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Kinetic Study on the Ring-Opening Polymerization of Tetrahydrofuran by Pyrosulfuryl Chloride Initiator[1)]

Shiro Kobayashi, Takeo Saegusa, and Yoshiaki Tanaka[2)]
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606

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This paper deals with a kinetic study of the ring-opening polymerization of tetrahydrofuran (THF) initiated by pyrosulfuryl chloride (PSC). The kinetic analysis was based on the determination of the concentration of propagating species, [P*], by the phenoxyl end-capping method. The rate constants of the three elementary processes, propagation (k_p), initiation (k_i), and termination (k_t), were determined. Activation parameters for the propagation were; $\Delta E_p^{\neq}=12$ kcal/mol, and $A_p=7.6\times10^6$ l/mol·sec. From the k_p values and the NMR study of the THF–PSC reaction, it is concluded that the propagation proceeds *via* the bis-oxonium species **5b**. The ester type species **5a** may be involved at a very early stage of polymerization. However, its contribution was quite small throughout the polymerization. The THF polymerization initiated by PSC was characterized by the fast initiation. The mechanism of termination was also examined. The THF polymerization by trifluoromethanesulfonic anhydride was also studied kinetically, which was characterized by a living propagation by bis-oxonium species.

Relatively few studies have been reported on the reaction of pyrosulfuryl halides in the organic chemistry. Very recently, however, attention has been paid on the reactions of pyrosulfuryl fluoride.[3)] We have recently reported a kinetic study of the polymerization of tetrahydrofuran (THF) by using superacid esters such as ethyl chlorosulfate, fluorosulfate, and trifluoromethanesulfonate.[4)] As an extension of our previous study we report in the present study the kinetics of the THF polymerization initiated by pyrosulfuryl chloride, Cl-SO_2–O–SO_2Cl, (PSC). PSC is a derivative of superacid, *i.e.*, an anhydride of chlorosulfuric acid. Furthermore, it could be a bifunctional initiator for the cyclic ether polymerization.

Results and Discussion

Determination of [P] by the Phenoxyl End-Capping Method.* The phenoxyl end-capping method has originally been developed by Saegusa and Matsumoto[5)] for the determination of [P*] in THF polymerization. Since then, this method has successfully been employed in kinetic analyses of polymerizations of various cyclic ethers including mono and bicyclic monomers.[6)] This

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[1)] "Superacids and Their Derivatives," Part II. For Part I, See Ref. 4.

[2)] Present Address: Industrial Research Laboratories, Kao Soap Co. Ltd., Wakayama-shi, Japan.

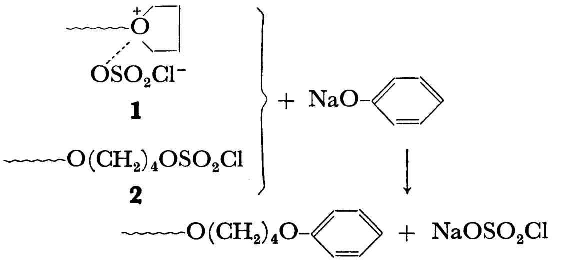
[3)] M. M. Boudakian, G. A. Hyde, and S. Kongpricha, *J. Org. Chem.*, **36**, 940 (1971).

[4)] S. Kobayashi, H. Danda, and T. Saegusa, This Bulletin, **46**, 3214 (1973).

