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Rates of Elementary Reactions in Cationic Polymerization of Tetrahydrofuran Catalyzed by Trialkyloxonium Salts

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SUMMARY

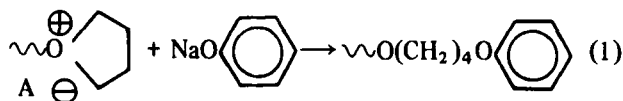
Kinetic studies are reported on the polymerization of tetrahydrofuran by trialkyloxonium salts. Triethyloxonium tetrafluoroborate (Et_3OBF_4) and -tetrachloroaluminate ($\text{Et}_3\text{OAlCl}_4$) were employed as the initiator. At various times the polymerization system was treated with excess sodium phenoxide. The propagating species of polymer and the remaining triethyloxonium of initiator were converted quantitatively into the corresponding phenyl ethers. Phenetole from the remaining catalyst was successfully separated from the polymer phenyl ether by vacuum distillation. The concentrations of propagating species and the remaining initiator were determined separately by UV analysis of the corresponding phenyl ethers. In the polymerization by Et_3OBF_4 a slow termination occurs to destroy the propagating species, i.e., this polymerization is not strictly a living system. The polymerization by $\text{Et}_3\text{OAlCl}_4$, on the other hand, is characterized by a very rapid termination. On the basis of the time-[P*] and time-conversion data in the polymerization by Et_3OBF_4 , the propagation rate constant k_p was calculated according to

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

where $[M]_t$'s and $[M]_e$ are the instantaneous and the equilibrium monomer concentrations, respectively. In addition, the rate constants of initiation (k_i) and termination (k_t) for the two initiators were roughly estimated on the basis of the above kinetic data. The k_t values for them were very much different from each other, whereas the k_i values were almost the same.

INTRODUCTION

The present paper describes kinetic studies of the polymerization of tetrahydrofuran (THF) initiated by trialkyloxonium salt. Triethyloxonium tetrafluoroborate (Et_3OBF_4) and tetrachloroaluminate ($\text{Et}_3\text{OAlCl}_4$) were employed as the initiators. The kinetic analysis is based on the determination of the instantaneous concentration of propagating species $[\text{P}^*]$ by means of the phenoxy end-capping method [1-3], in which the propagating species is quantitatively converted into the corresponding phenyl ether by treatment with excess sodium phenoxide (Eq. 1), and the phenyl ether group at the end of polymer molecule is determined by UV spectroscopy.



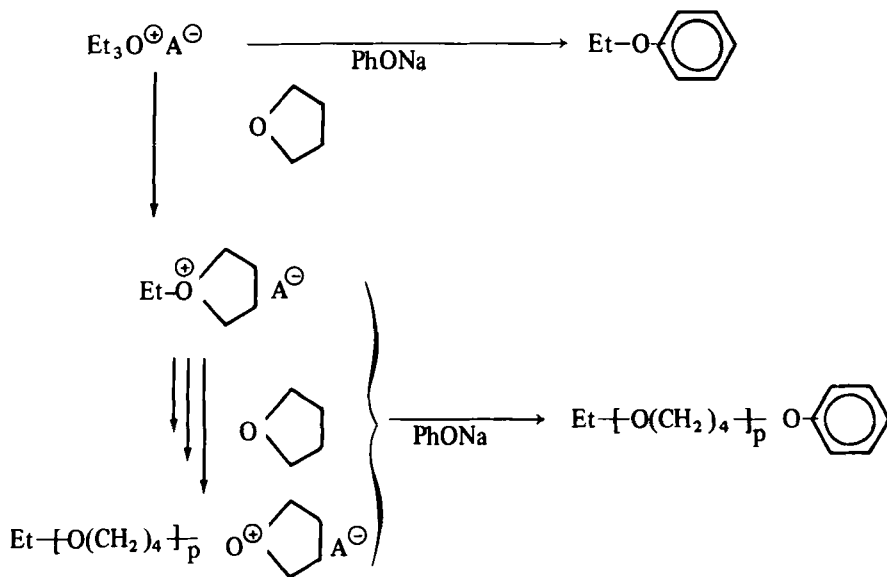
As to the oxonium-initiated polymerization of THF, several kinetic studies have been reported [4-7] in which triethyloxonium tetrafluoroborate (Et_3OBF_4) and hexachloroantimonate ($\text{Et}_3\text{OSbCl}_6$) were employed as the initiators. In these previous studies, a mechanism of living polymerization without termination was erroneously assumed and the molar concentration of the initiator was taken as the value of $[\text{P}^*]$.

