superacid esters and tetrahydropyran.[4] Generally, the cationic ring-opening polymerization of THF by Lewis acid catalysts proceeds *via* cyclic trialkyl oxonium propagating species.[5] In the THF polymerization by superacid ester initiators, however, an equilibrium between cyclic oxonium **1** and ester **2** species of the propagating end is involved during the course of polymerization.[2,6,7]

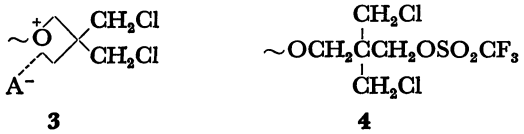


(1)

1 **2**

It was confirmed by means of ^{19}F NMR spectroscopy that equilibrium (1) takes place in the propagating species of the THF polymerization initiated by ethyl trifluoromethanesulfonate ($EtOSO_2CF_3$).[1]

In the cationic polymerization of four-membered cyclic ethers by acid catalysts, a mechanism involving a cyclic oxonium propagating species **3** is generally accepted.[5,8] As an extension of studies on the cationic polymerization of cyclic ethers initiated by superacid



3 **4**

esters, we examined the polymerization of 3,3-bis(chloromethyl)oxacyclobutane (BCMO) by $EtOSO_2CF_3$ initiator. Kinetics of the BCMO polymerization has been carried out by means of ^1H NMR spectroscopy. It was found that an ester type **4** is a propagating species. In the present paper we wish to give clear-out evidence for an ester type propagating species in the polymerization of cyclic ethers.

Results and Discussion

^1H NMR Studies. The polymerization reaction was monitored directly by ^1H NMR spectroscopy. Figure 1 shows examples of ^1H NMR spectra of the reaction system, in which the molar feed ratio of BCMO to $EtOSO_2CF_3$ is 6: 1. In the ^1H NMR spectrum after 5 min at 63 °C (Fig. 1(a)), 55% of the initial $EtOSO_2CF_3$ underwent reaction. A quartet at δ 4.82 (peak H) and a triplet at δ 1.60 (peak I) are due to methylene (2H) and methyl protons (3H) of $EtOSO_2CF_3$, respectively. Peaks H and I diminished with progress of the reaction, peaks A_1, D, E, F, and G increasing. $EtOSO_2CF_3$ was completely consumed at 63 °C within 15 min.

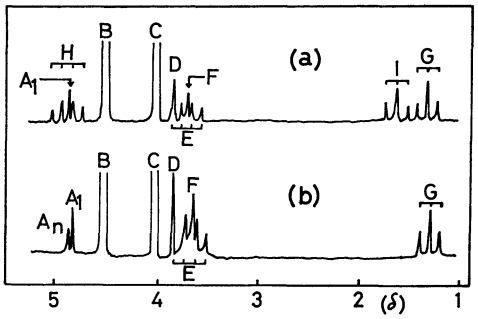
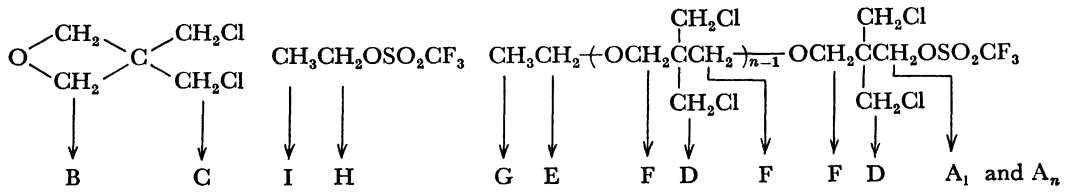


Fig. 1. ^1H NMR spectra of BCMO polymerization mixture by $EtOSO_2CF_3$ in nitrobenzene at 63 °C; (a) after 5 min and (b) after 180 min.

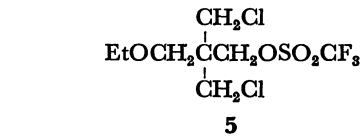
A new peak A_n appears in the ^1H NMR spectrum at a reaction time of 180 min at 63 °C (Fig. 1(b)). Singlet peaks, A_1 at δ 4.80 and A_n at δ 4.83, are assigned respectively to α-methylene protons (2H) of $-OSO_2CF_3$ group in ester type species **5** and **6** (*vide infra*). A signal of the open-chain chloromethyl protons (4H) appears at δ 3.82 (peak D). A peak due to α-methylene protons (2H) of open-chain ether group is observed at δ 3.64 (peak F). A quartet peak E at δ 3.67 and triplet peak G at δ 1.33 are ascribed respectively to methylene protons (2H) and methyl protons (3H) of

TABLE 1. SIGNAL ASSIGNMENTS IN THE POLYMERIZATION MIXTURE OF BCMO BY $EtOSO_2CF_3$ INITIATOR IN NITROBENZENE ((Fig. 1(a) and (b)).