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

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

method was used also in the present study. It has been established in the polymerization of THF that the conversion of the propagating species into the phenyl ether group is quantitative under the phenoxyl end-capping reaction conditions regardless of the nature of the propagating species, *e.g.*, oxonium type (**1**) or ester type (**2**).[7] The concentration of the phenyl ether group formed by the reaction of **1** or **2** with sodium phenoxide (Eq. (1)) was analyzed by its UV absorption at 272 mμ. The molar extinction coefficient value of the phenyl ether was obtained to be 1.93×10^3 l/mol·cm in the THF polymerization.[5,8]



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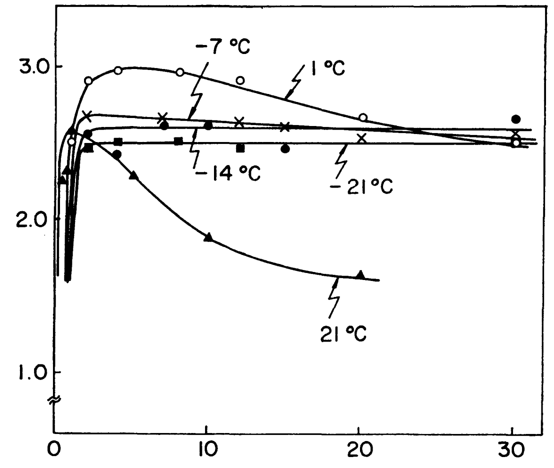


Fig. 1. [P*]-time plots in the polymerization of THF by PSC initiator in CH_2Cl_2: $[M]_0$, 9.9 mol/l; $[PSC]_0$, 0.0203 mol/l.

Polymerization of THF. The THF polymerization was carried out at five temperatures between −21 and 21 °C. The [P*] change during the THF polymerization was examined by means of the phenoxyl end-capping method. The time-[P*] relationships of the PSC-initiated polymerization are shown in Fig. 1. At −21 and −14 °C, P* was produced at an early stage of the polymerization, *i.e.*, within 3 min, and it remained constant thereafter. This indicates a rapid initiation and no occurrence of a termination at these temperatures. At higher temperatures [P*] reached to the maximum within few minutes, and then diminished slowly at 1 °C and fairly rapidly at 21 °C. The maximum concentration of P* during the polymerization is about 75% of the charged initiator concentration, based on the assumption that PSC is a bifunctional initiator.

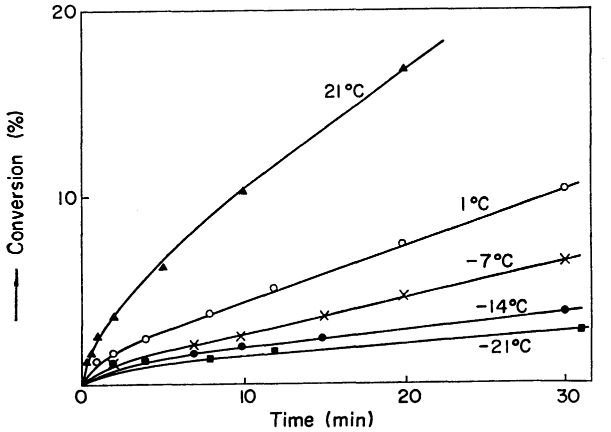
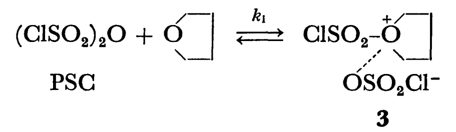


Fig. 2. Time-conversion curves in the THF polymerization by PSC initiator in CH_2Cl_2 at various temperatures: $[M]_0$, 9.9 mol/l; $[PSC]_0$, 0.0203 mol/l.

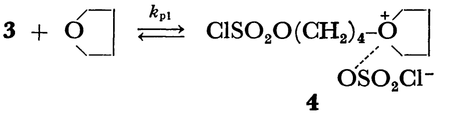
The time-conversion curves at five temperatures are shown in Fig. 2. From the time-[P*] and time-conversion relationships the propagation rate constant, k_p, was determined on the basis of the following procedure.

