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Time and Temperature Dependence of Macro-ion—Macro-ester Equilibrium in the Cationic Polymerization of Tetrahydrofuran by $HOSO_2F$*

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ABSTRACT

Reactivity and equilibrium of two active species–tertiary oxonium ion (TOI) and superacid ester (SAE)–in the system of cationic polymerization of tetrahydrofuran (THF) initiated

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*Dedicated to Prof. C. H. Bamford on the happy occasion of his 65th birthday.

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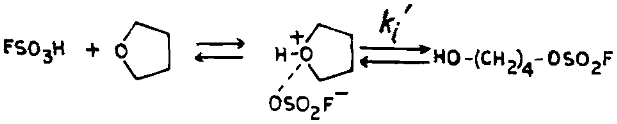
by fluorosulfonic acid (FSO_3H) in dichloromethane has been studied. In the given system, it was found that TOI is mainly responsible for the polymerization at the initial stage; however, the concentration of TOI decreases rapidly with the progress of polymerization and finally becomes almost untraceable. On the other hand, [SAE] monotonically increases as the polymerization proceeds. The stability of TOI appears less than that of SAE under the given reaction conditions. Results demonstrate that both the progress of polymerization and increase in temperature favor the formation of SAE.

INTRODUCTION

The polymerization of cyclic ethers, especially, that of tetrahydrofuran (THF) has received considerable attention recently [1-3]. The polymerization kinetics of THF initiated by superacid and their ester derivatives have been studied on the basis of direct measurement of the propagating species by proton [4-8], fluorine [9-10], and carbon [11] NMR spectroscopy. In these systems, the existence of an equilibrium between the active species, macro-ion and macro-ester, has been proposed [6, 7]. Both of the active species can be directly observed in high resolution proton NMR spectra. Considering the presence of such an equilibrium [Eqs. (1)-(6)],

Initiation:



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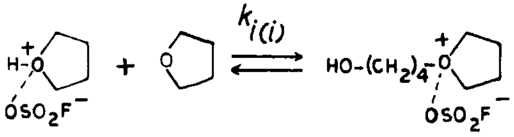

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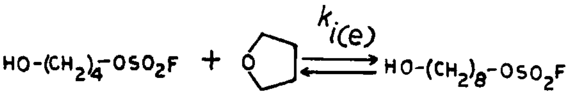

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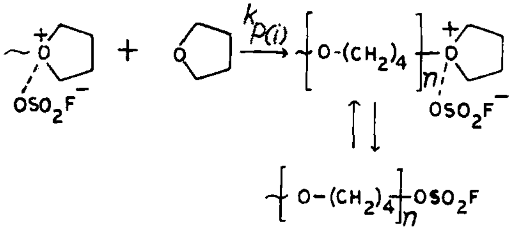

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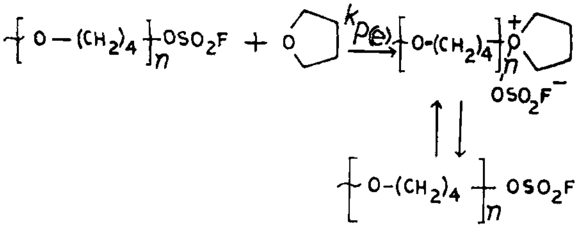

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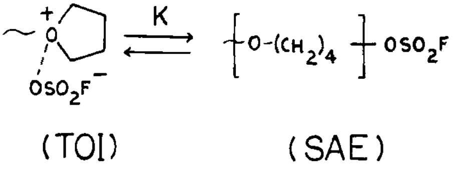

(6)

it has been assumed that the rate constant of propagation due to macro-ion $k_{p(i)}$ is much higher than that of macro-ester $k_{p(e)}$ [6-9]. It has also been reported [8, 9] that the propagation in media such as CH_2Cl_2, $CHCl_3$, or benzene, as well as in polar solvents such as CH_2NO_2 and $C_6H_5NO_2$, is predominantly promoted by the macro-ion [9]. However, quite recently Saegusa et al. [10] suggested that in the polymerization of THF in CCl_4 initiated by $EtOSO_2CF_3$ the rate constant of propagation due to macro-ester is much higher than assumed and is comparable to $k_{p(i)}$. Thus, it has not been completely clarified which form of the active species is responsible for the chain propagation in the medium of CH_2Cl_2.