Signal	Chemical shift in ppm[a] (from Me_4Si)
A_1	4.80 (s)
A_n ($n \geqq 2$)	4.83 (s)
B	4.56 (s)
C	4.07 (s)
D	3.82 (—)
E	3.67 (q)
F	3.64 (—)
G	1.33 (t)
H	4.82 (q)
I	1.60 (t)

a) Multiplicity: s=singlet, q=quartet, and t=triplet.



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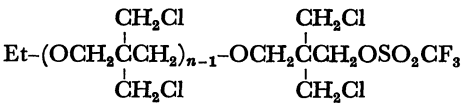


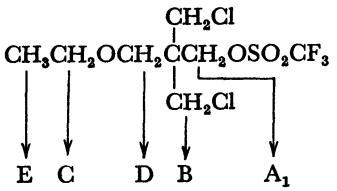
6, $n \geqq 2$

ethoxy group at the polymer end. Large singlets, B and C, are due to α-methylene protons (4H) and chloromethyl protons (4H) of BCMO monomer. Signal assignments given in Fig. 1(a) and (b) are summarized in Table 1.

For the sake of confirmation, a model compound of 3-ethoxy-2,2-bis(chloromethyl)propyl trifluoromethanesulfonate **5** was prepared by the reaction of $EtOSO_2CF_3$ and BCMO (see Experimental). **5** was isolated by distillation *in vacuo*, bp 45—46 °C (0.04mmHg). The NMR spectrum of **5** in nitrobenzene is shown in Fig. 2(a). Chemical shifts of **5** in $CDCl_3$ and in nitrobenzene are given in Table 2. It should be noted that the chemical shift of signal A_1 of **5** in nitrobenzene coincides with that of the polymerization system (Table 1). This provides a strong evidence that signal A_1 of the reaction system is due to α-methylene protons of ester type species ~~~$CH_2OSO_2CF_3$ of **4**. Chemical shifts of other signals in nitrobenzene (Table 2) are almost the same as those of corresponding peaks (Table 1).

An oligomer of **6** was prepared in order to confirm the assignment of peak A_n. The oligomer obtained did not contain **5** at all, and showed no signal at δ 4.80 (peak A_1 region). The average degree of polymerization of **6** was found to be n=2.30 (see Experimental). The signal due to α-methylene protons of ~~~$CH_2OSO_2CF_3$ in **6** appears at δ 4.83 (Fig. 2(b)), which is identical with the chemical shift of peak A_n of the

TABLE 2. SIGNAL ASSIGNMENTS OF THE MODEL COMPOUND **5**



Signal	Chemical shift in ppm[a] (from Me_4Si)	
	in $CDCl_3$	in nitrobenzene
A_1	4.56 (s)	4.80 (s)
B	3.63 (s)	3.84 (s)
C	3.48 (q)	3.67 (q)
D	3.45 (s)	3.65 (s)
E	1.15 (t)	1.34 (t)

a) Multiplicity: s=singlet, q=quartet, and t=triplet.

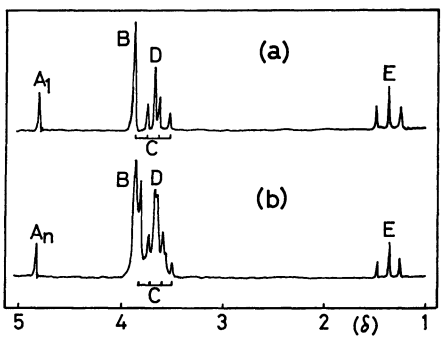


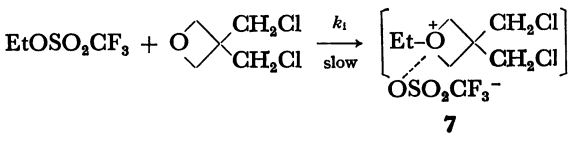
Fig. 2. ^1H NMR spectra in nitrobenzene at 35 °C of (a) **5** and (b) oligomer.

polymerization system. It is reasonable that the methylene proton signal due to ~~~$CH_2OSO_2CF_3$ of **6** appears at a field 0.03 ppm lower than that of **5**, since $Et\{OCH_2C(CH_2Cl)_2CH_2\}_{n-1}$ group in **6** is a little more electron-withdrawing than Et-group in **5**.

In coincidence with the observations of ^1H NMR spectroscopy, a signal due to the CF_3 group of **6** appeared at a lower field than that of **5** in ^{19}F NMR spectroscopy. The fluorine-19 chemical shift of a sharp singlet due to **6** was −3.58 ppm from the external standard of CF_3CO_2H capillary, whereas that due to **5** was −3.44 ppm in nitrobenzene.