The initiation of THF by PSC must be expressed as Eq. (2)



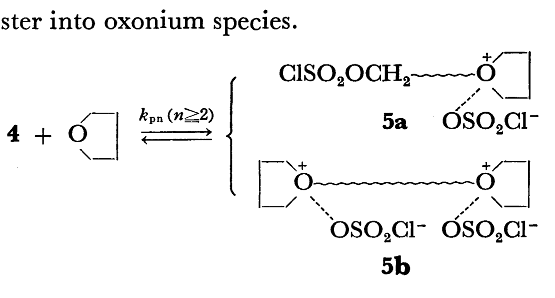
(2)

producing the oxonium species **3**. Then, the first propagation step takes place by the nucleophilic attack of THF monomer on **3**, by which the oxonium-ester type intermediate (**4**) may probably be produced



(3)

where k_{p1} represents the first propagation rate constant. In the later propagation stage, therefore, the growing chain end can be formulated as a bifunctional oxonium-ester (**5a**) and/or a bifunctional oxonium-oxonium type (**5b**) as shown in Eq. (4). As a matter of fact the formation of **5b** involves the conversion of ester into oxonium species.



(4)

It has been already established that the propagation of the THF polymerization proceeds *via* a bimolecular reaction between the propagating species and monomer, and hence obeys a following kinetic equation

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

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

$$-\frac{d[M]}{dt} = k_p[P^*]\{[M]-[M]_e\} \tag{5}$$

where [M] and $[M]_e$ denote the instantaneous and equilibrium monomer concentrations, respectively.[5] Integration of Eq. (5) with respect to time gives

$$\ln\frac{[M]_{t_1}-[M]_e}{[M]_{t_2}-[M]_e} = k_p\int_{t_1}^{t_2}[P^*]dt \tag{6}$$

where $[M]_{t1}$ and $[M]_{t2}$ are the monomer concentrations at time t_1 and t_2, respectively.

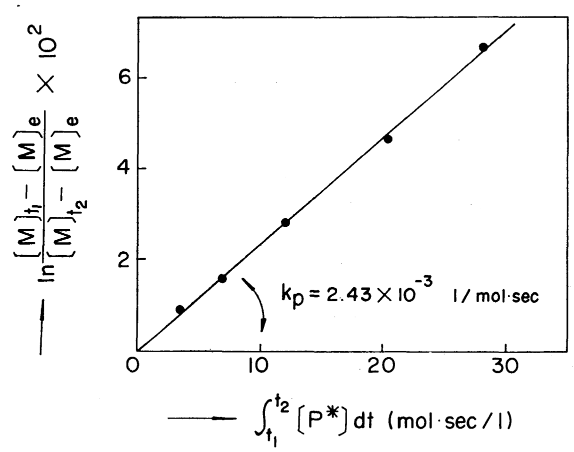


Fig. 3. Plots of Eq. (6) in the THF polymerization by PSC initiator at 1 °C: $[M]_0$, 1.7 mol/l; t_i, 8 min.

A linear plot of Eq. (6) gave a straight line passing through the origin as shown in Fig. 3, from which k_p at 1 °C was calculated. Similarly, k_p values at other temperatures were obtained and are summarized in Table 1.

TABLE 1. RATE CONSTANTS AND ACTIVATION PARAMETERS OF THE THF POLYMERIZATION BY PSC[a)]

°C	$10^3\times k_p$ (l/mol·sec)	$10^3\times k_i$ (l/mol·sec)	$10^4\times k_t$ (sec^{-1})
−21	0.42	—	—
−14	0.81	—	—
− 7	1.55	—	—
1	2.43	2.4	1.3
21	10.9(6.5)[b)]	10(∼15)[b)]	5.3
$\Delta E_p^{\ne}$ (kcal/mol)	12		
A_p (l/mol·sec)	7.6×10^6		

a) Polymerization conditions: $[M]_0$, 9.9 mol/l in CH_2Cl_2; $[PSC]_0$, 0.0203 mol/l.
b) Trifluoromethanesulfonic anhydride initiator at 21°C. Polymerization conditions were the same as those of PSC initiator.