This paper is concerned about the reactivity and equilibrium of two active species—tertiary oxonium ion (TOI) and superacid ester (SAE). It has been found that the stability of these active species is closely related not only to the solvent as mentioned earlier [9] but also to the conversion and temperature.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF), Merck analytical grade, was dried on potassium at its boiling temperature by refluxing for a period of 2 days in nitrogen atmosphere. After the removal of one-third by distillation, the middle fraction was collected from the deep blue-colored solution of THF in potassium and benzophenone.

Dichloromethane (CH_2Cl_2), Merck analytical grade, containing about 0.3% ethanol was treated with calcium chloride and allowed to stand overnight before filtration and subsequent purification by fractional distillation.

Fluorosulfonic acid (FSO_3H), by Fluka pure grade, was used without further purification.

The Meerwein salt (triethyloxonium tetrafluoroborate) was prepared by the interaction of epichlorohydrin and boron trifluoroetherate [12].

The superacid ester (propyl fluorosulfonate) was prepared by the simple condensation reaction of propyl alcohol and fluorosulfonic acid [13].

Polymerization

Polymerization was carried out under a nitrogen atmosphere in a three-necked flask. The reactants were added in the order: solvent, initiator, and monomer. The solution was stirred continuously with the aid of a magnetic stirrer and kept cool with a Dry Ice-acetone bath. The temperature of the reaction mixture was never allowed to rise above -20°C during the addition of the reactants.

NMR Spectroscopy

After mixing the reactants, about 1.0 ml of the polymerization mixture was transferred into an NMR tube and placed immediately into the spectrometer and a scan was taken at 10-15 min intervals. Later scans were taken at longer intervals. The samples were preserved at the specified temperature inside constant temperature chambers throughout the period of the study of the reaction. Concentrations of TOI, SAE, monomer, and polymer were determined by tracing the respective peaks on a uniformly thick paper with a constant moisture content, followed by cutting and weighing the paper by an analytical balance. The NMR spectra were recorded with Varian A-60, (60 MHz) or Brucker 60, (60 MHz) instruments.

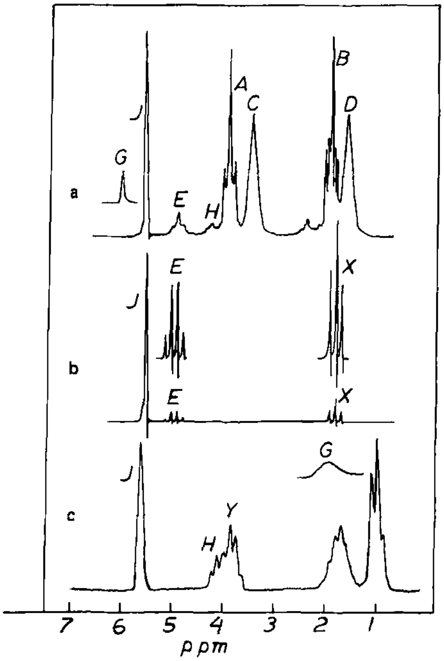

FIG. 1. ^{1}H-NMR spectra of (a) the polymerization mixture of THF in dichloromethane after 20 hr at 0°C, [FSO_3H] = 1.10 mole/liter, [THF] = 7.7 mole/liter; triethyloxonium tetrafluoroborate (Meerwein salt) in dichloromethane; (c) the reaction mixture of propanol and fluorosulfonic acid in dichloromethane.