Kinetics. The following scheme of reactions explains the course of BCMO polymerization.

Initiation



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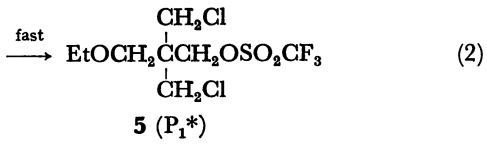
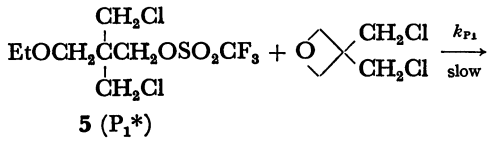


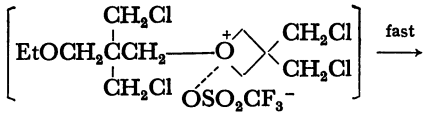
(2)

5 (P_1*)

Propagation



5 (P_1*)



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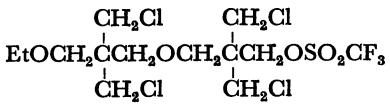
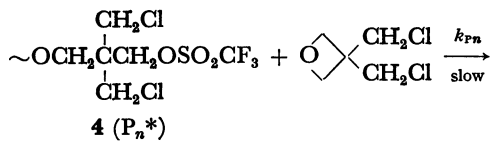


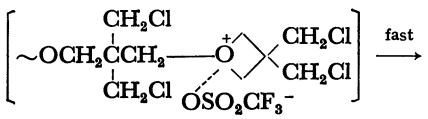
(3)

9 (P_2*)

Generally



4 (P_n*)



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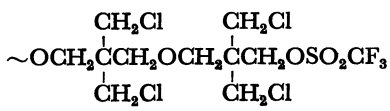


(4)

11 (P^*_{n+1})

Oxonium species **7**, **8**, and **10** might be involved as intermediates. However, these intermediates are not stable under the reaction conditions, undergoing rearrangement quickly to the ester type species **5**, **9**, and **11**, respectively.

The rate of initiation is given by

$$-\frac{d[I]}{dt} = k_i[I][M] \tag{5}$$

where k_i is the rate constant of initiation, and [I] and [M] are the concentrations of $EtOSO_2CF_3$ and BCMO, respectively. Integration of Eq. (5) gives

$$\ln\frac{[I]_0}{[I]_t} = k_i\int_0^t [M]dt \tag{6}$$

where $[I]_0$ is the initial feed concentration of $EtOSO_2CF_3$. The ratio $[I]_0/[I]_t$ was calculated from the integration values of peaks I and G in Fig. 1(a). The integrated value of [M] was obtained by graphical integration on the [M]-time curve. A linear plot of Eq. (6) is shown in Fig. 3, with a slope $k_i=1.4\times10^{-3}$ l/mol·s at 70 °C.

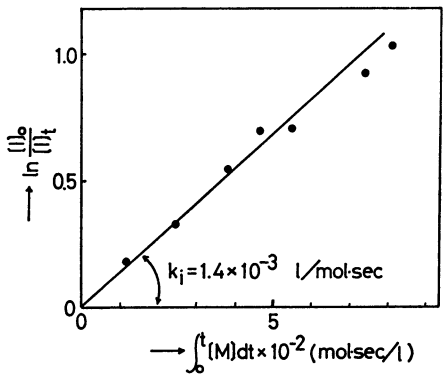


Fig. 3. Plots of Eq. (6) in BCMO polymerization by $EtOSO_2CF_3$ in nitrobenzene at 70 °C: $[I]_0=0.56$ mol/l, $[M]_0=3.90$ mol/l.

After the complete reaction of initiator, the consumption rate of the first propagating species P_1* is given by

$$-\frac{d[P_1^*]}{dt} = k_{p1}[P_1^*][M] \tag{7}$$

where k_{P1} is the rate constant of the first propagation. Integration of Eq. (7) with respect to time gives

$$\ln\frac{[P_1^*]_{t_1}}{[P_1^*]_{t_2}} = k_{p1}\int_{t_1}^{t_2}[M]dt \tag{8}$$

where t_1 and t_2 are reaction times longer than the time required for the complete reaction of initiator. The ratio $[P_1^*]_{t_1}/[P_1^*]_{t_2}$ was obtained by the integration values of peaks A_1 and A_n in Fig. 1(b). Figure 4 shows a linear plot of Eq. (8), with a slope $k_{p1}=1.4\times10^{-5}$ l/mol·s at 70 °C.