In the present study, $[\text{P}^*]$ as actually determined was differentiated from the initiator concentration. The time- $[\text{P}^*]$ relationship clearly demonstrated a slow termination in the tetrafluoroborate-initiated polymerization and a rapid termination in the tetrachloroaluminate-initiated polymerization. The combination of the time-conversion and the time- $[\text{P}^*]$ relationships enabled the determination of reliable values of the propagation rate constant k_p . In addition, the $[\text{P}^*]$ -time relation gave approximate values of the rates of initiation and termination reactions. The results are quite important in any consideration of the effect of counter anions upon the initiation, propagation, and termination reactions because the initiation is simple and the structure of the counter anion is comparatively clear in these cases.

RESULTS AND DISCUSSION

Method of [P*] Determination

The procedure for [P*] determination reported in our previous studies [1-3] was modified because the phenoxy end-capping treatment produces two phenyl ethers, the polymer phenyl ether from the propagating species and phenetole from the initiator (Scheme 1).



It has been established that the conversion of $\text{Et}_3\text{O}^{\oplus}$ into phenetole is quantitative under the present experimental conditions [1, 2].

Phenetole should be separated from the polymer phenyl ether. The separation was successfully carried out by vacuum distillation with the aid of Decalin as the distillation entrainer (see Experimental Section). Only phenetole was evaporated under the conditions of the present experiment.

The phenyl ether from the propagating species, even the species having a degree of polymerization of 1, was not evaporated. This was confirmed by reference experiments using mixtures of poly-THF and one of two phenyl ethers, phenetole and $\text{CH}_3\text{O}(\text{CH}_2)_4\text{OC}_6\text{H}_5$. The results are shown in Table 1.

As can be seen in Table 1, phenetole was removed almost completely

Table 1. Removal of Phenetole by Distillation with Decalin^a

Phenyl ether	10 ⁴ mole	After distillation ^b	
		10 ⁴ mole	%
EtOPh	2.1	<0.02	<1
EtOPh	2.2	<0.02	<1
CH ₃ O(CH ₂) ₄ OPh	2.4	2.4	100

^aSee Experimental Section.

^bThe amount of phenyl ether in the distillation residue.

from poly-THF by this procedure, whereas a model compound of phenyl ether of poly-THF having a degree of polymerization of 1 was not lost.

In the phenoxyl end-capping analysis of the polymerization system the amount of phenetole in the distillate corresponds to that of the remaining initiator of triethyloxonium salt, and the amount of phenyl ether in the distillation residue is equal to that of the propagating species.

Polymerization by Et₃OBF₄

Figure 1 shows the variations of [P*] (Curve 1) and of the

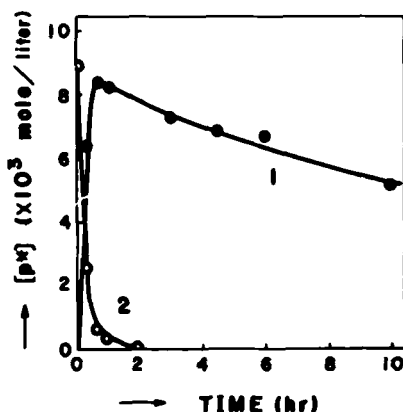


Fig. 1. Polymerization of THF by Et₃OBF₄: variations of [P*] (Curve 1) and of [Et₃O⁺] (Curve 2). Solution polymerization at 0°C. Solvent, CH₂Cl₂. [M]₀, 6.3 mole/liter [Et₃OBF₄]₀, 9.0 × 10⁻³ mole/liter.

