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Superacids and Their Derivatives. VI.[1] Kinetics of the Cationic Ring-Opening Polymerization of Tetrahydrofuran Initiated by Ethyl 2,4,6-Trinitrobenzenesulfonate

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Ethyl 2,4,6-trinitrobenzenesulfonate ("trinitate", EtOTn) was found to induce the ring-opening polymerization of tetrahydrofuran (THF). Kinetic studies of the THF polymerization by EtOTn initiator were carried out in CH_2Cl_2 solution by NMR spectroscopy. The instantaneous concentrations of the counteranion of the propagating oxonium species (**1**) and monomer were directly determined at the same time by the NMR measurement. The rate constants of initiation (k_i) and propagation ($k_{p(i)}$) due to **1** were obtained. Upon the view of $k_{p(i)}$ values with various initiators, it was concluded that the $k_{p(i)}$ values are changed significantly depending on the nature of the counteranion.

In recent several studies on the cationic ring-opening polymerization of tetrahydrofuran (THF) superacids and their ester or anhydride derivatives have been employed as initiator.[2–7] In these studies trifluoromethanesulfonic (TfOH),[2,3,5–7] fluorosulfuric (FSO_3H),[2,7] and chlorosulfuric acids ($ClSO_3H$)[2,4] were used as the superacid component. Primary alkyl esters of these acids are known to form oxonium ions with tetrahydropyran.[8] Generally, initiators are effective for the cationic ring-opening polymerization of THF, when they can form stable trialkyl oxonium ions. 2,4,6-Trinitrobenzenesulfonic acid (TnOH) is well known to be an only acid among organic acids except for TfOH to produce a stable trialkyl oxonium ion in the reaction with ether.[9,10] As an extension of our studies on the superacids and their derivatives, therefore, we examined the THF polymerization initiated by ethyl 2,4,6-trinitrobenzenesulfonate which we wish to abbreviate as "ethyl trinitate" (EtOTn). It was found that EtOTn induced the THF polymerization. Now, we wish to report kinetic results of this system. Kinetic analysis was performed by NMR spestroscopy.

Results and Discussion

NMR Spectroscopy. Figure 1 shows an example of NMR spectrum of the THF polymerization with EtOTn initiator after 60 min at 20 °C in CH_2Cl_2. The initial concentrations of monomer $[M]_0$ and of initiator $[I]_0$ were 6.78 and 0.167 mol/l, respectively. Among the signals in Fig. 1 peaks A at δ 8.84 and B at δ 8.56 should be noted. They are assigned respectively to aromatic protons (2H) of EtOTn (peak A) and of trinitate anion (peak B). The assignment of peak B is supported by the fact that the aromatic protons of triethyloxonium trinitate appears at the same chemical shift of peak B (See Experimental). The pattern of signals C–I is very similar to that of the polymerization mixture by EtOTf initiator, whose signal assignments were already performed.[2] Therefore, only the result of the assignment is shown here as follows;

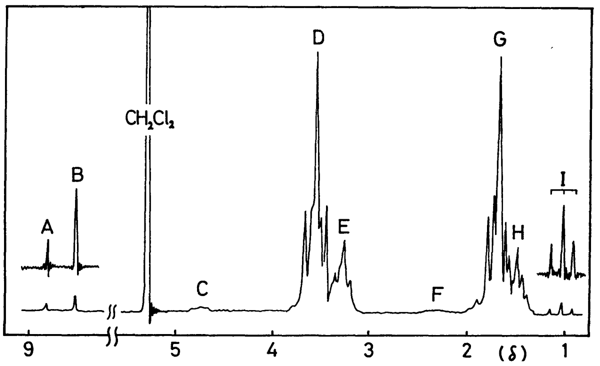
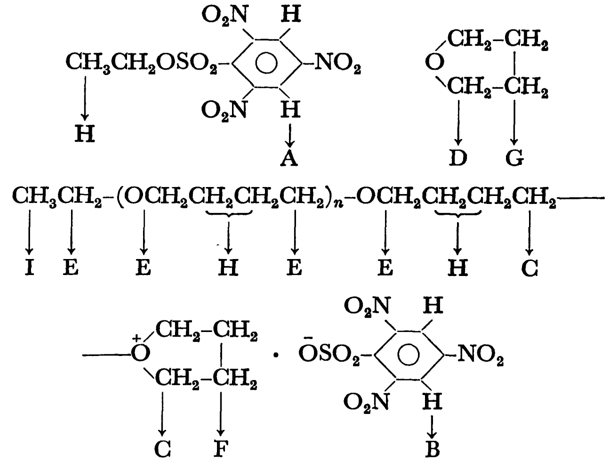