RESULTS AND DISCUSSION

Figure 1a shows an example of a ^{1}H-NMR spectrum of the system which was taken 20 hr after mixing of the reactants at 0°C. As well established, the signals A and B are due to α- and β-methylene protons of tetrahydrofuran monomer, signals C and D are due to α- and β-methylene protons of the polymer. It is suggested [6, 7] that peak E is due to α-methylene protons of the propagating tertiary oxonium species (TOI). Signal H, which developed slowly, is assigned [6, 7] to the α-methylene protons of the superacid ester of the polymer chain (SAE). Signals, especially that of TOI and SAE, were also confirmed by using Meerwein salt [12] (triethyloxonium tetrafluoroborate, $(C_2H_5)_3O^+BF_4^-$) and superacid ester [13] (propyl fluorosulfonate, $CH_3–CH_2–CH_2–OSO_2F$) as model compounds for TOI and

SAE, respectively. NMR spectra of these compounds are also presented in Fig. 1.

Assignments of these peaks are in agreement with those proposed earlier by other workers. However, it should be noted that the chemical shift of each peak changes continuously with time and concentration of the reactants. Thus, it is not possible to generalize the chemical shift of individual species unless concentration of the reactants and time period of reaction is mentioned. Table 1 shows some changes of chemical shift of various species with the progress of the reaction. The reason for this change in observed chemical shift is not clear but may be attributed to the change of polarity of the reaction medium.

This kind of movement of chemical shift does not, however, complicate the identification and subsequent computation, since the movement of the peaks generally occurs in the up-field direction and none of the peaks overlap.

The time-conversion curves for different initiator concentrations are given in Fig. 2. It can be seen that most of the polymerization occurred in the beginning, and equilibrium was eventually approached. The concentration of different active species as computed from the NMR-spectra is plotted as a function of time in Fig. 3. The concentration of TOI (Fig. 3a) increases in the early period of the reaction, decreasing later with the progress of the polymerization and finally becoming untraceable in the NMR spectra. On the other hand, the rate of formation of SAE, as shown in Fig. 3b, is slow in the beginning, increases gradually, and reaches a plateau at about 200 hr. This situation can be seen more clearly at higher temperature (Fig. 4). For example, at 38°C, TOI attains maximum growth within 20 min, then disappears rapidly, while SAE increases almost linearly until reaching equilibrium. From Figs. 3 and 4, it appears that increasing temperature is unfavorable for TOI in the reaction mixture.

Figure 5 presents the time dependence of the molar fraction of TOI. It is apparent that the molar ratio of TOI and SAE at 0°C reached a constant value of 48:52 after a short period of reaction. The presence of a similar equilibrium was also observed in CH_2Cl_2, $CHCl_3$, CCl_4, and in other solvents initiated by $EtOSO_2CF_3$ at 0°C [8-10].

In the early period of the reaction, when other competitive and consecutive reactions are neglected, the rate equation for the initiation is given by Eq. (7):

$$-d[I]/dt = k_i[I][M] \tag{7}$$

where I and M denote FSO_3H and THF, respectively and k_i is the rate constant of initiation and $k_i = k_{i(i)} + k_{i(e)}$.

TABLE 1. Observed Chemical Shift of Different Species in the THF-FSO_3H Polymerization Mixture in Dichloromethane[a]