concentration of the remaining $\text{Et}_3\text{O}^{\oplus}$ (Curve 2) in the course of the THF polymerization initiated by Et_3OBF_4 . The initiator was consumed fairly rapidly in an early stage of the polymerization with a corresponding increase of $[\text{P}^*]$. After about 1 hr, $[\text{P}^*]$ attained a maximum value that was close to the initial concentration of Et_3OBF_4 . However, the maximum value of $[\text{P}^*]$ was not identical with the initiator concentration. A slow decrease of $[\text{P}^*]$ after the maximum value was observed, which shows the occurrence of termination reaction in this polymerization. In essential agreement with a slow decrease of $[\text{P}^*]$, a plot of first-order rate law for monomer consumption (Fig. 2) showed a slight deviation from a straight line. This seems to disagree to the conclusion of the previous papers where a mechanism of living polymerization was given on the basis of the time-conversion and conversion-molecular weight relationships [5, 7]. To explain this disagreement it might be supposed that the polymerization system of the present study contains an adventitious impurity, e.g., water, which caused the termination. This possibility, however, is considered improbable because the same degree of purification of reagents as employed in the present study is

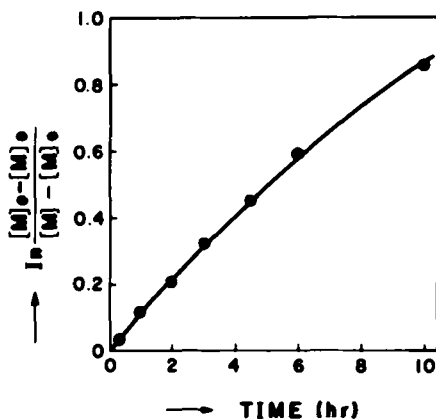
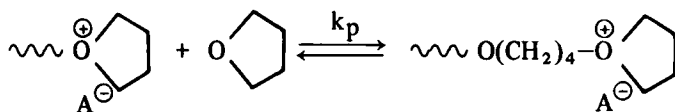


Fig. 2. Polymerization of THF by Et_3OBF_4 . First-order plot. Solution polymerization at 0°C . Solvent, CH_2Cl_2 . $[\text{M}]_0$, 1.7 mole/liter [9].

enough to exclude the termination in the THF polymerization by $\text{AlEt}_3\text{-H}_2\text{O}$ (2:1)-epichlorohydrin [1, 8] and BF_3 -epichlorohydrin [2]. For the present, the discrepancy may be explained by the fact that the $[\text{P}^*]$ change of the present study is more sensitive for detecting slow termination than the kinetic methods of the previous investigations which

were based on the time-conversion and conversion-molecular weight relationships. The deviation of the rate plot from a straight line in Fig. 2 is not definite enough to demonstrate a slow termination reaction. The direct determination of $[P^*]$, on the other hand, afforded a much more distinct result.

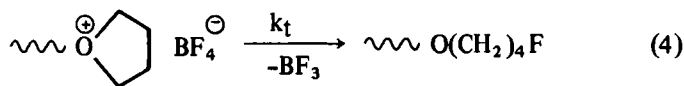
On the basis of the data in Figs. 1 and 2, the rate constants of elementary reactions in this polymerization were determined. The propagation rate constant k_p was calculated from the time- $[P^*]$ and the time-conversion data according to an equilibrium polymerization scheme.