The rate of initiation was estimated from the rate of the P* production. The rate equation is given by Eq. (7) according to the initiation reaction Eq. (2)

$$-\frac{d[PSC]}{dt} = k_i[PSC][M] \tag{7}$$

Thus, the initiation rate constant k_i was obtained from the slope of the linear plot of the integrated equation.

$$\ln\frac{[PSC]_0}{[PSC]_t} = k_i\int_0^t[M]dt \tag{8}$$

where $[PSC]_t$ was obtained on the assumption that $[PSC]_t=[PSC]_0-[P^*]$. From the [P*]-time relationship in Fig. 1 k_i was roughly calculated and given in Table 1.

A kinetic analysis of termination was also made on the basis of the [P*]-time curve. The termination of the THF polymerization has been assumed to be a unimolecular reaction.[9] Therefore, the following equation is derived

$$-\frac{d[P^*]}{dt} = k_t[P^*] - R_i \tag{9}$$

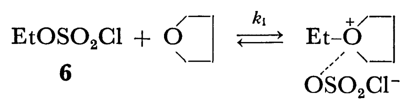
where R_i is the production rate of P* and k_t is the rate constant of termination. After the [P*] reaches to the maximum in few minitutes the production of P* ceases, *i.e.*, $R_i=0$. Hence, Eq. (9) becomes Eq. (10)

$$-\frac{d[P^*]}{dt} = k_t[P^*]$$

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

The plot of ln[P*] *vs.* time became a straight line after the [P*] maximum at 1 and 21 °C. These slopes gave k_t values, which are listed also in Table 1.

The k_p value initiated by PSC can reasonably be taken to represent the propagation *via* bis-oxonium species **5b** of Eq. (4) according to the following observations. Recently we have found that ethyl chlorosulfate (**6**) causes the THF polymerization *via* an oxonium ion (**7**) of Eq. (12).[4]



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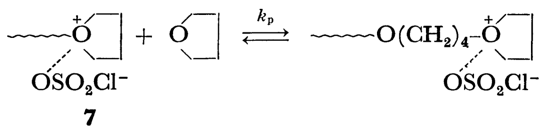

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(12)

The k_p value obtained in the above system was 1.4×10^{-3} l/mol·sec at 0 °C in CH_2Cl_2.[4] In the PSC-initiated polymerization the conversion of ester (**5a**) into oxonium (**5b**) is not impossible because the ester **6** is able to induce the THF polymerization. However, the rate of oxonium formation, k_i of Eq. (11), 3.8×10^{-6} l/mol·sec at 0 °C, is very slow compared with k_p of Eq. (12), 1.4×10^{-3} l/mol·sec at 0 °C, *i.e.*, k_i is about 3.7×10^2 times smaller than k_p. Since ester species of **5a** has longer alkyl chain group than ethyl group of **6**, it may be less reactive than **6** as usually seen in the similar type S_N2 reactions.[10] Therefore, ester species in **5a** is at least 3.7×10^2 times less reactive than oxonium species in **5a** or **5b**. In this respect **5a** behaves like a monofunctional species of the oxonium type although ester species of **5a** is inherently not a dead species. The [P*] obtained by the phenoxyl end-capping methods represents both the oxonium (**1**) and ester (**2**) type propagating species. If the propagation proceeds *via* **5a** the fraction of the oxonium

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[9] H. Meerwein, D. Delfs, and H. Morshel, *Angew. Chem.*, **72**, 927 (1960).

[10] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed., Cornell University Press. (1969), Chapter VII.

concentration is one half of the observed [P*]. Then, the k_p values should be twice as large as those in Table 1 since the propagation rate of the ester type is negligible small. The k_p value, for example, at 1 °C results in 4.86×10^{-3} l/mol·sec which is too large compared with the observed k_p value of 1.4×10^{-3} l/mol·sec at 0 °C initiated by ethyl chlorosulfate **6** (Eq. (12)). The k_p values should be equal in principle when the same counter anion is involved in the propagation. Both PSC and ethyl chlorosulfate **6** initiators provide a same counter anion, OSO_2Cl^-. Even so, the k_p value of 2.43×10^{-3} l/mol·sec is still fairly larger than that of Eq. (12). All these findings indicate most likely that the PSC-initiated polymerization proceeds *via* bis-oxonium type **5b**. The contribution of **5a** is, if any, very small throughout the propagation of THF polymerization.