Time (hr + min)	[FSO_3H] (mole/liter)[b]	[CH_2Cl_2] (mole/liter)	Chemical shift δ (ppm)							
			A	B	C	D	E	H	J	G
2 + 55	1.78	4.67	4.13	2.07	3.57	1.68	5.10	4.42	5.74	15.80
20 + 25	1.78	4.67	3.94	1.98	3.49	1.63	4.93	4.28	5.57	14.03
72 + 10	1.78	4.67	3.86	1.90	3.45	1.62	4.87	4.29	5.46	13.45
2 + 50	1.14	5.24	4.03	2.02	3.58	1.68	5.12	4.32	5.73	15.97
20 + 25	1.14	5.24	3.85	1.90	3.43	1.61	4.92	4.27	5.52	13.94
72 + 05	1.14	5.24	3.80	1.89	3.44	1.60	4.89	4.30	5.49	13.30
2 + 35	0.89	5.47	4.02	2.00	3.58	1.67	5.12	4.30	5.73	15.83
20 + 40	0.89	5.47	3.83	1.92	3.45	1.63	4.93	4.29	5.53	13.89
72 + 20	0.89	5.47	3.80	1.89	3.45	1.62	4.89	4.32	5.50	13.23
2 + 30	0.62	5.72	3.95	1.95	3.57	1.67	5.20	4.29	5.73	15.79
20 + 15	0.62	5.72	3.83	1.89	3.45	1.62	4.97	4.29	5.53	13.83
71 + 55	0.62	5.72	3.79	1.88	3.44	1.62	4.93	4.33	5.52	13.20
2 + 35	0.33	5.98	3.89	1.93	3.57	1.68	5.22	4.15	5.73	15.67
20 + 10	0.33	5.98	3.75	1.85	3.43	1.62	4.97	4.28	5.52	13.79
71 + 50	0.33	5.98	3.84	1.88	3.52	1.65	5.08	4.44	5.64	13.40
2 + 30	0.17	6.14	3.87	1.92	3.56	1.67	5.11		5.73	14.40
20 + 15	0.17	6.14	3.73	1.85	3.43	1.62	4.91	4.05	5.51	13.67
72 + 00	0.17	6.14	3.79	1.88	3.49	1.64	5.04	4.39	5.59	13.09

[a] THF = 7.31 mole/liter; internal standard TMS.

[b] Concentration of FSO_3H mentioned in the table is the initial concentration.

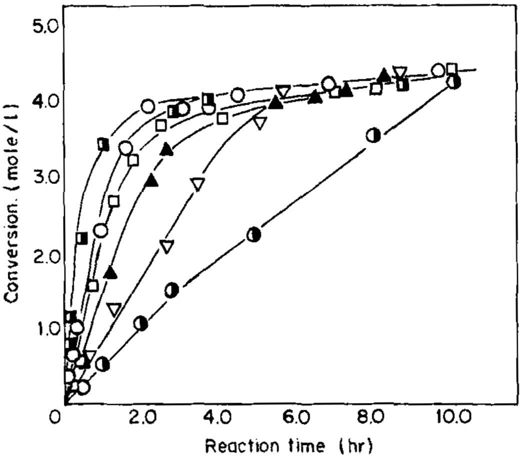

FIG. 2. Time-conversion curves of the polymerization of THF at 0° C at various [FSO_3H]: (◧) 1.80; (○) 1.10; (□) 0.80; (▲) 0.54; (▽) 0.27; (◑) 0.14 mole/liter; [THF] = 7.7 mole/liter.

Integration of Eq. (7) yields

$$\ln([I]_0/[I]_t) = k_i \int_0^t [M]\,dt \tag{8}$$

where $[I]_0$ and $[I]_t$ are the concentrations of the acid initially and at any time t, respectively. A plot of ln $([I]_0/[I]_t)$ against $\int_0^t [M]\,dt$ gives a straight line, and k_i was calculated from the slope - $k_i = 0.57 \times 10^{-5}$ liter/mole-sec.

If we assume that the magnitude of $k_{p(e)}$ is much smaller than $k_{p(i)}$ as suggested by other authors, $k_{p(i)}$ can be evaluated according to Eqs. (9) and (10):

$$-d[M]/dt = k_{p(i)}[TOI]\left([M]_t - [M]_e\right) \tag{9}$$

$$\ln\{([M]_0 - [M]_e)/([M]_t - [M]_e)\} = k_{p(i)} \int_0^t [TOI]\,dt \tag{10}$$