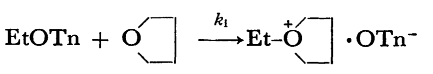
Fig. 1. NMR spectrum of the THF polymerization system initiated by ethyl 2,4,6-trinitrobenzenesulfonate in CH_2Cl_2 after 60 min at 20 °C.



A quartet signal due to methylene protons of EtOTn should appear around at δ 4.8—4.3. However, it is not detected clearly in Fig. 1 because of the low concentration of EtOTn.

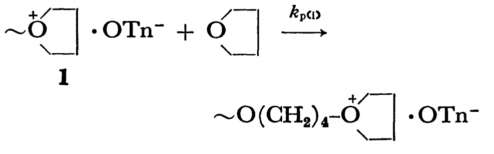
Kinetics. The course of the THF polymerization by EtOTn is given by the following reactions (Eqs. (1) and (2)).

Initiation



(1)

Propagation



(2)

Based on the above reactions of a bimolecular mechanism, the integrated rate equations of initiation and propagation are given by Eqs. (3) and (4), respectively[2,3]

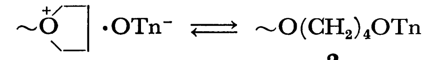
$$\ln \frac{[\mathrm{I}]_{t_1}}{[\mathrm{I}]_{t_2}} = k_\mathrm{i}\int_{t_1}^{t_2}[\mathrm{M}]\mathrm{d}t \tag{3}$$

and

$$\ln \frac{[\mathrm{M}]_{t_1}-[\mathrm{M}]_\mathrm{e}}{[\mathrm{M}]_{t_2}-[\mathrm{M}]_\mathrm{e}} = k_{\mathrm{p(i)}}\int_{t_1}^{t_2}[\mathrm{O}^+]\mathrm{d}t \tag{4}$$

where k_i and $k_{\mathrm{p(i)}}$ denote the rate constants of initiation and of propagation due to the oxonium ion species **1**, $[\mathrm{O}^+]$ is the concentration of the oxonium propagating species, and [I], [M], and $[\mathrm{M}]_\mathrm{e}$ are respectively the initiator, monomer, and equilibrium monomer concentrations.[2]

The peak area of B was equal to two-third of that of triplet peak I throughout the kinetic run, *i.e.*, the molar ratio between the counteranion (OTn^-) of the propagating polymer end **1** and ethyl group at the other polymer end was held unity, *i.e.*, $[\mathrm{O}^+]=[\mathrm{I}]_0-[\mathrm{I}]$. This indicates that the polymerization system was of living character without termination and in addition that the propagating end was mainly the oxonium ion type of **1** in CH_2Cl_2 solution, although the ester type **2** of the propagating end might be involved, as observed in the case of the EtOTf–initiated system.[3] However, the characteristic signal due to α-methylene protons of ~~~CH_2OTn **2** at δ 4.2 region[2] was not detected. It was difficult to determine precisely the concentration of the propagating species **1** directly from the oxonium proton peaks C and F, since both of them were very broad due to the low concentration of **1**.