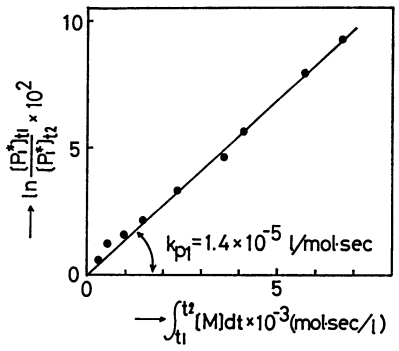


Fig. 4. Plots of Eq. (8) in BCMO polymerization by $EtOSO_2CF_3$ in nitrobenzene at 70 °C: $[I]_0=0.56$ mol/l, $[M]_0=3.90$ mol/l.

Kinetic runs of the BCMO polymerization by $EtOSO_2CF_3$ were similarly carried out at three other temperatures. At lower temperatures between 63—85 °C the reaction rate was small, and the polymerization was followed until P_1* disappeared. Arrhenius plots of k_i and k_{p1} values were linear, and activation parameters were calculated (Table 3). For higher conversions, the polymerizations were carried out at higher temperatures (*vide infra*).

Table 3. Rate constants and activation parameters of initiation (k_i) and the first propagation (k_{p1}) in the BCMO polymerization by $EtOSO_2CF_3$ in nitrobenzene solvent[a)]

Temp. (°C)	$k_i \times 10^3$ (l/mol·s)	$k_{p1} \times 10^5$ (l/mol·s)
63	0.87	0.90
70	1.4	1.4
78	2.1	1.9
85	3.1	3.1
$\Delta H^{\neq}$ (kcal/mol)	12.5	12.5
$\Delta S^{\neq}$ (e. u.)	−36	−46

a) Reaction conditions; $[M]_0=3.90$ mol/l, $[I]_0=0.56$ mol/l.

Polymerization by $EtOCH_2C(CH_2Cl)_2CH_2OSO_2CF_3$ (5). According to the scheme of the $EtOSO_2CF_3$-initiated polymerization of BCMO (reaction mechanism (2)—(4)), **5** corresponds to the smallest species of propagation (P_1*). Thus, the kinetics of polymerization by **5** was studied at higher temperatures. In this case, polymerization starts directly from the first propagating step (reaction mechanism (3)). Figure 5 shows the time-conversion curve of BCMO monomer at 128 °C.

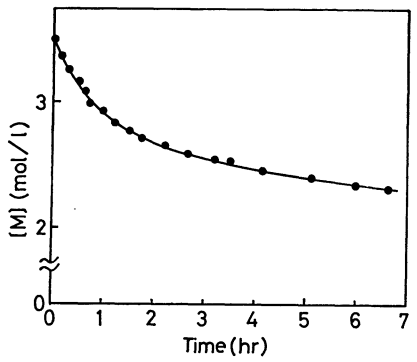


Fig. 5. Relationships between time and monomer conversion in BCMO polymerization initiated with **5** in nitrobenzene at 128 °C: $[5]_0=0.45$ mol/l, $[M]_0=3.50$ mol/l.

The rate of polymerization by **5** is given by

$$-\frac{d[M]}{dt} = k_{p1}[P_1^*][M] + [M]\sum_{n=2} k_{pn}[P_n^*] \qquad (9)$$

The combined value of $[P_1^*]$ and $[P_n^*]$ was found by integration of peaks A_1 and A_n to be constant throughout the kinetic run. This supports the view that the system is of living character under the kinetic reaction conditions. The stoichiometry between the combined value of peaks A_1 and A_n (total 2H) and peak G (3H) was found to hold, *i.e.*, $[P_1^*]+\sum_{n=2}[P_n^*]=[5]_0$. On the assumption that $k_{p2}=k_{p3}=\cdots\cdots=k_{pn}$, integration of Eq. (9) with respect to time from t_1 to t_2 gives

$$\ln\frac{[M]_{t_1}}{[M]_{t_2}} = k_{p1}\int_{t_1}^{t_2}[P_1^*]dt + k_{pn}\int_{t_1}^{t_2}[P_n^*]dt \qquad (10)$$

The $[P_1^*]$-time relationships were obtained by monitoring the reaction with ^1H NMR spectroscopy (peaks A_1 and A_n). Since peaks A_1 and A_n partly overlap with each other, the reaction was also followed by ^{19}F NMR spectroscopy. Signals due to the CF_3 group of **5** and **6** appeared as sharp singlets at −3.91 and −4.08 ppm, respectively, from an external standard of CF_3CO_2H capillary under the polymerization conditions. Results by both methods were in good agreement with each other (Fig. 6). A linear plot of Eq. (8) was made (Fig. 7), whose slope gave $k_{p1}=1.8\times10^{-4}$ l/mol·s at 128 °C.