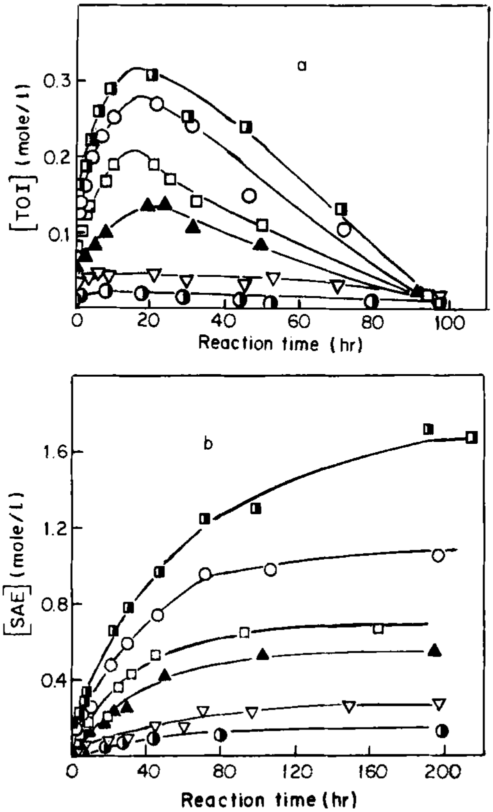

FIG. 3. Dependence of (a) [TOI] and (b) [SAE] on time at various concentrations of initiator. [Monomer] = 7.7 mole/liter, temperature: 0°C. Symbols are same as in Fig. 2.

A plot of the integrated value of [M] to that of [TOI] gives $k_{p(i)}$. A weighted average of the rate constant of propagation $k_{p(obs)}$ which is expressed by the Eq. was also calculated.

$$k_{p(obs)} = k_{p(i)}X_i + k_{p(e)}X_e \qquad (11)$$

where X_i and X_e are the molar fractions of TOI and SAE, respectively.

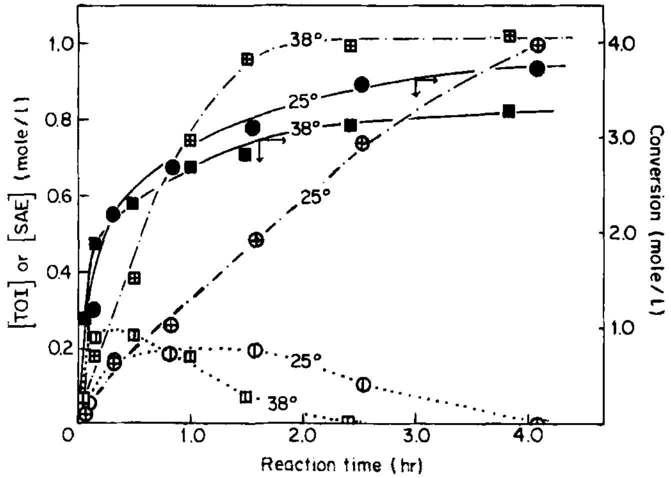

FIG. 4. Dependence of (···) [TOI], (-··-) [SAE], and (—) conversion on time at 25°C and 38°C. [FSO_3H] = 1.10 mole/liter; [THF] = 7.7 mole/liter.

The values of $k_{p(obs)}$ and $k_{p(i)}$ thus obtained are 1.6×10^{-3} and 2.3×10^{-3} liter/mole-sec, respectively. Although a direct comparison cannot be made because of the possible presence of chain transfer in our system, our figures for the rate constants are almost the same as found with systems initiated by ester derivatives of the superacid [9, 10]. Results are summarized in Table 2.

TABLE 2. Rate Constants of Initiation (k_i), Observed Propagation $k_{p(obs)}$, and Propagation by TOI $k_{p(i)}$ of the Polymerization of THF in Dichloromethane Solution at 0° C

Initiator	$k_{(i)} \times 10^5$ (liter/ mole-sec)	$k_{p(obs)} \times 10^3$ (liter/ mole-sec)	$k_{p(i)} \times 10^3$ (liter/ mole-sec)	Reference
$HOSO_2F$	0.57	1.6	2.3	Present work
$MeOSO_2F$	3.90	1.7	--	[10]
$EtOSO_2F$	0.76	1.4	--	[10]
$EtOSO_2CF_3$	1.20	1.7	2.0	[9]