$$-\frac{d[M]}{dt} = k_p [P^*] \{ [M] - [M]_e \} \quad (2)$$

$$\ln \frac{[M]_{t_1} - [M]_e}{[M]_{t_2} - [M]_e} = k_p \int_{t_1}^{t_2} [P^*] dt \quad (3)$$

where $[M]_{t_1}$ and $[M]_{t_2}$ are the monomer concentrations at time t_1 and t_2 , respectively, and $[M]_e$ is the equilibrium monomer concentration (1.7 mole/liter at 0°C [9]). The cumulative value of $[P^*]$ in Eq. (3) is given by graphical integration. From the linear relationship of Eq. (3) ($t_1 = 0$) (Fig. 3), a reliable value of k_p was obtained (Table 2). The k_p values for Et_3OBF_4 in Table 2 are very close to the values for $\text{BF}_3\text{-ECH}$ and other catalysts reported in the previous studies, whereas the initiation efficiency of Et_3OBF_4 is significantly higher [2, 3]. The rate of termination, on the other hand, is represented by the decrease of $[P^*]$ after 2 hr in Fig. 1, where the contribution of initiation is negligible. As to the mechanism of termination, self-decomposition of the propagating species by the counter anion may be assumed.



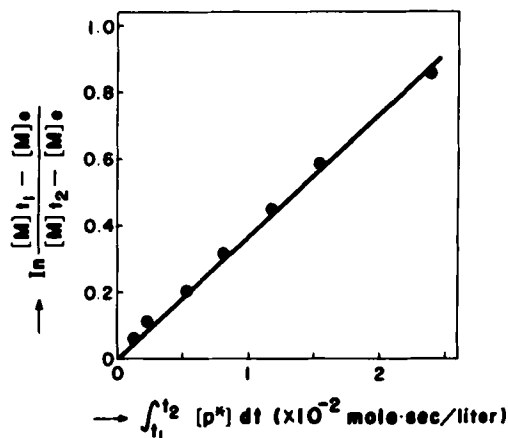


Fig. 3. Polymerization of THF by Et_3OBF_4 . Solution polymerization at 0°C . Solvent, CH_2Cl_2 . $[\text{M}]_e$, 1.7 mole/liter [9]. t_1 , 0.

Table 2. Rate Constants of Elementary Reactions^a

Initiator	$[\text{I}] \times 10^2$ (mole/liter)	$k_p \times 10^3$ (liter/mole sec)	$k_t \times 10^5$ (sec^{-1})	$k_i \times 10^4$ (liter/mole sec)
Et_3OBF_4	0.9	3.7	1	2
Et_3OBF_4	2.1	3.4	2	—
$\text{Et}_3\text{OAlCl}_4$	5.7	—	$\sim 10^3$	4

^aSolution polymerization in methylene dichloride: $[\text{M}]_0$, 6.3 mole/liter; temperature, 0°C .

According to this first-order decomposition mechanism, the rate constant of termination k_t was roughly estimated from the following equation.

$$-\frac{d[\text{P}^*]}{dt} = k_t[\text{P}^*] \quad (5)$$

The k_t value was of the order of magnitude of 10^{-5} sec^{-1} (Table 2).

Furthermore, the rate constant of initiation k_i was determined from the time- $[\text{I}]$ relation (Curve 2 in Fig. 1) according to

$$-\frac{d[\text{I}]}{dt} = k_i[\text{I}][\text{M}] \quad (6)$$

in which $[I]$ is the concentration of the remaining initiator. The value of k_i obtained (Table 2) is in agreement with the reported values of Tobolsky et al., determined by using a ^{14}C -labeled initiator [4]. The smaller value of k_i as compared with k_p is reasonable because the cyclic trialkyloxonium

ion $\text{~} \text{O}^{\oplus}$ is considered to be more reactive than $\text{Et}_3\text{O}^{\oplus}$ toward nucleophilic attack of the THF monomer.