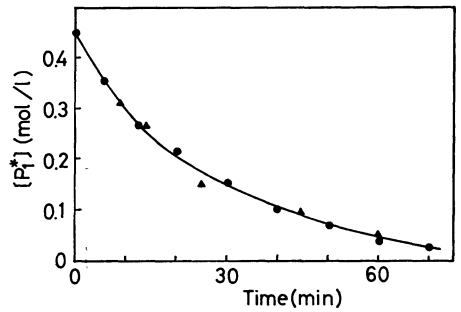


Fig. 6. $[P_1^*]$-time relationships in BCMO polymerization initiated with **5** in nitrobenzene at 128 °C monitored by ^1H NMR (-●-) and ^{19}F NMR (-▲-) spectroscopy: $[5]_0=0.45$ ml/l, $[M]_0=3.50$ mol/l.

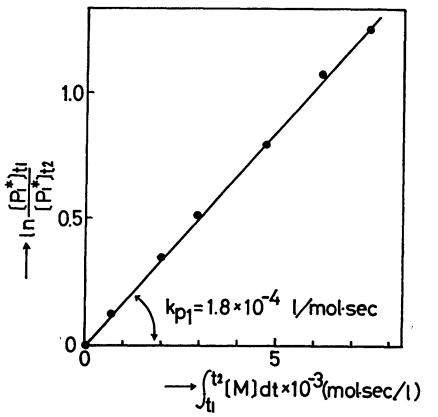


Fig. 7. Plots of Eq. (8) in BCMO polymerization initiated with **5** in nitrobenzene at 128 °C: $[5]_0=0.45$ mol/l, $[M]_0=3.50$ mol/l.

Equation (10) is converted into

$$\ln\frac{[M]_{t_1}}{[M]_{t_2}} - k_{p1}\int_{t_1}^{t_2}[P_1^*]dt = k_{pn}\int_{t_1}^{t_2}[P_n^*]dt \qquad (11)$$

Figure 8 shows a plot of Eq. (11), consisting of two straight lines A and B of different slopes. The plot indicates $k_{p2}>k_{p3}\simeq k_{p4}$. Line A was utilized to calculate k_{p2}, since the monomer consumption in its period corresponded to the stage of the second to third propagation step. Thus, $k_{p2}=5.7\times10^{-5}$ l/mol·s at 128

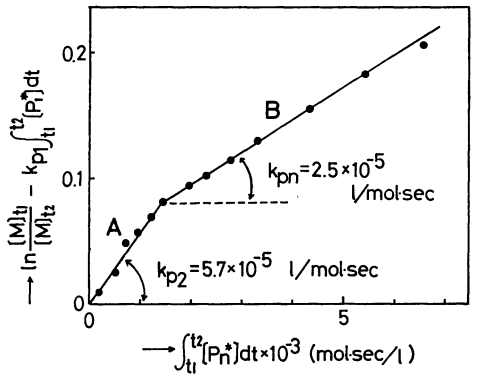


Fig. 8. Plots of Eq. (11) in BCMO polymerization initiated with **5** in nitrobenzene at 128 °C: $[5]_0=0.45$ mol/l, $[M]_0=3.50$ mol/l.

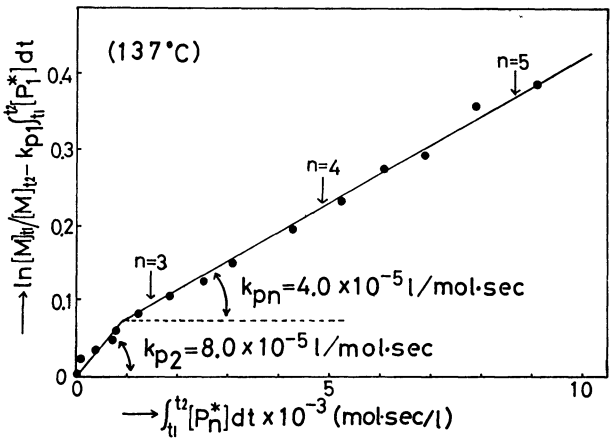


Fig. 9. Plots of Eq. (11) in BCMO polymerization initiated with **5** in nitrobenzene at 137 °C: $[5]_0=0.37$ mol/l, $[M]_0=3.80$ mol/l.

°C was obtained from the slope of line A. After the reaction stage of line A, the rate constant was calculated to be $k_{p3}=k_{p4}=k_{pn}=2.5\times10^{-5}$ l/mol·s at 128 °C from the slope of line B. It became clear in the polymerization at higher reaction temperature of 137 °C that k_{pn} does not change any more after the third propagation step (Fig. 9), *i.e.*, k_{pn} was constant from $n=3$ to at least $n=5$.

Similar results were obtained with $EtOSO_2CF_3$ initiator instead of **5** initiator at 128 °C. These data along with activation parameters are given in Table 4.