1 **2**

The instantaneous concentrations of EtOTn and **1** were determined by monitoring peaks A and B, respectively. The variation of the monomer concentration was obtained from peaks D and E. It should be noted that both the concentrations of the counteranion of the propagating species **1** and of monomer could directly be determined at the same time by the NMR measurement alone. Figures 2 and 3 show plots of Eqs. (3) and (4), respectively, the slopes of which gave the values of k_i and $k_{\mathrm{p(i)}}$. Similarly, the kinetics were carried out also at 0 and 10 °C in CH_2Cl_2. These results and activation parameters of initiation and propagation are shown in Table 1. The data scattered considerably because $[\mathrm{I}]_0$ was low due to the reduced solubility of EtOTn in the system. $[\mathrm{I}]_0$ was six times less than that of the previous kinetics of the EtOTf-initiated system.[2,3] The $k_{\mathrm{p(i)}}$ value (0.70×10^{-3} l/mol·s at 0 °C) of EtOTn initiator is smaller than that of EtOTf (2.0×10^{-3} l/mol·s at 0 °C).[3] The values of $\Delta H^{\ne}$ and $\Delta S^{\ne}$ are also very low in both initiation and propagation. This finding may be related to the bulkiness of OTn group; in both reactions of (1) and (2) the bulky OTn group causing an unfavorable geometry at the transition state (lower $\Delta S^{\ne}$ value).

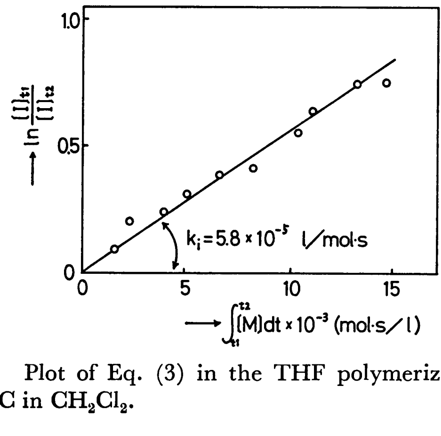


Fig. 2. Plot of Eq. (3) in the THF polymerization at 20 °C in CH_2Cl_2.

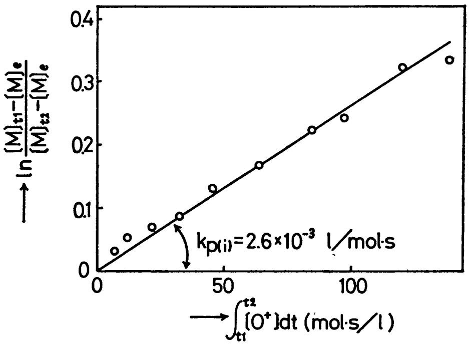


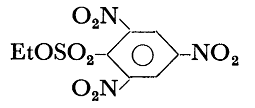
Fig. 3. Plot of Eq. (4) in the THF polymerization at 20 °C in CH_2Cl_2.

TABLE 1. RATE CONSTANTS OF INITIATION (k_i) AND OF PROPAGATION ($k_{\mathrm{p(i)}}$) AND ACTIVATION PARAMETERS IN THE THF POLYMERIZATION BY EtOTn INITIATOR IN CH_2Cl_2 SOLUTION[a]

Temp (°C)	$10^3\cdot k_{\mathrm{p(i)}}$ (l/mol·s)	$10^5\cdot k_\mathrm{i}$ (l/mol·s)
0	0.70	1.6
10	1.5	2.8
20	2.6	5.8
$\Delta H^{\ne}$(kcal/mol)	9±1	8±2
$\Delta S^{\ne}$(e.u.)	−41±3	−54±5

a) $[\mathrm{M}]_0=6.78$ mol/l, $[\mathrm{I}]_0=0.167$ mol/l.