Polymerization by $\text{Et}_3\text{OAlCl}_4$

Figure 4 shows the time- $[P^*]$ (Curve 1) and the time- $[I]$ (Curve 2) relationships in the THF polymerization by $\text{Et}_3\text{OAlCl}_4$. The time- $[P^*]$ profile of this polymerization is quite different from that of polymerization by Et_3OBF_4 . The $[P^*]$ value is very small throughout the polymerization

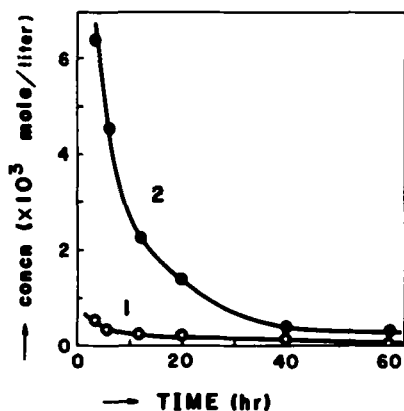
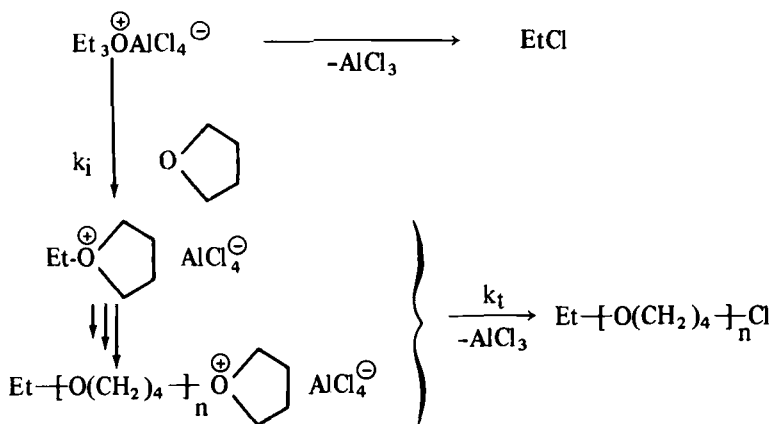


Fig. 4. Polymerization of THF by $\text{Et}_3\text{OAlCl}_4$: variations of $[P^*]$ (Curve 1) and of $[\text{Et}_3\text{O}^{\oplus}]$ (Curve 2). Solution polymerization at 0°C . Solvent, CH_2Cl_2 . $[\text{M}]_0$, 6.3 mole/liter. $[\text{Et}_3\text{OAlCl}_4]_0$, 5.7×10^{-2} mole/liter.

and decreases gradually. Correspondingly, the consumption rate of monomer was very small at a longer reaction time and the product was a liquid of very low molecular weight. Because of a large error in the time-conversion data, k_p could not be determined. The end group structure of the liquid product was investigated using a sample prepared with a large amount of $\text{Et}_3\text{OAlCl}_4$ (see Experimental Section). The product was shown to be a mixture of Cl-terminated oligomers, $\text{Et}-[\text{O}(\text{CH}_2)_4]_n\text{Cl}$, $\bar{n} = 3 \sim 4$. These findings indicate that in this system very rapid termination occurs by self-decomposition of the propagating species (Scheme 2).



The rate constants of termination and initiation were determined from Fig. 4. Neglecting the decomposition of the initiator, the rate of the change of $[P^*]$ is expressed by

$$\frac{d[P^*]}{dt} = - \frac{d[I]}{dt} - k_t[P^*] \quad (7)$$

in which $-d[I]/dt$ is the rate of initiation. Rearrangement of Eq. (7) gives

$$k_t[P^*] = - \frac{d \{ [P^*] + [I] \}}{dt} \quad (8)$$

Through the use of Eq. (8), approximate values of k_t which were in the order of magnitude of 10^{-2} sec^{-1} , were calculated at several reaction times (Table 2). It is very significant to note that the k_t value of the $\text{Et}_3\text{OAlCl}_4$ -initiated polymerization is much higher than that of Et_3OBF_4 -initiated one. The k_t value is taken as a measure of stability of the counter anion which is decisive on the duration of propagation of the THF polymerization. A rough calculation of k_i from the time- $[I]$ curve in Fig. 4 (Eq. 6) showed that the value did not differ very much from that for Et_3OBF_4 (Table 2).