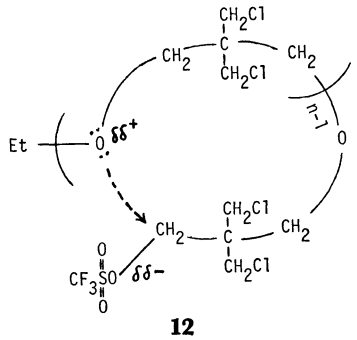
Table 4. Rate constants of propagation and activation parameters in the BCMO polymerization initiated by the compound (**5**) in nitrobenzene solvent

Temp. (°C)	$k_{p1}\times10^5$ (l/mol·s)	$k_{p2}\times10^5$ (l/mol·s)	$k_{pn}\times10^5$ (l/mol·s)
90[a]	3.7	—	—
119[a]	10	3.5	1.5
128[a]	18	5.7	2.5
128[b]	(17)	(6.0)	(2.8)
137[c]	~30	8.0	4.0
ΔH^* (kcal/mol)	13	13	14
ΔS^* (e. u.)	−45	−46	−45

a) Reaction conditions; $[M]_0=3.50$ mol/l, $[5]_0=0.45$ mol/l. b) $EtOSO_2CF_3$ initiator. c) Reaction conditions; $[M]_0=3.80$ mol/l, $[5]_0=0.37$ mol/l.

Reaction Mechanism. All the results are in line with the reaction mechanisms (2)—(4). In fact, the propagating species of ester type were observed directly by both ^1H and ^{19}F NMR spectroscopy during the kinetic run. The first propagating species **5** was isolated by vacuum distillation and the **5**-initiated BCMO polymerization commenced directly from the first propagation.

The rate of propagation varied during the course of polymerization *i.e.*, $k_{p1}>k_{p2}>k_{p3}=k_{pn}$ ($n\geqq3$) (Table 4). These values could be determined since P_1^* and P_n^* ($n\geqq2$) were directly observed by both ^1H and ^{19}F NMR spectroscopy. The difference in k_p is due to the difference in electrophilic reactivity of alkyl groups toward BCMO monomer for $n=1$, 2 and $\geqq3$ in **6**. The larger the alkyl chain ($n\geqq3$), the less the reactivity. This might be partly due to the increase of bulkiness of alkyl groups. It could be assumed that **6** is stabilized (deactivated) through an intramolecular coordination as given by **12**, *i.e.*, such cyclization probably becomes more profound for $n\geqq3$ whereas it is not possible for $n=1$.



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Examination of activation parameters (Tables 3 and 4) also supports the mechanisms (2)—(4). They are characterized by a general feature of activation parameters of S_N2 reaction between two neutral molecules producing an ionic species as a final product or a transient intermediate, the combination of low activation enthalpy (favorable for rate) and low activation entropy (unfavorable) taking place in each process.[4] The following reaction is reversible,

$$ROSO_2X + \text{O}\!\!\bigcirc \underset{}{\overset{k_{ox}}{\rightleftharpoons}} R\text{-}\overset{+}{\text{O}}\!\!\bigcirc \quad (12)$$

R = Me, Et, *n*-Pr; X = CF_3, F, Cl; OSO_2X^-

the process of oxonium formation (k_{ox}) having a relatively low ΔH^* (favorable for k_{ox}) and a low ΔS^* (unfavorable for k_{ox}).[4] A similar phenomenon is often observed in the Menschutkin reaction in which an ammonium ion is formed from alkyl iodide and amine (Eq. (13)).[9]

$$RI + R_3'N \longrightarrow RR_3'\overset{+}{N}I^- \quad (13)$$

The magnitudes of k_{p1} are about one-hundredth of those of k_i (Table 3). The small k_{p1} value is ascribed to the lower ΔS^* value; ΔH^* values being the same in both cases. The difference in rate of initiation and the first propagation is due to that of the electrophilic reactivity

of alkyl groups attached to OSO_2CF_3 toward the BCMO nucleophile, *e.g.*, CH_3CH_2-group for the former and $EtOCH_2C(CH_2Cl)_2CH_2$-group for the latter. A similar result was reported by Buncel and Millington[10] for the hydrolysis of primary alkyl chlorosulfates (**13**) in 85.3% aqueous dioxane, in which the reactivity of the ethyl group (**13a**) was 4.2×10^2 times as high as that of the

$ROSO_2Cl$

13a $R=CH_3CH_2-$
13b $R=(CH_3)_3CCH_2-$

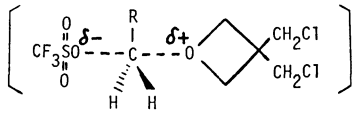
neopentyl group (**13b**). The alkyl group of propagating species is bulkier (unfavorable) than the neopentyl group of **13b**, whereas α-carbon atom of the former should be more positive due to electron-withdrawing chloromethyl groups (favorable) than that of the latter group. The combination of steric and electronic factors brings forth the reactivity difference of $k_i/k_{p1}\fallingdotseq100$.