TABLE 2. RATE CONSTANTS OF PROPAGATION ($k_{\mathrm{p(i)}}$) BY VARIOUS INITIATORS AT 0 °C

Initiator	$10^3\cdot k_{\mathrm{p(i)}}$ (l/mol·s)	$[\mathrm{M}]_0$ (mol/l)	Method[d–f]	Ref.
	0.70	6.78[b]	d	This work
$EtOSO_2F$	0.8	7.70[b]	d	2
$EtOSO_2Cl$	1.5	7.70[b]	d	2
$EtOSO_2CF_3$	2.0	7.70,[b] 5.30[b]	d,e	2, 3
$Et_3O^+BF_4^-$	3.7	6.3[b]	f	11
BF_3–ECH[a]	4.1	6.3[b]	f	12
BF_3–ECH[a]	4.6	12.6[c]	f	12
$SnCl_4$–ECH[a]	6.7	12.6[c]	f	12
$AlEtCl_2$	7.8	12.6[c]	f	12

a) ECH: epichlorohydrin as a promoter. b) Solution polymerization in CH_2Cl_2. c) Bulk polymerization. d) ^{1}H NMR spectroscopy. e) ^{19}F NMR spectroscopy. f) Phenoxyl end-capping method.[13]

As to the effect of the counteranion on the rate of the THF polymerization there are several data available. Table 2 lists the rate constants of propagation by various initiators, all of which were determined recently in our laboratory.[11–13] All the rate constants of propagation in Table 2 represent those due to the oxonium ion propagating species ($k_{p(i)}$). It has been presented that the value of $k_{p(i)}$ was not changed depending on the nature of the counteranion.[6,14] However, the $k_{p(i)}$ values in Table 2 vary from 0.70×10^{-3} to 7.8×10^{-3} l/mol·s at 0 °C. Our view is, therefore, that the $k_{p(i)}$ value changes significantly depending on the counteranion derived from the initiator.

Experimental

Reagents. THF and CH_2Cl_2 were purified as previously reported.[2,3] EtOTn was prepared according to Pettitt and Helmkamp[9,10] as follows. A commercial reagent of TnONa·$2H_2O$ was converted by concd HCl solution to the free acid of TnOH, mp 172—174 °C (lit,[10] 174—177 °C). A solution of 2.0 g (6.8 mmol) of TnOH dissolved in hot 15 ml of ethyl acetate was then kept at 5—10 °C. To this solution was added 1.2 g (6.3 mmol) of triethyloxonium tetrafluoroborate[15] in 2 ml of nitromethane and cooled in an ice-bath for 5 min with stirring. The mixture was poured into 25 ml of anhydrous ether. White precipitate was collected by filtration. The precipitate was washed with 5 ml of ether, finally with 3 ml of petroleum ether, and dried *in vacuo* to give 1.6 g of Et_3O^+ OTn^-, mp 88—90 °C (lit,[9] 88—89 °C). NMR (CH_3NO_2); δ 8.55 (sharp s, 2,4,6-$(NO_2)_3C_6H_2$–, 2H), 4.83 (q, $(-CH_2-)_3$ O^+ overlapping partly with CH_3NO_2), and 1.66 (t, $(CH_3-)_3$, 9H). EtOTn was obtained by the thermal decomposition of Et_3O^+ OTn^- at 40—50 °C under the reduced pressure (~0.5 mmHg) for 80 hr, mp 140—141 °C (lit,[9] 142—144 °C). NMR (CH_3NO_2); δ 8.85 (sharp S, 2,4,6-$(NO_2)_3C_6H_2$–, 2H) and 1.46 (t, CH_3–, 3H). The methylene proton signal overlapped with that of CH_3NO_2.

Kinetic Procedures. All operations were carried out under nitrogen. In an NMR sample tube were placed at −78 °C 24.2 mg (0.754 mmol) of EtOTn, 0.250 ml of THF, and 0.200 ml of CH_2Cl_2. The tube was sealed at the same temperature and shaked vigorously at room temperature until EtOTn was completely dissolved to give homogenous solution. The tube was then put into the NMR probe insert which was kept constant at the reaction temperature. Up to this step the reaction proceeded to a small extent. Therefore, this moment was taken to be t_1 when carrying out the kinetic analyses according to Eqs. (3) and (4). Then, the reaction was monitored by recording the spectrum several times on a Hitachi R-20B NMR spectrometer (60 MHz). The reaction temperature was kept constant within ±1 °C and the experimental error of the integration was within ±5%.

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