The k_p values obtained in the present study are interestingly compared with those initiated by typical Lewis acids.⁶⁾ For example, the k_p value at 0 °C by BF_3-epichlorohydrin initiator is reported to be 4.5×10^{-3} l/mol·sec,⁵⁾ the magnitude of which is about twice as large as that of the PSC-initiated polymerization.

Activation parameters of the propagation were also calculated. Arrhenius plot of k_p values gave a well-correlated straight line whose slope gave an activation energy $\Delta E_p^{\neq}$ of 12 kcal/mol. The same magnitude of $\Delta E_p^{\neq}$ was obtained in the BF_3-epichlorohydrin initiated polymerization.¹¹⁾ This is again taken to support the bis-oxonium process **5b**.

For comparison, kinetics of the THF polymerization was carried out also by trifluoromethanesulfonic anhydride (**8**) initiator. The results are shown in Fig. 4. [P*] reached to the maximum within 2 min and kept constant thereafter. The maximum of [P*] was 85% of the charged initiator on the assumption that **8** is a bifunctional initiator. It should be noted that in the polymerization by **8** no termination took place even at a higher temperature, *e.g.*, **21** °C. From the relationships in Fig. 4 k_p values were calculated (Table 1).

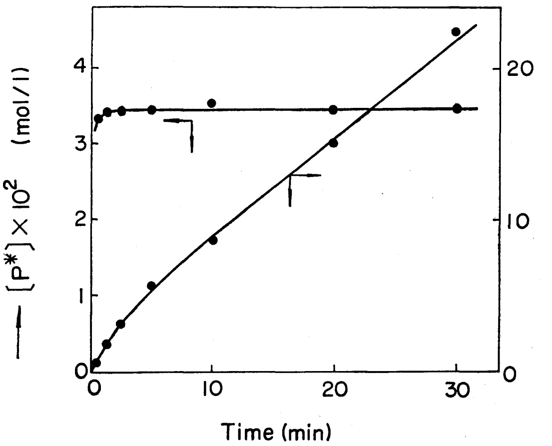
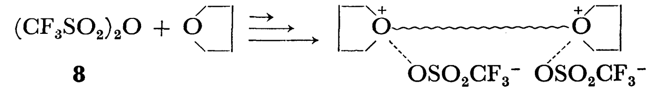


Fig. 4. Time-[P*], and time-conversion relationships in the THF polymerization initiated by trifluoromethanesulfonic anhydride at 21 °C in CH_2Cl_2: $[M]_0$, 9.9 mol/l; $[(CF_3SO_2)_2O]_0$, 0.0203 mol/l.

The k_p of **8** is smaller than that of PSC initiator. It is likely that the polymerization initiated by **8** proceeds *via* bis-oxonium type **9** as suggested previously by Smith and Hubin.¹²⁾



8 **9**

The PSC-initiated polymerization is characterized by a rapid initiation reaction as given in Table 1. The rate of the initiation is as fast as that of the propagation. Comparing k_i values between PSC and **6** of Eq. (11) PSC reacts with THF about 5.8×10^2 times faster than **6** at 1 °C. In addition the k_i value of PSC is also more than 10 times larger than that of triethyloxonium tetrafluoroborate in the THF polymerization.¹³⁾ The initiation rate of **8** is even faster than PSC. Therefore, the system initiated by **8** is recognized as that of a fast initiation but a slow propagation. This may account that polymer of very narrow molecular weight distribution ($M_W/M_N=1.08$) was obtained by **8** initiator.¹²⁾