TABLE 5. RATE CONSTANTS OF INITIATION (k_i) AND THE FIRST PROPAGATION (k_{p1}) IN THE BCMO POLYMERIZATION BY $EtOSO_2CF_3$ IN THREE DIFFERENT SOLVENTS AT 63 °C[a]

Solvent	$k_i\times10^3$ (l/mol·s)	$k_{p1}\times10^5$ (l/mol·s)
Nitrobenzene	0.87	0.90
Chlorobenzene	0.20	0.17
Methylcyclohexane	——[b]	0.10

a) Reaction conditions; $[M]_0=3.90$ mol/l, $[I]_0=0.56$ mol/l. b) The k_i value could not be determined since the solvent signals overlapped with methyl signals of peaks G and I.

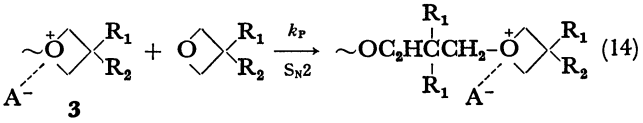
Solvent Effect. In order to obtain information on the mechanistic features, solvent effect was examined. Values of k_i and k_{p1} in the BCMO polymerization by $EtOSO_2CF_3$ initiator in three different solvents at 63 °C are given in Table 5. Both k_i and k_{p1} values increase in polar solvents, *e.g.*, k_{p1} is 5.3 times higher in nitrobenzene than in chlorobenzene. The results also provide evidence for the mechanisms (2)—(4). In the reaction between two neutral molecules of ester type species (electrophile) and BCMO monomer (nucleophile) the ionic transition state **14** will be



14 R = CH_3- or $\sim CH_2C(CH_2Cl)_2$

more stabilized by solvation in a polar solvent as compared with the initial state of two neutral molecules. Similarly the oxonium formation (Eq. (12)) was favored in polar solvents, *e.g.*, k_{ox} in nitrobenzene was 2.65 times larger than that in chlorobenzene for R=Et and X=Cl in Eq. (12).[4]

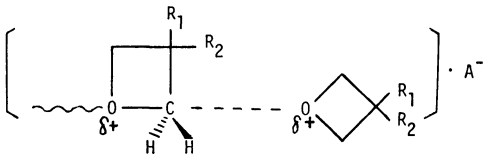
The solvent effect (Table 5) is in sharp contrast to that observed in the cationic polymerization of four-membered cyclic ethers by typical Lewis acids such as BF_3, *i.e.*, k_p values of both unsubstituted and 3-methyloxacyclobutanes by BF_3 initiator were about 9 times higher in a nonpolar solvent of methylcyclohexane than in a polar one of CH_2Cl_2.[8] It is generally accepted that the polymerization of oxacyclobutanes initiated by typical Lewis acids proceeds *via* an S_N2 reaction between the propagating cyclic oxonium **3** (electrophile) and monomer (nucleophile):[5,8]



(14)

3

where A^- represents the counter anion derived from initiator. In this case the transition state given by **15** is less solvated than the initial state, since the positive charge is more dispersed in **15** than in the initial state of oxonium. Thus, k_p decreases in a polar solvent with BF_3 catalyst.[8]



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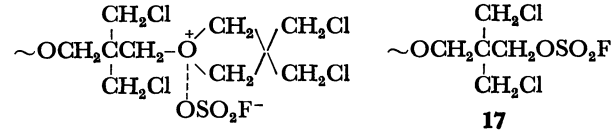
In the BCMO polymerization by BF_3, solvent effects were examined by Penczek and Penczek,[11] who found that the polymerization proceed through the oxonium propagating species and that the apparent overall rate of polymerization is greater in more polar solvents. The increase of the overall rate was ascribed to the increase in the rate of initiation, *i.e.*, concentration of the propagating species increased but the propagation rate did not.

In contrast to the present results it has been found that polymerization of oxacyclobutane and of 3-methyloxacyclobutane initiated by $EtOSO_2CF_3$ proceeds *via* oxonium propagating species.[12] The difference is due to two chloromethyl groups of BCMO, which brings about not only a destabilization of intermediate oxonium ions (**7**, **8**, and **10**) but also a decrease in the nucleophilic reactivity of BCMO monomer.