EXPERIMENTAL SECTION

Materials

THF and Methylene Dichloride. Commercial reagents were purified and dried as described previously [2, 8].

Decalin. Commercial reagent was treated with concentrated sulfuric acid, washed successively with an aqueous solution of sodium hydroxide and water, dried by calcium chloride, and distilled.

Oxonium Salts. The salts were prepared and purified immediately before use. All operations were conducted in an atmosphere of dry nitrogen. Et_3OBF_4 was synthesized from epichlorohydrin and BF_3OEt_2 in ether according to the method of Meerwein et al. [10]. It was further purified by reprecipitation (CH_2Cl_2 -ether) and dried in vacuo at room temperature. The tetrachloroaluminate salt $\text{Et}_3\text{OAlCl}_4$ was prepared similarly from epichlorohydrin and AlCl_3 in ether [10]. The precipitated salt was filtered at 0°C , washed several times with cold ether, and dried in vacuo at $-20 \sim -30^\circ\text{C}$. The dried salt was used without further purification.

Model Phenyl Ethers. Commercial phenetole was used directly. 4-Methoxybutyl phenyl ether $\text{CH}_3\text{O}(\text{CH}_2)_4\text{OPh}$ was synthesized in our previous study [1].

Polymerization and $[\text{P}^*]$ Determination

Polymerization was carried out in methylene dichloride solution at 0°C under a nitrogen atmosphere. A solution of initiator (ca. 0.3 ml) was added, by means of a syringe, to 10 ml of THF- CH_2Cl_2 mixture to start the polymerization. Short-stopping with excess sodium phenoxide and the subsequent treatment of the reaction mixture were carried out as described previously [1, 2]. The CH_2Cl_2 extract was diluted to 50 ml and the total amount of phenyl ether was determined by UV spectroscopy. A 10-ml portion of this CH_2Cl_2 solution was mixed with 8 ml of Decalin and the mixture was subjected to distillation at room temperature under reduced pressure (0.2 ~ 0.3 mm Hg). The distillation was continued until most of the Decalin had been distilled. The amount of phenyl ether at the polymer end was then determined by UV analysis of the distillation residue. In the reference experiments, Decalin (8 ml) was added to a solution of poly-THF

(ca. 0.5 g) and a model phenyl ether (ca. 0.2 mmole) in THF-CH₂Cl₂ (10 ml) and the mixture was subjected to vacuum distillation and UV analysis. Conversions by polymerization were determined gravimetrically.

Reaction of THF with Et₃OAlCl₄

Under a nitrogen atmosphere, a solution of Et₃OAlCl₄ (1.58 g, 5.8 mmole) in 5 ml of CH₂Cl₂ was allowed to react with 5 ml of THF at 0°C for 1.5 hr. The mixture was then decomposed by an aqueous solution of sodium hydroxide and the organic product was extracted by CH₂Cl₂. From the dried extract (K₂CO₃) the product was isolated by evaporation of the solvent. This gave 1.3 g of a liquid with an average molecular weight of 345 (vapor pressure osmometry). IR and NMR spectra together with v.p.c. and elemental analysis indicated that the product was a mixture of oligomers having the structure Et-[O(CH₂)₄] _{\bar{n}} -Cl. On the basis of this structure, the molecular weight gave 3.9 as an average value of \bar{n} and 1.3 g corresponded to 3.6 mmole (62% for Et₃OAlCl₄). The NMR spectrum of the product had a clear triplet at $\tau = 8.9$ ppm which was assigned to methyl protons of the terminal Et-group. From the relative peak area of this signal \bar{n} was calculated to be 3.7. On the other hand, the chlorine content of the product (12.2%) gave a value of $\bar{n} = 3.1$. The lower value of \bar{n} may be due to contamination by a small amount of CH₂Cl₂.

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