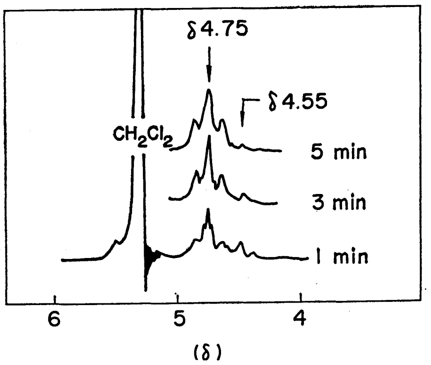


Fig. 5. NMR spectra of the reaction mixture of PSC with THF at 0 °C in CH_2Cl_2.
The molar ratio of PSC to THF was 1/5.

NMR Spectroscopy. To elucidate whether the ester type is involved or not, the reaction of THF with PSC in CH_2Cl_2 was examined by means of NMR spectroscopy. The THF to PSC molar ratio was 5/1. The reaction was carried out at 0 °C in an NMR sample tube under nitrogen. NMR spectra of the reaction system are shown in Fig. 5. After 1 min at 0 °C complex peaks appeared. Among them a triplet-like signal centered at δ 4.55 is reasonably assigned to α-methylene proton signal of the ester type **10** since that of an authentic tetramethylene bischlorosulfonate

$\sim\sim\sim CH_2OSO_2Cl$ $ClSO_2OCH_2CH_2CH_2CH_2OSO_2Cl$

10 **11**

11 appears at δ 4.60 in CH_2Cl_2 at 35 °C. Peaks centered at δ 4.75 is due to the α-methylene signal of oxonium type **12** whose assignment has already been established.⁴,⁷,¹⁴⁾ After 3 min at 0 °C, however, the

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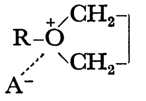
11) T. Saegusa, S. Matsumoto, M. Motoi, and H. Fujii, *Macromolecules*, **5**, 236 (1972).

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

13) T. Saegusa and S. Matsumoto, *J. Macromol. Sci. Chem.*, **A-4**, 873 (1970).

14) T. Saegusa, Y. Kimura, H. Fujii, and S. Kobayashi, *Macromolecules*, in press.



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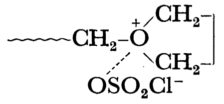

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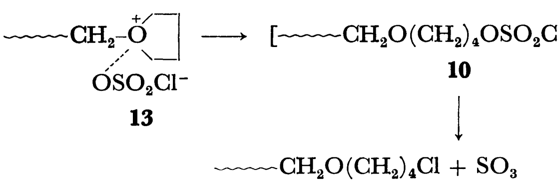
signal at δ 4.55 almost disappeared whereas the signal at δ 4.75 increased very much. It should be noted that the pattern of the signal at δ 4.75 changed from that of the reaction time of 1 min into a typical triplet-like one. The same triplet-like signal has been observed for the oxonium **13** at the same chemical shift.[4,14] After 5 min at 0 °C the ester signal has completely disappeared and only the oxonium signal was observed.

These findings indicate that the ester type species **10** converted into the oxonium species **13** at a very early stage to produce bis-oxonium species **5b**. This means that the contribution of ester type species **5a** is very small throughout the propagation stage which is in accordance with the kinetic results. It is interesting to note that in the PSC-initiated polymerization the reactivity of the ester involved at a very early stage is much enhanced probably due to the neighboring oxonium group.

Termination Mechanism. As seen in Fig. 1 considerable termination takes place at 21 °C in the PSC-initiated polymerization. Therefore, a reference reaction was carried out to examine the termination mechanism. At −78 °C THF was added to PSC in CH_2Cl_2 at a molar ratio of THF to PSC of 3: 1. The reaction system was allowed to warm up gradually to 25 °C and kept for 20 hr at this temperature. Then, the reaction mixture was treated with sodium phenoxide under the phenoxyl end-capping reaction conditions. White waxy polymer was obtained after work-up. The polymer was analyzed by elemental analysis, molecular weight measurement, iodometry, IR and NMR spectroscopy.