Recently, Pruckmayr and Wu[13] reported on a ^1H NMR study of BCMO polymerization initiated by superacid of fluorosulfuric acid ($HOSO_2F$). However, the rate constants were not determined since the system was complicated owing to the presence of "acidic" proton derived from $HOSO_2F$. Unlike their system the present polymerization with $EtOSO_2CF_3$ was clean, since no such acidic proton is involved. Thus, kinetic analysis was successfully made. Concerning ^1H NMR spectral assignments they ascribed peaks at δ 4.56 and 4.31 in CH_2Cl_2 (peaks A and C in Fig. 7[13]) respectively to the open-chain methylene and the ring methylene protons adjacent to the propagating oxonium **16**. However, it is unlikely that a trialkyl four-membered cyclic



16

17

oxonium such as **16** is observed as a long-lived species under their ^1H NMR measurement conditions. It is also very unlikely that ring methylene protons of **16** appear at higher chemical shift (δ 4.31) than those of BCMO (δ 4.41).[13] We propose here with that a peak at δ 4.56[13] is assigned to α-methylene protons of OSO_2F group of **17**. To support this assignment a signal due to α-methylene protons of OSO_2CF_3 of **5** appears at nearly the same chemical shift of δ 4.60 in CH_2Cl_2,[12] since the chemical shift of α-methylene protons of OSO_2X is not affected by X=F, Cl, and CF_3.[14] Thus, we believe that ester type **17** is involved as a stable propagating species also in the BCMO polymerization by $HOSO_2F$ initiator.

Experimental

Materials. BCMO and all solvents were purified as previously reported.[1,4,15] $EtOSO_2CF_3$ was prepared by the reaction of diethyl sulfate with CF_3SO_3H.[2]

3-Ethoxy-2,2-bis(chloromethyl)propyl trifluoromethanesulfonate **5** was prepared as follows. A mixture of 8.36 mmol of BCMO and 10.0 mmol of $EtOSO_2CF_3$ in 2.0 ml of CH_2Cl_2 was allowed to react for 10 days at 35 °C, in which BCMO was completely consumed. CH_2Cl_2 and excess $EtOSO_2CF_3$ were then removed, and **5** was isolated in 90% yield by vacuum distillation, bp 45—46 °C/0.04 mmHg. The data of the ^1H NMR spectrum are given in Table 2. ^{19}F NMR (nitrobenzene): −3.44 ppm (~~OSO_2CF_3) (from the external standard of CF_3CO_2H capillary). IR (neat): ν_{max} 1420, 1210, and 1150 cm^{-1} ($-SO_2-$).[16]

Found: C, 28.95; H, 3.94%. Calcd for $C_8H_{13}F_3O_4SCl_2$: C, 28.84; H, 3.90%.

Preparation of Oligomer. A mixture of BCMO (8.30 mmol) and $EtOSO_2CF_3$ (1.20 mmol) in 1.0 ml of nitrobenzene was allowed to react at 100 °C. After 10 hr, signal A_1 disappeared completely, and only signal A_n was observed in the ^1H NMR spectrum. Unchanged BCMO and nitrobenzene were removed *in vacuo*. The residue was an oligomer of oily material (0.60 g). The average degree of oligomerization was determined by ^1H NMR to be n=2.30 from the integration ratio of peaks B, C, and D to peak A_n of the ^1H NMR spectrum (Fig. 2 (b)). ^{19}F NMR (nitrobenzene): −3.58 ppm (~~OSO_2CF_3) (from the external standard of CF_3CO_2H capillary). IR (neat): ν_{max} 1420, 1210, and 1145 cm^{-1} ($-SO_2-$).[16] The molecular weight of oligomer was determined to be 510 by vapor pressure osmometry, which is close to the calculated value of 535 with n=2.30 in **6**. Thus, the 0.60 g oligomer obtained corresponds to 1.12 mmol, which does not differ much from the concentration of the initiator of $EtOSO_2CF_3$. This indicates that each initiator produces 1 mol of oligomer.

Found: C, 32.56; H, 4.26; F, 10.68; S, 6.45; Cl, 30.60%. Calcd for $C_{14.50}H_{23.40}F_3O_{5.30}SCl_{4.60}$ (n=2.30 in **6**): C, 32.58; H, 4.41; F, 10.66; S, 6.00; Cl, 30.50%.

NMR Measurement. A typical example is as follows. Into an NMR sample tube were introduced 1.67 mmol of BCMO, 0.24 mmol of $EtOSO_2CF_3$ and 0.20 ml of nitrobenzene at −78 °C under nitrogen. The tube was sealed and stirred at the same temperature. The extent of the reaction was negligible at this point. The tube was then inserted into the NMR probe which was kept at a constant temperature. The reaction was then monitored. A Hitachi R-20B NMR spectrometer equipped with radio frequency counters of ^1H (60 MHz) and ^{19}F (56.456 MHz) nuclei was used. The reaction temperature was kept constant within ±1 °C and the experimental error of the NMR analysis was within ±2%.

Molecular Weight Determination. The molecular weight of the oligomer was determined by a vapor pressure osmometer (Hitachi Perkin-Elmer model 115) in dimethylformamide at 55 °C.

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