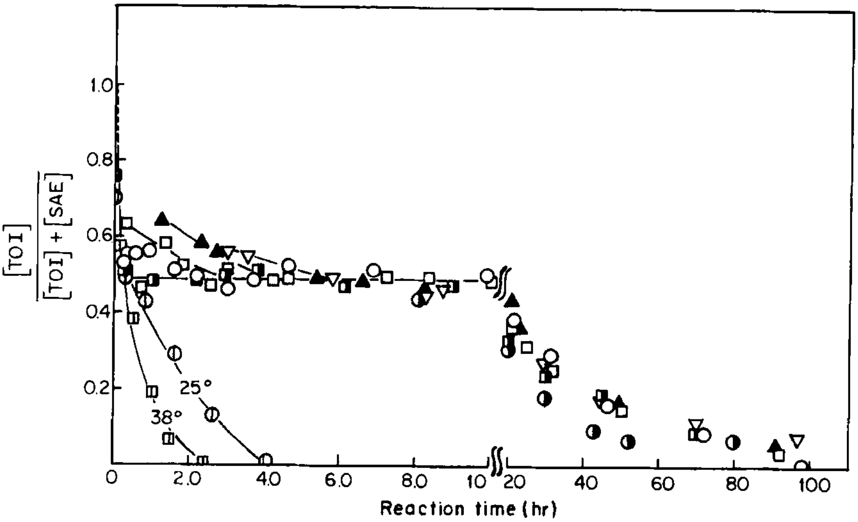

FIG. 5. Time dependence of molar fraction of TOI. Symbols are same as in Fig. 2.

It should be noted that the equilibrium in Eq. (6) is attained only after a definite period of reaction and at a low polymerization temperature (0° C), as shown in Fig. 5. At higher temperatures, (25° C and 38° C) no equilibrium is attained during the polymerization. In these cases the equilibrium between TOI and SAE in Eq. (6) is greatly shifted in the direction of TOI at the beginning of polymerization. These results suggest that polymerization in this region proceeds predominantly through TOI. A deviation from the equilibrium can be seen even in the polymerization at 0° C, especially in the early stages at lower concentrations of the initiator. As shown in Fig. 6, in cases of lower initiator concentration SAE could not be observed for an initial period of polymerization. It was found that $k_{p(obs)}$ calculated from the kinetic run where SAE is zero or very low agrees with values calculated after the formation of SAE. This findings supports the fact that $k_{p(e)}$ is indeed much smaller than $k_{p(i)}$, as assumed before. It is, therefore, quite reasonable that the addition of monomer after the attainment of the equilibrium monomer concentrations, $[M]_e$ did not give a rapid increase of molecular weight as indicated by Pruckmayr and Wu [4]. By that time, active species have been transformed to SAE, the reactivity of which is much less in comparison to that of TOI. Thus, it is possible under present reaction conditions that the contribution of SAE in the

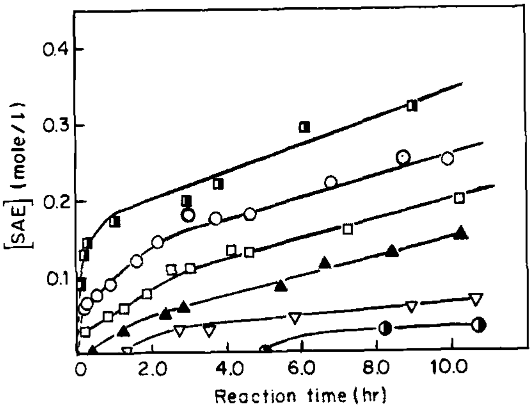

FIG. 6. Concentration of SAE as a function of time in the initial stage of the reaction. [THF] = 7.7 mole/liter; 0° C. Symbols and [FSO_3H] are same as in Fig. 2.

polymerization can be ignored not only because of its small value of $k_{p(e)}$ but also due to low concentration, at least, in the initial stages of polymerization (i.e., $X_e \simeq 0$). Thus $k_{p(obs)}$ in this region of polymerization becomes equal to $k_{p(i)}$.

The reason for the transformation of TOI to SAE at higher conversion is not yet clear. However, it could be related to the decrease of dielectric constant of the medium with the progress of the polymerization, since SAE should be more stable in a medium of low dielectric constant than TOI.

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