The results of elemental analysis was as follows: C, 66.56; H, 8.82 and Cl, 10.6%, respectively. The iodine value was null, *i.e.*, the polymer has no olefinic group. The molecular weight measurement by vapor pressure osmometry gave 309. From these data the polymer composition was proposed as $(C_6H_5)_{1.07}(OC_4H_8)_{2.68}Cl_{0.95}$ for the polymer. In addition, the NMR measurement of the polymer gave a polymer composition of $(C_6H_5)_{1.01}(OC_4H_8)_{2.6}$ from an integral ratio of phenyl protons *vs.* aliphatic protons. The IR spectrum of the polymer showed an absorption band at 650 cm^{-1} due to C–Cl stretching indicative of the presence of alkyl chloride.

Based on the above findings the termination mechanism is reasonably formulated as Eq. (13) which involves the nucleophilic attack of chloride anion of the counterion on the α-carbon of oxonium **13** with the liberation of SO_3. In this process it is not clear if the ester type intermediate **10** is involved or not. The termination of the PSC-initiated polymerization is in sharp constrast to that of the trifluoromethanesulfonic anhydride **8** initiated one where no termination was observed even at a higher temperature of 21 °C. This is obviously due to the stability difference between the counter anions, OSO_2Cl^- and $OSO_2CF_3^-$.



(13)

Experimental

Materials. The THF monomer and methylene dichloride solvent were commercial reagents and were purified in the same manner as described previously.[5,8] PSC was prepared by the reaction of sulfur trioxide with carbon tetrachloride according to the literature procedure,[15] bp 147 °C (lit,[15] 147—148 °C). Trifluoromethanesulfonic anhydride **8** was prepared by the dehydration of trifluoromethanesulfonic acid with excess phosphorus pentoxide,[16] bp 84 °C (lit,[12] 84 °C).

Tetramethylene bischlorosulfate **11** was prepared by the following procedure. To 0.1 mol of 1,4-butanediol in 10 ml of CH_2Cl_2 0.26 mol of sulfuryl chloride in 30 ml of CH_2Cl_2 was added dropwise at −20 °C. During the addition nitrogen gas was bubbled into the reaction mixture to remove sulfur dioxide and hydrogen chloride in the system. The addition took 20 min. Then, the reaction mixture was gradually warmed up to 0 °C, and kept for 4 hr at 0 °C and for 12 hr at −78 °C. A white solid precipitated. The solid was isolated and recrystallized from CH_2Cl_2, mp 49—50 °C. The NMR spectrum in CH_2Cl_2 showed two triplet-like signals centered at δ 4.60 (4H) and at δ 2.06 (4H).

Polymerization Procedure and Determination of [P].* Polymerization was carried out in CH_2Cl_2 solution under nitrogen. The reaction was initiated with the addition, at polymerization temperature, of a CH_2Cl_2 solution of PSC to a monomer solution. After a desired time of reaction, the polymerization system was short stopped by the addition of a 0.5 mol/l THF solution of sodium phenoxide. The procedure for the determination of [P*] was the same as that of the reported previously.[4,7]

The analogous procedures were taken in the polymerization of trifluoromethanesulfonic anhydride initiator.

NMR Measurement. To 0.03 mol of THF monomer in 2 ml of CH_2Cl_2 0.006 mol of PSC in 1 ml of CH_2Cl_2 was added with vigorous stirring at −78 °C under nitrogen. A portion of the reaction mixture was transferred into an NMR sample tube by using a hypodermic syringe at −78 °C. Then, the NMR spectrum was recorded at 0 °C on Hitachi R-20B NMR spectrometer.

Molecular Weight Determination. The molecular weight of the polymer was measured by a vapor pressure osmometer (Hitachi Perkin-Elmer model 115) in benzene at 35 °C.

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15) M. Sveda, "Inorganic Syntheses," Vol. 3, p. 124 (1950).

16) T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, **1957**, 4069.